UNIVERSIDADE DE TAUBATÉ
PROGRAMA DE PÓS-GRADUAÇÃO
EM CIÊNCIAS AMBIENTAIS

Revista Ambiente & Água

An Interdisciplinary Journal of Applied Science

ISSN = 1980-993X (Online)
<http://www.ambi-agua.net>

43th Edition of Revista Ambiente & Água - An Interdisciplinary Journal of Applied Science,
Taubaté, V. 13, N. 2, p. 1-13 Mar./Apr. 2018. ([doi:10.4136/ambi-agua.v13.n2](https://doi.org/10.4136/ambi-agua.v13.n2))

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Revista Ambiente & Água - An Interdisciplinary Journal of Applied Science / Instituto de Pesquisas Ambientais em Bacias Hidrográficas. Taubaté. v. 13, n.2 (2006) - Taubaté: IPABHi, 2018. Quadrimestral (2006 – 2013), Trimestral (2014 – 2016), Bimestral (2017), Publicação Contínua a partir de Janeiro de 2018.

Resumo em português e inglês.
ISSN 1980-993X

1. Ciências ambientais. 2. Recursos hídricos. I. Instituto de Pesquisas Ambientais em Bacias Hidrográficas.

CDD - 333.705

CDU - (03)556.18

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Rev. Ambient. Água, Taubaté, vol. 13 n. 2, p. 1-13, 2018. [doi:10.4136/ambi-agua.2120](https://doi.org/10.4136/ambi-agua.2120)

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Social and environmental innovations of Brazilian companies

ARTICLES doi:10.4136/ambi-agua.2145

Received: 07 Jun. 2017; Accepted: 06 Feb. 2018

**Celso Machado Junior^{1*}; Maria Tereza Saraiva de Souza²; Roberto Bazanini³;
Daielly Melina Nassif Mantovani⁴; Cristiane Jaciara Furlaneto⁵**

¹Faculdades Metropolitanas Unidas (FMU), São Paulo, SP, Brasil

Mestrado Profissional em Administração em Governança Corporativa (MPAGC)

E-mail: celsomachado1@gmail.com

²Fundação Educacional Inaciana Pe. Sabóia de Medeiros (FEI), São Bernardo do Campo, SP, Brasil

Programa de Mestrado e Doutorado em Administração (PMDA). E-mail: mariateresasaraivas@gmail.com

³Universidade Paulista (UNIP), São Paulo, SP, Brasil

Programa de Mestrado em Administração. E-mail: roberto.bazanini@terra.com.br

⁴Faculdades Metropolitanas Unidas (FMU), São Paulo, SP, Brasil

Programa de Pós-Graduação em Administração (PPGA). E-mail: daimantovani@gmail.com

⁵Universidade Paulista (UNIP), São Paulo, SP, Brasil

Conselho Superior de Ensino, Pesquisa e Extensão. E-mail: crisjaciara@gmail.com

*Corresponding author

ABSTRACT

This paper focuses on the social and environmental innovations of Brazilian companies, rather than on merely economic innovations. These innovations are discussed within the context of sustainability. Data were collected via a qualitative and descriptive study from the annual Guia Exame de Sustentabilidade magazine (2014 Edition). The magazine stated that 228 companies responded to the questionnaire. Of these, 61 companies stood out in Brazil for their policies and practices in sustainability and had their results published. The social innovations were geared towards meeting the needs of the surrounding communities. Environmental innovations appeared in greater numbers, connoting a higher stage of attention and interest from Brazilian companies. Environmental innovations were intended to evolve or improve processes and products and to reduce the consumption of resources.

Keywords: efficient processes, reduction of greenhouse gases, socio-technical context.

Inovações sociais e ambientais das empresas brasileiras

RESUMO

Neste artigo, se investiga as inovações voltadas para aspectos sociais e ambientais, ao invés da análise de aspectos meramente econômicos, proporcionando assim o contexto da sustentabilidade. Este propósito é estabelecido para identificar as inovações sociais e ambientais desenvolvidas pelas empresas brasileiras. Os dados foram coletados através de um estudo qualitativo e descritivo da revista anual Guia Exame de Sustentabilidade (edição de 2014). A publicação de 2014 da revista identificou que 228 empresas responderam ao questionário. Destas, 61 empresas se destacaram no Brasil por suas políticas e práticas de sustentabilidade e publicaram seus resultados. As inovações sociais foram voltadas para atender às necessidades das comunidades vizinhas. As inovações ambientais apareceram em maior

número, em estágio mais elevado de atenção e interesse em relação as sociais pelas empresas brasileiras. As inovações ambientais foram destinadas a desenvolver ou melhorar processos e produtos, bem como para a redução do consumo de recursos.

Palavras-chave: contexto sócio técnico, processos eficientes, redução de gases de efeito estufa.

1. INTRODUCTION

Social and environmental innovations, rather than merely economic innovations, are of interest to society. This research identifies Brazilian companies' social and environmental innovations through an investigation of 61 companies that disclosed details of their performance in the magazine *Guia Exame de Sustentabilidade* (2014).

The theory of economic development proposed by Schumpeter (1997) explains the elements that support the evolution of markets, countries and companies. According to this author, innovation has a close relationship with the establishment of new markets and the emergence of entrepreneurs. It is important that a government support research and development for its country's economic growth. In this way, Dosi (2006) argues that the growth and competitiveness of an industrial society can be encouraged by carrying out scientific and technological research, confirming Schumpeter's approach.

Through the Oslo Manual, the Organization for Economic Co-operation and Development (OECD, 2005) classifies innovation into four areas: product, process, marketing and organization. This division positions an innovation in the area from which it originated or in the area that had greater participation in it.

The Oslo Manual (OECD, 2005) is an international benchmark to measure innovation. Despite the greater attention paid to innovation in the industrial sector, the Oslo Manual enables the interpretation of innovation in various spheres of society. However, it focuses primarily on economic development, moving away from social and environmental issues, which, together with the economic variable, lay the foundations of sustainability.

In the context of economic innovation, Schumpeter (1997) argues that this can be achieved by producing new things, producing the same things in a new way (in various combinations of materials and forces) and making new combinations that bring financial returns.

The innovations that occur within the companies are thus important for the whole of society and influence the development of the country. Thus, this research identifies innovations of Brazilian companies that had social and environmental impact.

Design innovation based solely on financial returns is far from a sustainable development proposal. Concern for sustainability is a reality in most companies, whose management teams focus not only on economic aspects but also social and environmental aspects. The engagement of enterprises in the context of sustainability involves the need to change practices to address sustainable development. Barbieri et al. (2010) point out that in the process of innovation, organizations should incorporate the mitigation of social and environmental aspects. In this sense, besides benefiting the economy, innovation should contemplate society and the environment, consolidating the concept of sustainable development.

Authors like Bhatt and Altinay (2013) and Maclean et al. (2013) indicate that research on social innovation is in the embryonic stage, lacking theoretical and empirical studies. To Cajaiba-Santana (2014), social innovation studies are fractionated and diluted among various fields of knowledge. Bignetti (2011) identifies that research on social innovation is rare and rudimentary. The research field is still emerging. Bouchard (2012) proposes that social innovations aimed at social change present a new vision – a new way to evaluate and define problems and possible solutions.

While sustainable development is a scientific field still developing, there are important studies with the potential to direct relevant research on this topic. Within the existing body of research, this study highlights contributions that support the discussion to be developed with the collected data. It is worth noting that the definition of social innovation is viewed as an innovative resolution that is designed to meet human needs (Mulgan, 2006) and to help to solve the social and environmental problems that afflict humanity (Maurer and Silva, 2014).

The innovation can be incremental that stems from improving or complementing something that already exists in the market, or radical that occurs abruptly implanting novelties in the market and discontinued what was in force. Foster and Heeks (2013) highlights the importance of the diffusion of new technologies in the economy and points out that such diffusion has four dimensions: management or technological trajectory; rhythm or rate of diffusion; conditions; and economic, social and environmental factors.

According to Chambon et al. (1982), social innovations are dynamics that allow an individual or a group of individuals to meet social demands or sets of social needs that are currently not met satisfactorily. Also, according to the authors, social innovation gives individuals a better condition than at present, characterizing a degree of novelty. For the authors, social innovation has four dimensions: (i) form – it is immaterial, represented by actions and practices; (ii) process – it requires involvement and commitment from conception to implementation; (iii) actors – consider people and their interaction with the environment; and (iv) change objectives – it solves social problems, allowing the unfolding of everyday life.

For Kanter (1999), social problems are also economic problems. The author points out the existence of companies that identify a favorable environment for social innovation and migrate corporate social responsibility to corporate social innovation. Thus, the author proposes that the commitment of companies to change involves the whole of society but differently than philanthropy; it identifies opportunities for learning and business development via research and development (R&D). According to the author, social innovation seeks to solve the problems that affect society, such as those related to health, education and economic development.

The study of Holmes and Smart (2009) reviews open innovation in the context of corporate social responsibility, which approximates social innovation and social entrepreneurship. The authors also highlight the importance of businesses expanding their borders as a phenomenon that strengthens the process of innovation and social legitimacy.

The existence of links among diversity management, the process of innovation and superior performance in companies with greater attention to social aspects was observed in research conducted by Bridgstock et al. (2010). The authors position social innovation as the convergence of cultural aspects, in which the emphasis is on the importance of ideas and the understanding that social conditions could be different and better. Thus, social innovation meets currently unmet human and social needs, differing from business innovation that worries only about the consumer and the market. Attention to people and communities, not commercial gain, is what characterizes social innovation, according to Dawson and Daniel (2010). It is distinguished by developing concepts, strategies and tools to support social aspects in the improvement process. For these authors, social innovation is developed collaboratively in order to tackle social problems and relies on the generation and implementation of ideas undertaken collectively.

The aforementioned theoretical context establishes the first hypothesis of this research:

H1 – Social innovations made by companies are aimed at solving social problems.

Within the context of sustainability is also a concern for the environment. The environmental approach considers aspects related to energy consumption, reduction in the consumption of natural resources, and in the generation of pollution. Thus, new products and processes must contemplate innovative solutions that are not restricted to benefits for users, but

also for the environment. Concern about environmental innovation comes from various segments of society. In the academic context, the journal *Environmental Innovation and Societal Transitions* (EIST) is exclusively dedicated to environmental innovation. In addition, magazines such as the *Journal of Cleaner Production*, the *Journal of Industrial Ecology*, *Ecological Economics*, *Revista de Gestão Social e Ambiental* and *Revista Metropolitana de Sustentabilidade* deal with issues related to environmental sustainability. Magazines such as *Policy Research*, *Technological Forecasting and Social Change* and the *Journal of Evolutionary Economics* deal with innovation. The areas of sustainability and innovation also manifest in the dissemination of research regarding environmental innovation.

Kemp and Pearson (2007) present environmental innovation as a concern surrounding the entire product lifecycle or service. For the authors, environmental innovation includes a new product, production process, service, management type or business model for the organization, causing a reduction in environmental risk, pollution and other possible negative impacts resulting from the use of resources in comparison with relevant alternatives.

Rennings (2000) defines environmental innovation or eco-innovation as innovation that contributes to sustainable development. Thus, in the industrial context, the development and use of environmental innovations have the potential to be mechanisms to achieve sustainability. Coenen and Díaz López (2010) propose that environmental and social innovations undertaken responsibly provide technological, institutional and organizational shifts, which modify the basis of knowledge of production systems. Thus, to Van den Bergh et al. (2011), in industry, the significant transition towards sustainability is based on new forms of environmental innovation. Incremental improvements that seek to increase the environmental efficiency of existing production technologies and systems are not sufficient to achieve the demanded radical changes to establish sustainable development. However, the authors believe that environmental innovation is now incremental.

Environmental innovation designed to provide sustainable development in the industrial sector incorporates a systemic approach (Coenen and Díaz López, 2010) involving socio-technical systems that cover manufacturing, consumption and distribution. For Jacobsson and Bergek (2011) and Markard et al. (2012), environmental innovations contribute to sustainability, which in turn is positioned as an important large-scale transformation inductor, involving users, institutions, technological advances, the economy, political structures and other aspects. Markard et al. (2012) emphasize that research into socio-technical systems (such as power supply, water supply and urban transport) enhances the understanding of how different green technologies, competing with each other, enable the creation of new products, services, business models and organizations. In this regard, environmental innovation is established as an important component of sustainability and differentiation in the market.

As noted, the benefits resulting from environmental innovation are significant. However, studies identify the importance of considering the costs involved in the implementation of environmental improvements. Jorgenson et al. (2009) emphasize that the development of innovations involves long periods of research and costly investments. Their analysis indicates that the reduction of pollutant emissions in the coming decades will be more related to environmental regulation than to the intention of developing new products or services. In this conception, environmental innovation is a response of companies to meet legislation, not a natural vocation of the companies. Van den Bergh et al. (2011) emphasize that environmental innovations are geared towards meeting the pressing problems of society, which, however, are associated with external costs and do not enter the calculation of the direct cost to the polluter, for example, air pollution and solid waste disposal. If an industrial agent (a polluter) is not encouraged to invest in environmental innovations or new environmentally friendly technologies, it will affect its internal costs. In this context, the existence of laws is an important

incentive for environmental innovation, as it includes variable social costs that are borne by society in general.

Van den Bergh et al. (2011) also point out that several empirical studies on environmental innovation have focused on variable costs. In this sense, cost (present and future projections) materializes as an important factor affecting both producers and consumers, who are more sensitive to initial costs than long-term costs.

From this context emanates the second hypothesis of this research:

H2 – Environmental innovations are geared towards meeting the demands of the socio-technical system.

Combined with innovation focused on economic growth, social and environmental innovations are important variables for sustainable development. Thus, the innovation process must consider all the variables involved in order to ensure the sustainable development of society and that the demands of society are met in full.

2. METHODOLOGY

This study, according to its general purpose, can be characterized as qualitative and descriptive, using secondary data. Data were collected from the annual magazine *Guia Exame de Sustentabilidade* (2014 edition), published by Editora Abril publishing company. The first edition was published in 2000, and the magazine follows a methodology developed by the Center for Sustainability of the Fundação Getúlio Vargas (*Guia Exame de Sustentabilidade*, 2014). The publication has focused attention on the process of establishing a ranking of companies that declare that their management teams focus attention on sustainability. The 2014 magazine stated that 228 companies responded to the questionnaire. Of these, 61 companies stood out in Brazil for their policies and practices in sustainability and had their results published.

In addition to the indicators presented, the 2014 magazine allowed companies to describe three recently deployed sustainability reports, which described the benefits and results in 2013/2014 and those that were incomplete. The reports could discuss projects, programs, initiatives and practices related to sustainability. Each company was able to offer three accounts of sustainability along the following themes: governance and sustainability, human rights, community relations, supplier management, water management, biodiversity management, waste management, climate change (including management energy), relationships with customers/consumers, and transparency and fighting corruption. If a company wished, it could be exempted from presenting a sustainability report.

This study develops content analysis that, through pre-analysis, in line with the work of Bardin (2009), makes it possible to establish the categorization and codification of the reports submitted by the companies. This process seeks to identify social and environmental innovations. All reports presented in the 2014 *Guia Exame de Sustentabilidade* are referenced in a new list and classified into two categories, namely, social innovation and environmental innovation. The search for a framework for reports based on environmental and social innovation is justified both by the reporting approach of reports that should portray recent activities and incomplete activities, and the demand for companies to present new solutions that meet the paradigms of sustainability. Table 1 presents the concepts used to frame the reports submitted by the companies. Note that these concepts were presented in the theoretical chapter.

Table 1. Concepts used to classify sustainability reports.

Category	Concept
Social Innovation	<p>Proposals aimed at social change present a new vision – a new way to evaluate and define problems and possible solutions (Bouchard, 2012).</p> <p>Social innovations are dynamics that allow an individual or a group of individuals to meet social demands or sets of social needs that are currently not met satisfactorily (Chambon et al., 1982).</p> <p>Social innovation is the convergence of cultural aspects, in which the emphasis is on the importance of ideas and the understanding that social conditions could be different and better (Bridgstock et al., 2010).</p>
Environmental Innovation	<p>Environmental innovation includes a new product, production process, service, management type or business model for the organization, causing a reduction in environmental risk, pollution and other possible negative impacts of resource use in comparison with relevant alternatives (Kemp and Pearson, 2007).</p> <p>Environmental innovation is designed to provide sustainable development in the industrial sector and incorporates a systemic approach (Coenen and Díaz López, 2010).</p> <p>Environmental innovations contribute to sustainability, which in turn is positioned as an important large-scale transformation inductor, involving users, institutions, technological advances, the economy, political structures and other aspects (Jacobsson and Bergek, 2011; Markard et al. 2012).</p> <p>In environmental innovation, cost (present and future projections) materializes as an important behavioral factor of producers and consumers, who are more sensitive to initial costs than long-term costs (Van den Bergh et al., 2011).</p>

Source: Prepared by the authors, based on the references cited.

The next chapter presents the data observed in the content analysis through the classifications of environmental innovation and social innovation.

3. PRESENTATION AND ANALYSIS OF DATA

The synthesis of the collected data is presented in Table 2. All the data obtained can be seen in Appendix A, presented at the end of this article, with the classification of the reports of companies into environmental innovation (EI) or social innovation (SI).

The data show 49 environmental innovations and 22 social innovations, and it was established that 11 companies had both environmental and social innovations. Bradesco was the only company not to present environmental or social innovations. The innovations highlighted by the company related to the technological field, with the potential to result in environmental and social benefits; however, the account of the company did not make this relationship clear. Figure 1 shows the distribution of companies with environmental and/or social innovations.

The data present four groups of companies. The first group presents only environmental innovations with 38 companies (62.3%); the second group with 11 companies (18%) present both environmental and social innovations; the third group with 11 companies (18%) present only social innovations; and the last group with a company that presents an innovation that does not fit as environmental or social. Thus, in the aggregate of the companies of the first group with those of the second group, a total of 49 companies (80.3%) are identified investing in environmental innovations, showing that this practice is of most interest to companies.

Table 2. Synthesis of reports highlighted by companies, from Appendix A.

Sector	Number of firms	Number of innovations introduced	% of innovation in the sample	Number of environmental innovation introduced	Number of Social Innovation introduced
Agribusiness	3	3	4,22%	2	1
Auto Industry	2	2	2,82%	2	0
Capital Goods	2	2	2,82%	2	0
Consumer Goods	6	7*	9,86%	5	2
Construction	1	2	2,82%	1	1
Consulting and IT Management	3	4*	5,63%	3	1
Electronics	5	6*	8,45%	5	1
Energy	8	9*	12,68%	7	2
Hotels	1	1	1,41%	1	0
Infrastructure	2	2	2,82%	1	1
Financial Institutions	4	3**	4,22%	1	2
Construction Materials	2	3*	4,22%	2	1
Mining and Steel Mills	7	9*	12,68%	7	2
Paper and Cellulose	2	3*	4,22%	2	1
Chemistry	5	5	7,05%	4	1
Health Services	4	4	5,63%	1	3
Telecommunications	2	3*	4,22%	1	2
Transportation and Logistics	1	1	1,41%	1	0
Small and medium enterprises.	1	2*	2,82%	1	1
Total	61	71	100%	49	22

Source: Prepared by the authors, based on the references cited.

Note: * there are institutions that present more than one innovation, ** One of the institutions presented innovation, but it does not fit as either environmental or social.

Figure 1. Distribution of companies with environmental and/or social innovations.

Source: research data.

Table 3 indicates the benefit themes of the social innovations of the companies. Social innovations present unique benefits. The social actions developed by the companies result in more social benefits than those listed; however, for the purposes of this research, the data are restricted to those reported by the companies. The relation of social innovations and their respective benefits can be seen in the Appendix A.

Supporting the community with nine occurrences (41%) was established as a major focus of the companies that carried out social innovations. Next was enhancing professional capacity: in two situations, the target audiences were outside the companies, and in one situation it was the employees themselves. Next were establishing partnerships with collectors and mitigating the effects of the activities of the companies. With just one occurrence each were working with local suppliers, providing education for transit, providing financial education, fighting corruption, ensuring gender equality and improving digital inclusion.

Table 3. Benefit themes of the social innovations.

Theme	Quantity	%	Theme	Quantity	%
Support the community	9	41,0	Education for transit	1	4,5
Enhance professional capacity	3	13,6	Financial education	1	4,5
Partnerships with collectors	2	9,2	Fighting corruption	1	4,5
Mitigate the effects of activities	2	9,2	Gender equality	1	4,5
Local suppliers	1	4,5	Digital inclusion	1	4,5

Source: research data.

Table 4 shows the benefit themes of the environmental innovations of the companies. Note that environmental innovations can address various topics related to the environment; thus, Table 4 expresses all the benefits from the changes reported by the companies. Thus, an innovation can generate more than one benefit. It is worth mentioning that a total of 100 benefits were identified because of environmental innovations. The relationship of environmental innovations and their respective benefits can be observed in the Appendix A.

Table 4. Benefit themes of the environmental innovations.

Theme	Quantity	%	Theme	Quantity	%
Efficiency	20	20	Mitigate environmental impacts	4	4
Electricity	20	20	Environmental certification	3	3
Water	10	10	Environmental education	2	2
Reuse/recycling	8	8	Good habits	1	1
Reduction of GGEs	7	7	Carbon credit	1	1
Supply chains / suppliers	6	6	Biotechnology – genetic improvement	1	1
Waste reduction	6	6	Risk assessment	1	1
Reduction in resource consumption	5	5	Forest recovery	1	1
New products	4	4			

Source: research data.

The data show greater attention paid to the search for efficiency and electricity management. The quest for efficiency in most cases was related to improvements that resulted in a lower consumption of natural resources and lower impacts of the byproducts and processes involved. Electricity was positioned as one of the resources that receives most attention from companies, followed by water. Reuse/recycling was in fourth position, which involves repurposing the leftovers or waste produced by the activities of the companies. The reduction of GGEs had seven occurrences. With six occurrences were improving supply chains / suppliers and ensuring waste reduction. The reduction in resource consumption had five occurrences, and new products had four occurrences. Environmental certification had three occurrences, while

environmental education had two. With one occurrence each were good habits, carbon credit, biotechnology – genetic improvement, risk assessment and recovery of forests.

The following chapter discusses the survey data using the theoretical framework developed to support the research.

4. DISCUSSION

The data relating to social innovation indicate that it receives less attention from these companies than environmental innovation does. The data confirm the embryonic position of social innovation, as pointed out by Bhatt and Altinay (2013) and Maclean et al. (2013). In this sense, not only is social innovation research embryonic but the innovation process is also geared towards social change.

Supporting the community with nine occurrences represented 41% of the social innovations and was thus positioned as the subject of a greater volume of innovations. This theme incorporates, in most cases, actions that occur in the surroundings of companies and that aim to improve the social conditions of people nearby. This position matches the approach of Chambon et al. (1982), in which social innovation is intended to meet social needs that are not yet answered satisfactorily, or, as Mulgan (2006) proposes, is intended to meet human needs.

Enhancing professional capacity and creating partnerships with collectors have more-direct relationships with the need to provide people with their own conditions of subsistence. In this sense, social innovations are also configured as economic innovations, as proposed by Kanter (1999). In this case, the author indicates that social innovations offer opportunities for learning and business development, moving away from philanthropy. Actions to mitigate the effects of the company's activities are intended to prevent possible future problems; however, they are also a form of social innovation, based on the understanding that social conditions could be better and different, as proposed by Bridgstock et al. (2010).

Other matters dealt with by the companies' social innovations were quite diluted and addressed the following topics: local suppliers, education for transit, financial education, fighting corruption, gender equality and digital inclusion. This diversity of themes converges with the approach of Cajaiba-Santana (2014), who indicates that social innovation studies are diluted across different areas. Thus, the great diversity of social innovation studies is probably due to the multiplicity of subject matters of social innovation.

The accounts of social innovations developed by the companies did not point to obtaining commercial profit from these – a condition that adheres to the proposal of Dawson and Daniel (2010), for whom social innovation is developed collaboratively in order to solve social problems. This context confirms the first hypothesis established by this research.

The environmental innovations identified by the companies were geared towards efficiency, electricity, water, reuse/recycling, supply chains/suppliers, reduced consumption of resources, new products, mitigating environmental impacts, environmental education, biotechnology and the recovery of forests. These are types of sustainable development, according to the definition provided by Rennings (2000). This context confirms the proposition of Van den Bergh et al. (2011), that industry relies on innovation to achieve environmental sustainability.

The data show three companies, indicating their implementation of environmental certification processes. This was probably related to legal requirements, mainly due to wood exports. This mirrors the approach of Jorgenson et al. (2009), which highlights the influence of environmental regulations as a stimulating factor.

It was possible to identify a set of 20 innovations aimed at electricity consumption, matching the data of Van den Bergh et al. (2011), which highlights the concerns of producers and consumers with cost in the current context and in the future. Markard et al. (2012) found

that environmental research is focused on socio-technical systems, which focus on electricity, water and urban transport. This research found that the organizations identified energy and water as company management elements, but urban transport was not identified. For Coenen and Díaz López (2010) environmental innovations fall within the socio-technical context but they expand to a larger universe, which incorporates manufacturing, distribution and consumption. Thus, this research identified the main forms of environmental innovation as relating to efficiency, the consumption of electricity and water, reuse/recycling, the reduction of GGEs, supply chains / suppliers, waste reduction and reducing resource consumption. All of these actions relate to manufacturing, consumption and distribution. The results obtained confirmed the second hypothesis.

5. CONCLUSION

This paper proposed to identify Brazilian companies' social and environmental innovations. The developed research enabled us to identify several actions of social and environmental innovations practiced by Brazilian companies. Because the data used in this study were made available in a trade magazine accessible to any interested party, it can be inferred that the Brazilian companies disclosed their social and environmental innovations with this in mind.

Social innovations were presented in a smaller volume and were largely geared towards meeting the needs of surrounding communities. Social innovation actions also related to learning and business development, a condition that is far from a philanthropic approach.

Environmental innovations appeared in greater numbers than social innovations did, connoting a higher stage of attention and interest from Brazilian companies. Environmental innovations fall within the socio-technical context, with measures to develop or improve processes and/or resources. Among the topics of interest of the identified environmental innovations were searches for efficiency, reduced consumption of energy and water, reuse/recycling, the reduction of GGEs, supply chains / suppliers, reducing waste and reducing the consumption of resources.

One limitation of this study was the retrieval of data from a single publication. However, this limitation was due to the scarcity of publications dedicated to the area of sustainable innovation. This context limited the search for other sources of data.

This study reflects the current stage of social and environmental innovation of companies. However, because it is a topic of growing interest to companies, this study establishes the merit for further research to replicate this study in order to identify the progress and expansion of the interest in the subject. It is worth noting that a possible Brazilian economic contraction and increased disputes between businesses could result in reduced interest of companies in the issue, but there remains a need for studies to identify the variations that occur and the possible causative agents behind these changes.

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Appendix A. Reports highlighted by the companies.

Sector	Company	Featured Actions	Class*
Agribusiness	Bunge	Efficiency, reducing greenhouse gas emissions (GGEs), logistics – invested in logistics, with a 20% reduction in the route of grain and a 20% reduction in the emission of carbon originating from transport – reduction of 100,000 truck trips. Restrictions on suppliers that violate environmental and labor standards.	EI
	Amaggi	Environmental and social certification – invested in international certification to avoid the risk of having products barred abroad for social or environmental issues.	EI
	Odebrecht Agro-industrial	Supported communities – invested in the training of bricklayers and bakers, to meet labor shortages in the cities where they are installing their industries.	SI
Auto Industry	Volvo	Efficiency, energy, reduction in GGEs, reuse – invested in productive efficiency. Decrease of 63% in the energy needed to manufacture a vehicle and a 50% reduction in GGEs. Currently, 90% of the waste of raw materials – iron and plastic – is processed at the factory.	EI
	Eaton	Efficiency, power, water – searched for more-efficient uses of resources, causing a 15% reduction in water consumption and a 28% reduction in electricity consumption.	EI
Capital Goods	Tetra Pak	Using sustainable resources – the use of renewable materials in 2014 went from 75% to 82%. Expanded the use of recycled materials in the production process.	EI
	Weg	Energy efficiency – became one of the first companies in the country to apply international standards of energy management: ISO50001. A reduction of 13% of electricity consumption in the assembly lines.	EI
Consumer Goods	Unilever	Supplier certification – working with its suppliers to achieve the target of 100% of agricultural raw materials having certification of origin by the end of the decade.	EI
	Brasil Kirin	Reduction of materials in packaging, collectors – has programs to reduce raw materials in packaging. In 2013, it saved 4,000 tons of plastic resin. Works with partnership collectors for collecting discarded packaging material.	EI SI
	Coca-Cola	Development of poor communities – invested in the development of small-scale suppliers of extractive communities in the Amazon.	SI
	Grupo Boticário	Energy efficiency – invested in the efficient use of natural resources. In the reform of its first plant, it reduced the consumption of electricity by 20%, and its new plant has been designed with attention to the better use of natural resources.	EI
	Kimberly-Clark	Reduction in water consumption – invested in reducing water consumption in the paper manufacturing process. In 2013, it needed 5,000 liters of water to produce 1 ton of paper.	EI
	Natura	Efficiency, mitigation, networking – The company proposes a business management that makes possible a positive impact on the environment.	EI
Construction	Even	Efficiency, energy, water, mitigation of problems caused by its operations – has a program to alleviate the inconvenience that the construction of its buildings causes for those who live nearby. Invested in new properties that have a lower consumption of water and electricity.	EI SI
Consulting and IT Management	Promon	Efficiency, water, collectors – specializes in developing environmental solutions with positive social impacts. Implemented a recycling system that benefits recycling cooperatives and a closed-loop water system that eliminates the need for the collection and disposal of water.	EI SI
	Ecofrotas	Carbon credits – developed a methodology that allows the sale of carbon credits with the adoption of ethanol in the car fleet.	EI
	EY	Sustainable logistics chain – created a methodology for building sustainable supply chains and applied its knowledge in planning the 2016 Olympics in Rio de Janeiro.	EI
Electronics	Philips	Efficiency of products – invested in the development of products with higher energy efficiency and lower costs. One example is LED lamps – the price dropped 70% in two years.	EI
	Embraco	Reuse – invested in its business based on the reuse of material that would be discarded. Reused 96% of solid waste from industrial processes.	EI
	HP	Efficient products and processes, reuse – implemented the circular economy concept and developed partnerships with suppliers to reduce resource consumption and increase the efficiency of products. Its products were also made more energy efficient.	EI
	Schneider Electric	Supplier development, GGE reduction, supporting the community – developed the sustainability of its suppliers. Reduction in GGEs. Training 15,000 people from disadvantaged communities through electrician courses.	EI SI
	Whirlpool	Water saving – saved water in appliance manufacturing and encouraged consumers to do the same by purchasing its washing machines.	EI

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Energy	AES Brasil	Sustainable energy – diversified its sources of power generation. Installed solar plants with hydroelectric plants to take advantage of the structure. It aimed to double the capacity of its power generation via sustainable energy by 2016.	EI
	Ampla	Electricity consumption hours – by 2015, it aimed for customers in the city of Buzios to be able to choose appropriate tariffs based on their spending habits.	EI
	Coele	Consumer awareness, supporting communities – implemented programs offering discounts in exchange for recyclable waste and the replacement of inefficient electric appliances. Encouraged customers to use less electricity.	EI
	CPFL Energia	Alternative energy – expanded investments in renewable sources of electricity and imposed sustainability goals for its executives.	EI
	EPD	Energy, supporting communities – invested 430 million reais (162 million dollars as of December 31, 2014) in social and environmental programs in communities affected by its new hydroelectric plants.	EI SI
	Elektro	Local suppliers – promoted the economy in its concession areas. In 2014, 75% of business was done with local partners.	SI
	Itaipu Binacional	Use of electricity – invested in sustainable forms of electricity use. Supported the development of electric cars.	EI
	Light	Reduction in energy theft – invested in the fight against energy theft, which drains 16% of the energy distributed by the company in Rio de Janeiro.	EI
Hotels	Grupo Rio Quente	Environmental education – educational programs are the foundation of the sustainability policy of Rio Quente Group. Sourced alternative energy – heating shower water was done by solar panels.	EI
Infrastructure	CCR	Education for transit – has a program that contributes to training future drivers and decreasing accident rates on the roads.	SI
	Ecoro-dovias	Energy efficiency – its road modernization includes energy efficiency with the introduction of LED lamps and solar panels.	EI
Financial Institutions	Itaú Unibanco	Financial education – offered financial education for internal employees and business clients in order to reduce default rates.	SI
	Bradesco	Investment in technology – invested in digital channels to keep customers away from the rows of bank tellers. The cost of digital transactions is 5% of that in banks.	
	Grupo BB and Mapfre	Risk assessment in contracts, reduction of resources – included sustainability issues in risk assessments. It simplified the terms of the contracts, reducing paper usage by 88%.	EI
	HSBC	Fighting corruption – improved its internal controls and trained employees to prevent bribery cases.	SI
Construction Materials	Masisa	Integration of suppliers, professional training – achieved integration of the supply chain by establishing a focus on sustainability. It operated in the training of professionals in the area and the growth of the furniture sector.	EI SI
	Duratex	Waste reduction – aimed to reduce industrial waste sent to landfill. In 2013, it recycled 33% of its waste.	EI
Mining and Steel Mills	Arcelor-mittal	Energy efficiency, water consumption, reduction of GGEs – initiated a project to take advantage of the gases from the burning charcoal used in the production process to generate electricity. Achieved GGE reduction. Reused and treated water.	EI
	Alcoa	Forest recovery – invested in a mined area rehabilitation technique in Pará and created an alternative income for the community.	EI SI
	AngloGold Ashanti	Water saving – its wastewater treatment facility in underground mining helped to save water, achieving a 7% rate of water reuse and a 58% reduction in the volume of water pumped.	EI
	Aperam	Waste reduction, efficiency – in six years, the steel mill Aperam halved the generation of waste in the manufacture of steel. The goal was to clear the remains of the production process.	EI
	Vale	Efficiency, reducing consumption of natural resources – aimed to extract iron ore while having a minimal impact on the environment. In the new plant, there was a 90% reduction in the volume of water used. Ore transportation was done by electric mats, not by 300 trucks.	EI
	Voto-rantim Metais	Efficiency, waste reduction, supporting the community, public managers – invested in recycling electric arc furnace dust, the main waste generated in its plants. The goal is zero waste from productive activity by 2020. The Forest Ecos program focuses on developing public awareness and training entrepreneurs and managers.	EI SI
	Yamana	Efficiency, reduced energy consumption – the company's strategy was to streamline costs, seek efficiency and reduce electric and diesel power consumption.	EI
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Paper and Cellulose	Fibria	Efficiency, waste reduction, supporting the surrounding community – invested in biotechnology in the genetic improvement of eucalyptus in order to reduce the area planted. Reduced solid waste going to landfill. It has social actions aimed at improving the lives of neighboring communities.	EI SI
	Klabin	Environmental certification – invested in FSC (Forest Stewardship Council) certification of good practices in forest management for small providers acting in the form of associations.	EI
Chemistry	Beraca	Social project – developed a project to support low-income communities in Piauí through access to clean water and education.	SI
	Basf	Efficiency, reducing consumption – performed a review of the processes of its unit in São Bernardo do Campo to improve the consumption of water and electricity and to reduce environmental impacts, waste generation and GGEs.	EI
	Braskem	Product innovation – invested 200 million reais (75 million dollars as of December 31, 2014) in the year to drive innovation in green products. Developed raw materials derived from sugar cane to replace oil.	EI
	Dow Brasil	Product innovation – developed a filter system that promises to reduce water treatment costs by 40%. The technology began to be used on the São Paulo coast.	EI
	White Martins	Product innovation, efficiency – developed products and services to increase the efficiency of its customers. It has also internally acted to increase its efficiency.	EI
	Sabin	Female work – supported female-dominated labor with constant training.	SI
Health Services	Fleury Group	Employee training – encouraged employees to give suggestions to improve business processes. In 2013, the program generated savings of 4 million reais (1.5 million dollars as of December 31, 2014).	SI
	Albert Einstein Hospital	Supporting needy communities – the hospital provided care to more than 10,000 children in the second largest slum in São Paulo.	SI
	Sírio-Libanês Hospital	Reducing the impacts of activities – adopted an international agenda to reduce the impact of its activities in ten themes, including sustainable construction technologies, green hospitals and a health-based international network.	EI
Telecommunications	Algar Telecom	Environmental design, supplier development – developed a recycling project that combines environmental, educational and social objectives. Collected banners and transformed them into school materials, which were then donated to the public. It ensured its suppliers were committed to sustainability.	EI SI
	Telefônica Vivo	Digital inclusion – provided Internet access to rural schools. In 2014, its digital inclusion program benefited 4,000 rural schools. The goal was to connect 22,000 rural schools.	SI
Transportation and Logistics	Libra Group	GGE reduction, replacing diesel with electricity – invested in electrical equipment for the transport of loads to reduce the GGEs in port operations.	EI
SMEs	Zanzini	Relationships with society, recycling – invested in relationships with social actors and the use of recycled materials.	EI SI

Source: Authors based on Guia Exame de Sustentabilidade (2014).

Notes: Class* = classification: EI or SI.

SME: Small and medium enterprises.

Surface albedo in different land-use and cover types in Amazon forest region

ARTICLES doi:10.4136/ambi-agua.2120

Received: 04 Apr. 2017; Accepted: 20 Jan. 2018

**Thiago de Oliveira Faria¹; Thiago Rangel Rodrigues^{2*};
Leone Francisco Amorim Curado¹; Denilton Carlos Gaio¹; José de Souza Nogueira¹**

¹Universidade Federal de Mato Grosso (UFMT), Cuiabá, MT, Brasil

Programa de Pós-Graduação em Física Ambiental. E-mail: thiagofaria@ufmt.br,

leonecurado@gmail.com, dcgaio@fisica.ufmt.br, nogueira@ufmt.br

²Universidade Federal do Mato Grosso do Sul (UFMS), Campo Grande, MS, Brasil

Laboratório de Ciências Atmosféricas (LCA). E-mail: thiago.r.rodrigues@ufms.br

*Corresponding author

ABSTRACT

Albedo is the portion of energy from the Sun that is reflected by the earth's surface, thus being an important variable that controls climate and energy processes on Earth. Surface albedo is directly related to the characteristics of the Earth's surface materials, making it a useful parameter to evaluate the effects of original soil cover replacement due to human occupation. This study evaluated the changes in the surface albedo values due to the conversion of vegetation to other land uses and to analyze the applicability of the use of albedo in the spatial delimitation of land-use classes in the transitional region between the Cerrado and Amazon biomes. Surface albedo measurements were obtained from processing of Landsat Thematic Mapper data in the Geographic Information System (GIS), and land-use information were collected using Google Earth high-resolution images. The results show that human activities such as the cultivation of crops and burning have contributed substantially to variations in the surface albedo, and that albedo estimates from Landsat imagery have the potential to help in the recognition and delimitation of features of land use and cover.

Keywords: Landsat 5, reflectance, remote sensing.

Albedo de superfície em diferentes classes de uso e cobertura do solo em região de floresta amazônica

RESUMO

Albedo é a porção de energia solar refletida pela superfície terrestre, sendo assim, uma importante variável que controla os processos climáticos e energéticos sobre a Terra. Albedo da superfície está diretamente relacionado com as características dos materiais da superfície da Terra, tornando-se um parâmetro útil para avaliar os efeitos da substituição de cobertura do solo original devido à ocupação humana. Este estudo objetivou avaliar as alterações nos valores de albedo da superfície em função da conversão da vegetação em outras formas de uso do solo, e analisar a aplicabilidade do uso do albedo na delimitação espacial de classes de uso do solo em região de transição entre os biomas Cerrado e Amazônia. As medidas de albedo da superfície foram obtidas a partir de processamento de dados Landsat Thematic Mapper em sistema SIG e as informações de uso do solo foram obtidas usando imagem de alta resolução do Google Earth.

Os resultados demonstram que ações antrópicas sobre a superfície, como desenvolvimento de lavouras e queimadas contribuem substancialmente para as mudanças no albedo de superfície, e que as estimativas de albedo a partir de imagens Landsat apresentam potencial para auxiliar na identificação e delimitação de feições de uso e cobertura do solo.

Palavras-chave: Landsat 5, reflectância, sensoriamento remoto.

1. INTRODUÇÃO

The Amazon rainforest exchanges large amounts of water and energy with the atmosphere, and is therefore important in controlling the regional and global climate (Meir and Grace, 2005). However, the spatial distribution and temporal variation of rainfall (Curado et al., 2016), as well as duration of droughts (Rodrigues et al., 2016a), can have a profound impact on the dynamics of energy exchange by affecting the partitioning of energy between sensible and latent heat fluxes (Vourlitis et al., 2008; 2014; Rocha et al., 2009; Rodrigues et al., 2013; 2014). Because our current knowledge of the climate system is still insufficient to solve some of the divergent predictions about this topic, it is important to improve the understanding of mechanisms of vegetation-climate interaction in forested regions such as the Amazon (Gonçalves et al., 2013), whose seasonal patterns of certain biophysical and climatic parameters show complex interactions (Vourlitis et al., 2014; Rodrigues et al., 2016b).

The process of agricultural expansion and deforestation taking place in the Amazon, mainly in the region known as the ‘Arch of Deforestation’, has resulted in more intensive land-use and forest disturbance as a consequence of the conversion of original vegetation to different forms of land use and cover (Neeff et al., 2005; Soares-Filho et al., 2006; Costa and Pires, 2010).

One of the biophysical parameters influenced by the modification of original vegetation in forested regions is the surface albedo, which is the fraction of incident radiation reflected by a surface that acts as a factor for distribution of solar radiation and energy flow between the surface and atmosphere (Wang et al., 2006; Novais et al., 2015). Albedo is a parameter that varies both spatially and temporally given changes in surface properties, such as soil moisture and vegetation cover as well as changes in local natural light conditions (Franch et al., 2014). It influences the prediction of variables like near-surface temperature and relative humidity (Boussetta et al., 2015). Studies relating landscape features to land cover transformation may help in the understanding and planning of changes in landscape conditions over time, including projections of future land use as well as comparisons between alternative landscape scenarios (Paudel and Yuan, 2012; Swann et al., 2015).

Strongly influenced by anthropic occupation affecting land use in originally natural environments, the surface albedo is a parameter that both influences the radiation balance and modifies the absorption of shortwave radiation (Betts et al., 2007).

Thus, studies on albedo changes as a consequence of modifications in land use and land cover may contribute to the understanding of impacts resulting from human-environment interaction (Barnes et al., 2013; Boisier et al., 2013). There are still many regions, such as the Amazon region of the Brazilian state of Mato Grosso (Schwaiger and Bird, 2010), that require further investigation of the effects caused by land use and cover, since this region has experienced an expansion in economic activity over the last decades (Roberts et al., 2003).

Remote-sensing techniques can contribute to obtaining different information about the earth’s surface in relatively large areas (Ban-Weiss et al., 2015) by allowing, for example, the investigation of albedo variations along different land-use and cover scenarios (Gao et al., 2014). Some researchers have explored the advantages of the use of biophysical parameters from satellite imagery in studies in the vast territory of the Brazilian Amazon. Some examples

of this are the publications of Tartari et al. (2015), Querino et al. (2016), and Silva et al. (2016), who used surface albedo among the investigated parameters. Such studies have increased the level of knowledge of the interactions between the Earth's surface and the atmosphere in this important biome.

Taking into account that albedo presents specific values for certain classes of land use and land cover (Wickham et al., 2015), it is possible to evaluate the effectiveness of this parameter in the identification and distinction of different forms of land use and occupation in order to promote future work on land-use evolution (Salifu and Agyare, 2012).

Although there are many studies showing the applicability of medium spatial resolution images in surface albedo behavior due to changes in land use classes, there are still very few studies evaluating the use of surface albedo in distinguishing land-use classes. Among the few studies with this focus, Salifu and Agyare (2012) showed that the use of surface albedo offers potential to distinguish different land-use and cover types in Volta Basin region, Ghana.

This study evaluated the effect of conversion of native forest to different types of land use and cover (LUC) on the surface albedo values in the Amazon-Cerrado transition region, as well as the applicability of surface albedo to the identification and delimitation of different land-use classes.

2. MATERIALS AND METHODS

2.1. Study Area

The total study area encompasses approximately 20,000 ha and is located between the towns of Ipiranga do Norte and Sorriso, a region of Amazon-Cerrado transition in northern Mato Grosso (Figure 1). The selected area shows several types of land use and presents an opportunity to perform studies on the behavior of biophysical variables in the different classes of land use from satellite imagery.

2.2. Image Pre-Processing

Land-use and cover data were collected and analyzed with high spatial resolution images from Google Earth Pro®, and albedo measurements of different land-use classes were retrieved from Landsat-5 TM. Thus, the study required combining images with the same date from Landsat and Google Earth Pro® to allow comparison of the results. The date of 30 September 2009 was selected as there were images available both from Google Earth Pro® and from Landsat-5 TM. Therefore, the results of this study refer to this date.

The image from the Google Earth Pro® software was acquired at the maximum resolution and then georeferenced using a high-resolution SPOT image through control points in both images. The Landsat-5 TM image used corresponds to the orbit and Point 227/68 in the Landsat Universal Reference System, and was acquired from the website espa.cr.usgs.gov, which provides a surface reflectance image that had undergone atmospheric correction and is cloud-free.

2.3. Surface albedo survey

The surface albedo estimates were calculated according to Liang (2001), who establishes equations for several orbital sensors that allows calculating the albedo through simulations of radiation transport using MODTRAN (Moderate Resolution Atmospheric Transmission). This work applies Equation 1 to Thematic Mapper (TM) images.

$$\text{Albedo} = 0.356\alpha_1 + 0.130\alpha_3 + 0.373\alpha_4 + 0.085\alpha_5 + 0.072\alpha_7 - 0.0018 \quad (1)$$

In which α_i corresponds to the surface reflectance that is intrinsic to the bands “i” of the sensor Landsat-5 TM.

Figure 1. Top left: State of Mato Grosso in mid-western Brazil; Top right: towns of Sorriso and Ipiranga do Norte; Bottom: study area.

2.4. Land use and land cover

In order to identify and outline the types of soil use and cover, a high-resolution image dated 30 September 2009 was obtained from the Google Earth Pro® software for which vectorization class was later carried out using ArcGIS 10.1® at a scale of 1:5,000.

The following classes of land use and cover were considered for the study area: crop, forest, burned area and water. Crop areas were targeted through characteristic polygons that occur in the region in the form of squares, rectangles and circles in which the cultivation process is carried out. This class was not distinguished in terms of the different steps involved in the production process, such as planting and harvesting. The class mapped as forest corresponds to areas of dense vegetation, with visual appearance similar to those of the Amazon forest observed in high-spatial resolution images. The burned-area class is identified due to the characteristic visual appearance of an area that underwent combustion in which several band compositions of the Landsat-5 TM were further attempted following the procedures of Roza and Ribeiro (2013). Water areas are represented especially by water courses and abandoned meander channels.

The analysis of the surface albedo in each one of the classes of land use and occupation was carried out at a scale of 1: 25,000, and all the geoprocessing routines were performed using the ArcGIS 10.1® software.

3. RESULTS AND DISCUSSION

Land-use and land-cover mapping shows a large predominance of crop and forest classes (Figure 2) that occupies 48.75 and 47.45% of the total study area, respectively. Burned areas and water bodies occupy a more restricted portion of the study area, making up 2.74 and 1.06%, respectively.

Figure 2. Soil use and soil cover.

Burned area mapping included analysis of false-color composites (RGB: 4,3,1) and (RGB: 5,4,3) of Landsat-5 TM, which allowed recognition of burned areas through dark (almost black) and purple tones, respectively, according to the criteria adopted by Roza and Ribeiro (2013) to identify burned areas using Landsat-5 TM images.

Figure 3 shows the surface albedo map of the study area with color-coded values. This map has an overall mean of 0.153 and a standard deviation of 0.021.

Figure 3. Surface albedo.

Summary statistics with mean, median and standard deviation of the surface albedo for each land use class are shown in Table 1. Figure 4 presents a box-plot of the summary statistics of the surface albedo for all classes of land use.

Table 1. Summary statistics of surface albedo for the classes of soil use and cover.

Land use and cover	Mean	Median	Standard Deviation
Crop	0.163	0.164	0.013
Forest	0.142	0.140	0.011
Burned area	0.094	0.090	0.010
Water	0.083	0.075	0.029

Figure 4. Box-plot showing summary statistics of surface albedo in each land use class.

The regions occupied by forests presented a mean albedo value of 14.2%, which is similar to that of albedo of tropical rainforests (Berbet and Costa, 2003; Querino et al., 2006; Liberato, 2011). The results indicate that the variation of the albedo values for forest is relatively low, suggesting that forest has albedo with substantially homogeneous behavior in the study area. The small variation of albedo values for forest regions can be caused by variation of vegetation types in this class of land use.

The mean albedo of the crop areas was 16.7%, which represents the highest mean among the classes of land use and cover. This land use class showed a large range between the values of albedo, which can be due to the presence of different stages of agricultural production in the study area, such as planting and harvesting.

The burned area was the class that presented the lowest variation of surface albedo values, and its standard deviation was 1.0%. The mean albedo for burned area was of 9.4%, which is significantly lower than the classes of crop and forest. This low value is explained by the decrease in reflectance due to the loss of photosynthetically active material and by the accumulation of ashes on the soil (Cardozo et al., 2014).

Albedo values for burned areas vary according to the time elapsed after burning, but the mean value found in this study is relatively similar to the values for burned areas identified by other authors, although for different types of vegetation. Pereira et al. (2007) found a mean albedo value of 9.3% for recently burned areas in the Pantanal region of Mato Grosso do Sul, whereas Cardozo et al. (2014) identified a mean albedo value of 6% for burned areas in the state of Rondônia.

The water class shows a mean albedo value of 8.3%, which is the lowest value among all of the land-use classes studied. This value is within the range found by other authors (Giongo et al., 2010; Liberato, 2011). The water class presented a standard deviation (2.9%) and variation of albedo values significantly higher than the other studied classes. The highest standard deviation is largely due to pixel contamination given the limited spatial resolution of Landsat images. This was mainly observed in the area of the Rio Branco River, an affluent of the Rio Verde River, whose mean width is around 20 meters and, therefore, below the spatial resolution of Landsat TM images used in the study. The appearance of mixed pixels is a consequence of albedo values influenced by other features of the terrain other than water.

The differences in albedo values among the land-use classes (forest, crop, water and burned area) mapped by Google Earth images (Figure 5) shows that surface albedo retrieved from medium-spatial resolution images has the potential to help in the characterization of land use classes in the Amazon region.

Figure 5. "Zoom" on the study area showing an overlay of albedo estimates and Google Earth Pro® image (transparency of 65%).

In general, surface albedo mapping allowed for the identification of water surfaces on the basis of their lower values in comparison to the other classes of land use. In addition, it was possible to identify features such as abandoned meander channels and water courses with a mean of over 30 m in width. It was also possible to infer traces of water surfaces with a mean width lower than 30 m, as is the case for the Rio Branco River, when some pixels of the image show typical values of a wet surface.

The mapping of albedo also allowed for distinguishing forests and crop areas from other forms of soil use and occupation; however, the distinction between forest and crop areas was more challenging to identify since these two classes may present subclasses that are only better classified after field work and since they consist of native forest, regenerating forest and planted forest, as well as different types of crops in their respective production phases.

The albedo survey was shown to be effective in identifying and delimiting burned areas, which have overall values lower than those of crops and forests. However, it is important to

pinpoint that a reliable interpretation of burned areas requires a complementary analysis using band composites able to highlight this soil cover class.

Therefore, the results showed that the estimation of surface albedo from orbital sensors, which was calculated according to Liang (2001), in combination with the resulting interpretation of band combinations as proposed by Roza and Ribeiro (2013), favors the identification and delimitation of burned areas in forests of the Amazon-Cerrado transition region.

The comparison between surface albedo values calculated for forests and crop classes shows that the conversion of forests to agriculture produced an albedo increase of 0.025. This increase due to large-scale deforestation, as suggested by other studies (Culf et al., 1996; Giambelluca et al., 1997), tends to have a direct effect on the radiation budget and energy partition given the lower amount of energy absorbed by the earth's surface.

4. CONCLUSIONS

The values of albedo surveyed for classes of soil use and cover in the Amazon-Cerrado boundary in Mato Grosso are reasonably similar to those found in the literature in previous studies. Concerning areas of crops and forests, due to their heterogeneity there may be areas where the boundary between these two classes is difficult to establish using only albedo estimates. However, as a rule-of-thumb, crops have significantly higher albedo values than those of forest areas and other land-use classes studied here.

The albedo estimates calculated from the Landsat image show a significant potential to help in the identification and delimitation of anthropic and natural features in the Amazon-Cerrado transition region once the classes of soil use and cover have distinctive albedo values that allows them to be distinguished from each other using medium-spatial resolution images. Among the classes considered in this study, albedo estimates were more effective to spot burned areas as well as water features, such as abandoned meander channels and water courses, especially when these features have a mean width of over 30 meters.

5. ACKNOWLEDGEMENTS

The research was supported by the Universidade Federal de Mato Grosso (UFMT), Programa de Pós Graduação em Física Ambiental (PPGFA) IF/UFMT, Coordenação de Aperfeiçoamento de Pessoal do Ensino Superior (CAPES) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support to the research project: CNPq/407998/2016-0 and CNPq/424915/2016-2.

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Production of energy (biodiesel) and recovery of materials (biochar) from pyrolysis of urban waste sludge

ARTICLES doi:10.4136/ambi-agua.2128

Received: 27 Apr. 2017; Accepted: 05 Jan. 2018

Arianna Callegari¹; Petr Hlavinec²; Andrea Giuseppe Capodaglio^{1*}

¹Università degli Studi di Pavia, Pavia, Italy

E-mail: arianna.callegari@unipv.it, andrea.capodaglio@unipv.it

²Brno University of Technology, Brno, Czech Republic

E-mail: hlavinec.p@fce.vutbr.cz

*Corresponding author

ABSTRACT

Safe disposal of sewage sludge is one of the most pressing issues in the wastewater treatment cycle: at the European Union level, sludge production is expected to reach 13 Mt by year 2020. Sludge disposal costs may constitute up to, and sometimes above, 50% of the total cost of operation of a WWTP, and contribute to over 40% of its GHGs emissions. The most common disposal options at the moment are landfilling, disposal in agriculture (about 40% EU-wide), incineration or co-incineration, and use in the industrial production of bricks, asphalts and concrete. Sewage sludge, however, still contains beneficial resources such as nutrients, that can be recovered through specific processes (e.g. precipitation as struvite) and energy, recoverable through a variety of approaches. Microwave-assisted pyrolysis of urban waste sludge was applied for the production of oil, (Syn)gas, and biochar that were afterwards characterized and compared to mainstream alternative fuels (biodiesels) and other material recovery options. Sustainability issues related to the production of biodiesel/biochars from urban wastewater treatment sludge are also discussed. The paper shows that waste urban sludge can indeed be a full component of the urban circular economy by allowing, if properly processed, recovery of energy resources at multiple levels: bio-oils (biodiesel), syngas and biochar, all having definite advantages for final residues use and disposal. Biodiesel, in particular, allowing energy recovery as liquid fuel, offers a much more flexible and efficient utilization.

Keywords: biochar, biodiesel, materials, microwaves, pyrolysis, sustainable energy, urban waste sludge.

Produção de energia (biodiesel) e recuperação de materiais (biochar) a partir da pirólise de resíduos de lodo urbano

RESUMO

A eliminação segura das lamas de esgoto é uma das questões mais urgentes no ciclo de tratamento de águas residuais: a nível da União Europeia, espera-se que a produção de lamas atinja 13 Mt até o ano 2020. Os custos de disposição das lamas podem constituir-se e às vezes acima de 50% Custo total de operação de uma ETAR e contribui para mais de 40% das emissões de GEEs. As opções de eliminação mais comuns no momento são: aterro, eliminação na agricultura (cerca de 40% em toda a escala), incineração ou co-incineração, uso na produção

industrial de tijolos, asfaltos, concreto. As lamas de esgoto, no entanto, ainda contêm recursos benéficos, como nutrientes, que podem ser recuperados através de processos específicos (por exemplo, precipitação como estruvita) e energia, recuperável através de uma variedade de abordagens. A pirólise assistida por microondas de lama de lixo urbano foi aplicada para a produção de petróleo, gás (Syn) e biochar que posteriormente foram caracterizados e comparados aos principais combustíveis alternativos (biodiesels) e outras opções de recuperação de materiais. São discutidos os problemas de sustentabilidade relacionados à produção de biodiesel / biochars de lamas de tratamento de águas residuais urbanas. O documento mostra que o lodo urbano residual pode de fato ser um componente completo da economia circular urbana, permitindo, se devidamente processado, a recuperação de recursos energéticos em vários níveis: bio-óleos (biodiesel), gás de síntese e bio-carbon, todos com vantagens definidas para o uso e eliminação de resíduos finais. O biodiesel, em particular, que permite a recuperação de energia como combustível líquido, oferece uma utilização muito mais flexível (e eficiente).

Palavras-chave: biochar, biodiesel, energia sustentável, lodo de resíduos urbanos, micro-ondas, pirólise.

1. INTRODUCTION

Residual urban sludge disposal costs may constitute up to, and sometimes above, 50% of the total cost of operation of Wastewater Treatment Plants (WWTPs) and contribute more than 40% of the total greenhouse gas (GHG) emissions associated with their operation (Liu et al., 2013). The safe disposal of such sludge is literally a “big” issue in urban wastewater treatment: at the European Union level, the 2020 sludge production is expected to reach close to 13 Mt by year 2020, an increase of more than 30% from today’s levels. According to Machado (2001), urban waste sludge production in Brazil is much lower (about 150 Kt per year) since about 80 million people in Brazil do not have their wastewater collected by centralized systems, but disposed of through separate unitary (septic tanks) systems, in which there is no centralized control over the final destination of excess organic solids. Part of the population have their wastewater collected by communal systems, but not yet treated. In practice, only less than 45 million Brazilians get their wastewater treated. Clearly, the size of the issue will inevitably increase as wastewater collection and treatment in Brazil increases, as has been seen elsewhere in the world. In 2008, the United Nations Human Settlement Programme more than doubled the previous estimate by Machado for the country, updating it to 370 kt per year (Mateo-Sagasta et al., 2015).

Traditionally, wastewater sludges are processed for: a) reduction of total weight and volume to facilitate their transport and subsequent treatments; b) stabilization of contained organic material and destruction of pathogenic microorganisms, elimination of noxious odours, and reduction of putrefaction potential; and, for the last few decades, and at an increasing degree, c) value addition by developing economically viable recovery of energy and residual constituents, such as nutrients, that can be recovered through specific processes (e.g. precipitation as struvite), and energy, recoverable through a variety of approaches.

Wastewater still contains significant amounts of resources (i.e. nutrients) and energy; most of these end up, after treatment, immobilized in residual sludge. According to Shizas and Bagley (2004) the theoretical chemical energy content of wastewater is approximately 3 kJ/g (dry w.), which is roughly 10 times the energy expenditure necessary to treat the same wastewater in a current-technology WWTP. As of today, conventional technology allows the recovery, through anaerobic sludge digestion, of just a small fraction of that estimated value, allowing WWTPs to cover at most $\frac{1}{4}$ to $\frac{1}{2}$ of their energy needs (Capodaglio et al., 2017). By

sheer mass balance proportions, wastewater sludge can be shown to contain about 5 times the energy stored in wastewater. Table 1 illustrates some figures reported by different researchers.

Table 1. Energy content estimates (kJ/g dry w.) for different sludge types.

Primary Sludge	Secondary Sludge	Digested Sludge	Source
15.9	12.4	12.7	Shizas and Bagley (2004)
15	13.5	11.4	Zanoni and Mueller (1982)
n.a.	n.a.	12.6	Vesilind and Ramsey (1996)

In Table 1, digested sludge refers to sludge processes through secondary (anaerobic) digestion after a first-stage liquid treatment. In Brazil and other South American countries, it is common practice nowadays to treat urban wastewaters through UASB processes (Capodaglio, 2017) as this process is much less energy-intensive, and could be almost as efficient as traditional aerobic processes used in EU and the USA, due to the local, favorable climatic conditions. UASB processes can, in theory, also allow energy recovery from wastewater; however, in the few full-scale applications visited by the authors, this was rarely implemented in practice. In any case, the residual energetic value of anaerobic sludge after a UASB process should be comparable to the values indicated in Table 1 for digested sludge.

The EU Landfill Directive 99/31/EC sets restrictions (quantitative targets) for biodegradable municipal wastes (such as sewage sludge) disposed of in landfills; in addition, the national legislation of some Member States have set very strict limits for organic matter or total organic carbon (TOC) contained in disposed-of sludge, prohibiting *de facto* its landfilling. According to recent Eurostat data, in fact, significant abandonment of sludge landfilling practices is occurring in most of Europe, except for Italy, Denmark, and Estonia. Sewage Sludge Directive 86/278/EEC, concerning beneficial use of sludge on soils, initially sought to encourage safe use of sewage sludge in agriculture, regulating this form of disposal to prevent harmful effects. After concerns raised about possible harmful accumulation of compounds in soils, 16 (out of 27) EU countries have set more stringent requirements for heavy metals in sludge, compared to the Directive's provisions, and 10 countries set stricter limit values for heavy metals in soil. Such restrictions are being strengthened periodically, while most EU countries have outright prohibited the disposal of untreated sludge in soil. Composting is applied more often in the new EU-12 countries, compared to the old EU-15.

Finally, incineration is enforced in most EU-15 countries. Greece, Slovenia, Germany and Netherlands present the greatest increasing trends, even though the first two countries export sludge for incineration; Denmark, Austria, Belgium and Italy show instead decreasing incineration trends (Kelessidis and Stasinakis, 2012).

Thermal processing of sludge remains, however, a convenient and efficient approach for the disposal of waste urban sludge without causing excess secondary pollution, which is used as much as possible in many countries. Thermal utilization of sludge comes into play when the sludge does not comply with, or is in excess of, requirements for disposal in agriculture, and allows forms of energetic recovery. Thermal processing of sludges can take several forms. Co-firing in power plants and heating plants with coal (approximately 5% sludge) does not significantly decrease the temperature of the combustion process, and usually does not require extra investment costs for off-gas cleaning, as existing filters and separators can handle this extra component. Co-firing in cement kilns was considered the most convenient technology in terms of both sludge disposal and utilization: one ton of dried sludge can substitute up to 0.33 t of raw material and, since ash from sludge is bound to cement clinker, this can actually be considered a waste-less technology. This is also considered a “waste-to-energy” system, and is acceptable if no other environmentally friendly technology can be applied (Capodaglio et al.,

2016a). Incineration (with urban solid waste, or in special sludge incinerators) is another option, where the energy contained in the sludge contributes to the energy balance of the process.

Sewage sludge is usually processed, prior to disposal, in anaerobic tanks to produce biogas, a mixture of CH_4 and CO_2 that can be used as such, or further refined to obtain bio-methane, a renewable fuel with characteristics practically identical to those of fossil methane (Capodaglio et al., 2016b).

However, recent work has demonstrated that the production of biodiesel using lipids extracted from sewage sludge could be economically feasible because of the remarkably high yield of oil and low cost of this feedstock.

Recent work has demonstrated that production of biodiesel from lipids contained in sewage sludge, largely regardless of its upstream production processes (i.e. WWTP technology), could be an alternative, economically feasible technique for energy recovery from waste biological sludges, as compared to conventional biodiesel feedstocks (Bharathiraja et al, 2014), thanks to high oil yields, as shown in several studies (Olkiewicz et al., 2012; Capodaglio et al., 2016c).

Furthermore, while conventional biodiesel feedstocks is usually expensive and competing with other uses (e.g. food for animals, or people), waste sludge is abundant, costly to dispose of under traditional schemes, and therefore should be available almost everywhere at very low, or no cost, as a feedstock.

Brazil has a standing tradition of biodiesel uses, derived from both food and non-food crops, and from various food-waste products (e.g. spent frying oils). This type of solution is widely supported by the Brazilian government within its Biodiesel Production and Use Program (BPUP), which favours renewable energies, specifically addressing energy self-sustainability of isolated rural communities (Torres et al., 2013). No references were found, however, concerning the recovery of biodiesel and materials from urban waste sludge in Brazil. This is probably due to the fact that the sludge disposal problem has not reached critical proportions as it did in several in several EU member states.

Several technologies have been studied for this purpose worldwide. While transesterification is perhaps the most-used biodiesel-extraction process in Brazil, pyrolysis could be a technology to consider, not only in urban waste sludge processing, but also in other energy/materials recovery chains, as it allows useful recovery of energy and materials at different levels. These include pyrolysis, hydrothermal liquefaction, wet oxidation, supercritical water oxidation, sequential methane/hexanol distillation (Demirbas, 2001). These, once process-validated and industrially tested, could be considered not only as viable alternative processes for sludge disposal, but also sustainable, environmental-compliant biodiesel production processes. In addition to biodiesel, waste urban sludge may provide, as by-products, other substrates of notable energetic and material values, such as biochar.

Studies show that for oil extracted from waste sludge, the energy gain is up to 29.7 GJ/ton (Zhang et al., 2013). Furthermore, GHG emissions studies show that biodiesel production from sludge is a net carbon dioxide capture process, with the highest capture being around 40 t CO_2 /t biodiesel produced. Sludge-derived biodiesel, finally, has a lower Global Warming Potential (GWP) than most other renewable biodiesels (Table 2) with the exception of biodiesel derived from waste vegetable oils (Dufour and Iribarren, 2012).

Table 2. Comparison of GWP (kg CO_2 equivalent) of different biofuels.

Biodiesel type	Waste vegetable oil	Beef tallow	Poultry fat	Sewage sludge	Soybean	Rapeseed	Low-sulphur Fossil Diesel
GWP (kg CO_2 -eq)	16.97	23.32	23.55	20.84	26.18	63.23	83.69

This paper illustrates experimental findings from the application of pyrolysis treatment to urban waste sludge, and describes possible recovery pathways of energy and materials from that feedstock. In addition to the benefits in potentially contributing to solve the significant problem of the ultimate disposal of urban waste sludge, this technology could be instrumental in supporting current government commitments (e.g. EU's under Directive 2003/30/EC, on the promotion of biofuels for transport) to achieve in the next coming years higher fractional targets of bio-oils' content in commercial fuels (e.g. 10% by 2020 in the EU) (Raboni et al., 2015).

2. MATERIALS AND METHODS

Pyrolysis is a thermal-decomposition process, carried out in the absence of O₂, that converts biomass into solid charcoal (biochar), bio-oil (biodiesel, or SSPO, Sewage Sludge Pyrolysis Oil), and gaseous products (syngas) at elevated temperatures (generally more than 500°C) and atmospheric pressure. It is one of the most efficient processes for biomass conversion discovered and industrially adopted to date. Recovered SSPOs are a complex mixture of aliphatic, aromatic and poly-aromatic hydrocarbons, long carbon-chain organic acids and alcohols, etc. (Pokorna et al., 2009), very similar in properties to diesel fuel (hence the alternative term, "biodiesel").

Pyrolysis not only can be used to transform biomass of various origins and other waste materials (e.g. rubber tyres) into bio-oil, biochar, and syngas, of varied characteristics (depending on initial feedstock and actual process operating conditions), but also allows for variation in the ratios between different product fractions, according to process temperature profiles and duration. In a sense, pyrolysis allows the user to choose among the three possible final products, according the best-fitting combination required by local reuse/recycle needs (Capodaglio et al., 2016c).

While the advantage of obtaining sludge-derived liquid fuels is easily obvious to most, more so than gaseous fuel, which is subject to greater transportation and use challenges than the former, the solid fraction residue from the process (biochar) also has been found to have several useful, unexpected applications. Biochar is a new technical term indicating "*the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment*" (Shackley et al., 2012). Biochar could in theory be used to generate energy (it has an energy content that, depending on the process used for its production, can be even > 18 MJ/kg); however, biochar is recently getting much attention from the scientific community due to its various use potentials. Given its properties, it is clear that the concept of biochar production from sewage sludge has become increasingly popular in recent years.

Microwave technology has recently emerged as one of the most promising methods of enhancing and accelerating chemical reactions, due to efficient heat-transfer profiles. It is therefore being adopted as one of the best technologies available in pyrolytic processes, since it reduces residence time and brings significant energy savings (Motasemi and Azfal, 2013). Microwave-assisted pyrolysis (MAP) technology is an alternative heating method already in use in biomass pyrolysis for biofuels production, presenting several advantages over conventional pyrolysis, including: uniform internal heating for material particles, since electromagnetic energy is directly converted into heat at a molecular level; ease of control due to its instantaneous response; simple set-up, facilitating its adaptation to large-scale industrial processes; reduced need for feedstock grinding; and low cost, as microwave is a mature and energy-efficient technology. The different heating mechanisms make MAP products retain different characteristics from those obtained with conventional heating. In addition, MAP takes a much shorter process time than conventional pyrolysis (Menendez et al., 2002; Leszczynski, 2006), as the heating of the feedstock biomass is more uniform.

Using monomodal microwave synthesizers (MMS) instead of multimodal ones, the need for preliminary mixing dry sludge with microwave receptors additives reported by earlier researchers could also be eliminated, and the process temperature needed for process completion is significantly lowered (as low as 270°C), allowing the production of a larger liquid product (biodiesel) fraction (Capodaglio et al., 2016c). Detailed description of pyrolysis, MAP and MMS-driven pyrolysis are given by Masek et al. (2013).

The apparatus shown in Figure 1 was used to expose sludge samples to MAP. The experimental apparatus consists of a pure quartz cuvette (Fig. 1[a]), capable of withstanding high temperatures exceeding 1000°C, with a cavity (Fig. 1 [b]) containing the sludge sample (15-25 g) being treated. A MMS, unlike a conventional (multimodal) cooking microwave oven, is capable of matching the impedance between the load to be irradiated and the microwave-generator (magnetron), thus maximizing the power transfer to the samples. With an MMS appropriately tuned, it is also possible to irradiate dry samples, eliminating the need reported by previous researchers to add microwave receptors to the sludge, a task impossible to achieve with traditional microwave ovens that heat contents indirectly, by agitation of the water molecules contained in the samples. A triple-stub matching device (MD, Alter Systems, Fig. 1[e]) connected with the magnetron was used to balance reflective coefficients within the system, allowing the creation of an optimal electric field intensity in the cavity containing the sample.

Sludge samples were prepared from dewatered waste sludge obtained from the local municipal WWTP that had already undergone an anaerobic digestion process. Samples were further desiccated at 60°C for 24 hours in order to further reduce their water content to around 73.5%, while minimizing any possible reaction that could modify their organic content. This desiccation phase will be the object of additional considerations about the sustainability of the process at the full-scale. The desiccated sample was then ground to a fine powder, and pyrolyzed in this apparatus.

Determination of oil content was made after condensation of process evaporate with a Soxhlet extractor after each test (See Tests 1-7 in Table 3), and its chemical characterization was then performed by GC-MS spectrometry. Test conditions varied according to maximum temperature achieved in the cuvette, time of sample exposure to maximum temperature, time-to maximum temperature (heating rate of sample). Biochar characterization was achieved after grinding and sieving to < 0.5 mm the resulting product. Determination of volatile matter and ash content was conducted according to ASTM-D1752-84, elemental composition (C, H, N) assessed by an elemental analyser (Thermo Fisher Scientific, MA. USA), O content by Vario El Cube (Elementar Analysensysteme, GmbH).

Table 3 shows temperature, duration and quantity of extracted oils from the tests conducted. The greatest oil yields were observed between 270 and 500°C. Below 200°C, the oil quantity obtained is very small; over 500°C, there is still some production.

3. RESULTS AND DISCUSSION

The highest oil yield was obtained at the test temperature of 280°C (25.0% oil to organics sludge fraction, 12.52% oil to total sludge, weight basis) and short process duration. Higher temperatures and longer process times tend to increase the amounts of generated gaseous and solid fractions.

GC-MS analysis of extracted oil samples, diluted with dichloromethane, show the following composition (Figure 2). Toluene and styrene do not show in some of the graph lines due to the high dilution ratio adopted for analysis; however, they were detected in the raw oil samples. From lower to higher retention times (left to right in the graphs) MS identifies aromatic

hydrocarbons (containing one or more aromatic rings in their molecular structure), nitrogenous compounds, alkanes, carboxylic acids (containing the $-\text{COOH}$ or the $-\text{OH}$ groups linked to a carbonyl group C=O), sterols and derivatives.

The lower calorific value (LCV) of the biodiesel obtained, is slightly lower than the one obtained from energy crops. Sludge-derived biodiesel LCV was about 33 kJ/g (in the range 33-35 kJ/g for all tests), against that from corn and safflower at 42-43 kJ/g, or the one from coconut feedstock at 38 kJ/g commonly reported (Capodaglio et al., 2016c). Compared with fossil diesel, therefore, this sludge-derived oil has an LCV that is about 30% lower. LCV will vary according to process conditions: at higher process temperatures, the LCV of obtained bio-oil will tend to be lower for the same feedstock.

Figure 1. The experimental MMS apparatus.

Table 3. Tests conditions and oil yields.

	Max Test Temp. °C	Time at T_{MAX} [min]	Total process Time [min]	% oil to total sludge	% oil to sludge org. fraction
SLUDGE AS IS	60	=	=	3.57*	7*
TEST 1	180	28	50	3.30	7
TEST 2	270	20	55	9.68	19
TEST 3	280	2	8	12.52	25
TEST 4	400	2	18	10.77	22
TEST 5	490	1	54	10.25	21
TEST 6	600	3	56	8.71	17
TEST 7	650	-	60	7.38	15

*extraction with solvent from original sample.

Figure 2. Superimposed GC-MS analytical results for the oil extracted in the different tests (From Capodaglio et al., 2016c).

Syngas is primarily composed of H_2 and CO , with smaller quantities of CH_4 , CO_2 , H_2O , and other low molecular-weight volatile organics. While its heating value is low ($\sim 6 \text{ MJ kg}^{-1}$) compared to natural gas ($\sim 54 \text{ MJ kg}^{-1}$), it can provide fuel for hot water, sludge pre-drying or electricity onsite. Given the low LCV and its “dirty” composition, it is usually not considered worthy of further processing (unless purposefully generated in high quantities). Some time ago, before widespread availability of natural gas, syngas was generated to provide energy for home heating, cooking, street lighting, etc. (a.k.a. “town gas”). At the moment, although providing some residual energetic value, syngas is the least interesting product of waste sludge pyrolysis.

Biochar is the solid residue of the process, with high energy content, that can be therefore burned in systems fed with pulverized coal. NO_x emissions from biochar combustion are comparable to those of coal, requiring similar abatement technologies. Some types of feedstock (i.e. urban sludge) may contain relatively high levels of metals that concentrate in the biochar after pyrolysis. Biochars, however, may also have many other attractive, high value uses, in fields such as chemistry, metallurgy, agriculture, waste treatment, etc. Table 4 shows characteristics of biochar derived from sewage sludges with traditional and microwave-assisted pyrolysis, by the authors and in other studies. As it can be seen, the characteristics of the material vary according to the process adopted and depending on the origin of the feedstock material. Table 5 shows some of the main ash components of sewage sludge biochar from different origins. Process operational temperature has a substantial effect on the quality of biochar produced: biochar produced at low temperatures is most suitable for agricultural uses, due to carbon content and nutrient availability, while higher temperatures can improve its porosity and thus enhance its effectiveness in adsorbing contaminants present in soils (Agrafioti et al., 2013). Researchers have also shown that the pyrolysis process can suppress heavy metal release by non-impregnated biochars, resulting in an extremely low environmental risk using sludge-derived biochar as soil amendment (unlike the case of sludge as is). Biochars can be obtained under different processes and feedstocks; they significantly differ from one to another in their properties, depending on the type of biomass used to produce them, its growth conditions and also on pyrolysis operating conditions.

It has already been recognized that oils derived from wastewater sludge are comparable replacements of traditional biodiesel production feedstock (Bharathiraja et al., 2014). In order to assess the sustainability of biodiesel production from this source, energy balance and greenhouse gas (GHG) emissions are also essential factors to consider.

It has been reported that biodiesel produced from two major food crop feedstocks, soybean and sunflower oils, has an energetically unfavorable energy balance, due to the low-oil yield of the crops, translating to a process energy loss of 32% for soybean, and 118% for sunflower (Pimentel and Patzek, 2005). Therefore, replacement of traditional feedstock with better-suited raw or recovered materials is continuously being investigated. Wastewater sludge fulfils the basic general requirements of alternative feedstocks, that should be abundant, sustainable, and energetically favorable (i.e. generate a positive energy balance).

Sludge-derived biodiesel thus has a lower Global Warming Potential (GWP) than most other renewable biodiesels with the exception of biodiesel derived from waste vegetable oils (Dufour and Iribarren, 2012; Capodaglio and Callegari, 2017). Compared to conventional low-sulphur diesel as a benchmark, a 75.1% reduction for use of sludge-derived biodiesel can be achieved.

The transformation of waste sludge in biochar by pyrolysis has also some relevant environmental advantages. In the introductory section a brief review of the existing methods of excess sewage sludge disposal was presented. In addition to the saved costs for the otherwise necessary disposal of sewage sludge, this section shows the beneficial (added-values) uses by which biochar can become a resource.

The most appealing feature of biochar is the fact that it is an inexpensive, sustainable and easily-produced material with potentially extensive applications. Even though most of those applications are still in their infancy, biochar already has a number of identified applications with potentially extraordinary effects, including soil amendment, catalysis, water purification, and many others still to be invented or discovered.

Beneficial effects of biochar on agricultural crops yield and properties of soil have been studied, showing significant improvement in the yield of crops (Chan et al., 2008). Biochar addition is known to improve nitrogen fertiliser-use efficiency by improving the chemical properties of soil. It significantly increases soil C content, and improves crop productivity. Wastewater sludge biochar application was specifically found to increase soil cation exchange capacity (CEC) by up to 40%, and soil pH by up to one unit (Hossain et al., 2010), with improvement of plant available nutrients, and carbon sequestration.

Biochars are receptive to complex metal ions present in the soil on their surfaces and therefore reduce their bioavailability, resulting in a reduced risk. Studies detected insignificant bioaccumulation in crops of metals present in wastewater-sludge biochar. In addition, biochar is known to have positive effects on soil quality, as it enhances soil aeration, increasing water holding capacity and improved environmental conditions for the growth and development of plant root systems.

Table 4. Characteristics of biochar derived from sewage sludges with traditional and microwave-assisted pyrolysis.

Source	Zielinska et al. (2015)				Lu et al. (2013)			Agrafioti et al. (2013)			Antunes et al. (2013)			Authors (this paper)		
Type of sludge	Municipal WWTPs (4)				Municipal WWTPs (3)			Municipal WWTP			Municipal WWTP			Municipal WWTP		
Pyrolysis process	Traditional slow				Traditional slow			Traditional			MAP			Monomodal Microwave-assisted		
Sample/Temp. °C	Original	500	600	700	Original	300	600	Original	300	500	Original	300	800	Original	270	500
Yield (% dry w.)	-	45-54	43-51	40-49	-	n.d.	n.d.	-	58.1-64	27-31	-	91	77	-	-	-
Ash content (%)	55.8-61.3	64-73	63-77	68-79	n.d.	n.d.	n.d.	25.9	n.d.	n.d.	55.5	55.8	63.3	52-55	54-57	58-61
Carbon (C, %)	21.6-26.2	18.9-26.6	18.4-27.7	18.1-27.8	23.8-33.2	21.7-31.5	15.2-26	37.9	39.7	9.8	19.9			22-25	20-22	17-21
(O+N)/C	0.32-0.66	0.25-0.29	0.15-0.28	0.09-0.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1			-	-	-
S_{micro} (m ² g ⁻¹) (Micropore surf.)	-	7.1-19.4	2.8-7.7	1.4-27.7	-	4-6.7	6.3-18.2	-	0.5-18	4-90	16.64	50.06	64.67	-	-	-
pH	7.01-7.39	7.08-7.25	80.5-11.4	12.2-13.1	6.08	6.2	9.6	5.9	6.0	11.6	6.13	6.42	6.6	7.2-7.45	7.3-7.55	7.5-7.88

Table 5. Main ash components for some reported biomass feedstocks.

Source	Zielinska et al. (2015)				Lu et al. (2013) (note different data units)			Authors (this paper)		
Sample/Temp °C	Original	500	600	700	Original	300	600	Original	270	500
Fe (% d.w.)	1.1-6.8	2.4-11.5	2.37-12.5	2.6-13.2	0.8-23.2*	18.6-37.6*	0.06-43.2*	2.2-4.9	2.8-7.3	3.68-9.4
Si (% d.w.)	2.5-5.8	4.8-9.1	5.1-9.4	5.5-97	-	-	-	2.8-5.3	3.6-8.6	4.6-10.2
P (% d.w.)	3.4-4.9	5.4-9.6	5.3-9.2	5.6-9.5	20-28.4*	29.5-42.6*	35.5-57.6*	3.6-4.5	4.72-7.18	5.2-9.82
S (% d.w.)	1.5-3.8	1.37-4.6	1.2-3.97	1.37-5.2	0.7-1.1	0.5-0.67	0.43-0.57	1.65-4.02	1.88-4.5	1.85-4.3
Al (% d.w.)	1.8-2.5	2.3-3.3	2.6-3.7	2.7-3.9	26.2-31*	38.1-52*	50.8-55.2*	1.98-2.75	2.17-2.94	2.15-3.33
Mg (% d.w.)	0.57-2	0.9-3.3	1.08-2.6	1.1-2.4	4.1-6.3*	8.2-11*	9.3-14.5*	0.8-2.3	0.85-2.87	1.03-3.06
K (% d.w.)	0.5-0.8	0.9-1.4	1.0-1.55	1.1-1.64	0.8-1.2*	1.6-2.1*	2.6-2.8*	0.6-0.95	0.7-1.1	0.69-1.6

Benefits associated with applying biochars to soils, comparable to those of activated carbon, have been reported (Beesley et al., 2011). It was shown that increasing the pyrolysis temperature of biochars increases their degree of carbonisation, surface area, and reduces the abundance of amorphous organic matter. This also increases biochars' capability to also adsorb organic contaminants (Yu et al., 2009). Biochars obtained at high temperatures ("activated") will have the highest organic contaminant remediation potential.

Lately, biochar has been indicated as a possible substitute resource for several industrial applications in electronic and industrial applications (Huggins et al., 2014; Liu et al., 2012; Tan et al., 2015).

4. CONCLUSIONS

It has been herein shown that waste urban sludge can be a full component of the urban circular economy by allowing, if properly processed, recovery of energy resources at multiple levels: bio-oils (biodiesel), syngas and bio-char. These have properties that make them particularly attractive as secondary resources: bio-oils are similar in characteristics to diesel fuels, and could be used as transportation fuel or as a source of chemicals extraction; biochar has some very interesting agricultural and non-agricultural applications, and these will undoubtedly increase in the future. Biofuels' future production and use in the transport sector will be much more diversified, with biodiesel playing a greater role. The estimated growth of biodiesel production presents a fundamental issue of social sustainability due to land use for energy crops rather than food. The use of alternative renewable feedstocks such as wastewater sludge could provide support to the development of this sector, while solving a specific problem. Quantities of sewage sludge produced worldwide are increasingly growing, demanding environmentally and economically sound management in compliance with laws and regulations. Traditional disposal pathways are increasingly costly and may not be practicable in the future, due to new regulations or to diminishing public acceptance.

Use of urban waste sludge as oil-and-char feedstock has definite advantages for final residues' use and disposal; energy recovery as liquid fuel offer much more flexible (and efficient) utilization possibilities. Flexibility and multiple possibilities in the use of biochar may soon become an interesting economic issue in orienting the production of pyrolysis by-products towards economic maximization of possible returns, while significantly reducing overall GHGs emissions due to urban waste sludge disposal.

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Characterization of controlled landfill leachate from the city of Guaratinguetá - SP, Brazil

ARTICLES doi:10.4136/ambi-agua.2136

Received: 21 May 2017; Accepted: 07 Jan. 2018

**André Luis de Castro Peixoto¹; Rodrigo Fernando dos Santos Salazar^{2*};
Jayne Carlos de Souza Barboza³; Hécio José Izário Filho³**

¹Instituto Federal de Educação, Ciência e Tecnologia de São Paulo (IFSP), Capivari, SP, Brasil
Departamento de Química. E-mail: alcpeixoto@ifsp.edu.br

²Universidade de Cruz Alta (UNICRUZ), Cruz Alta, RS, Brasil
Centro de Ciências da Saúde e Agrárias (CCSA), Departamento de Engenharia Ambiental e Sanitária
E-mail: r.f.s.salazar@gmail.com

³Escola de Engenharia de Lorena (EEL-USP), Lorena, SP, Brasil
Departamento de Engenharia Química. E-mail: jayne@dequi.eel.usp.br, helcio@dequi.eel.usp.br

*Corresponding author

ABSTRACT

This research evaluated the physicochemical parameters of a leachate sample from a controlled landfill in the city of Guaratinguetá-SP. The evaluation was conducted using spectrometric and spectrophotometric methods in order to assess the formation of persistent compounds. The selection of parameters was based on the CETESB Article 18 and CONAMA 357/05 Article 34, as well as organic characterization methods, such as FTIR, NMR (1H-NMR, 13C-NMR and APT), GC-MS, molar mass distribution and elemental analysis (CHN). Chemical and physical stability were also verified. The ammoniacal nitrogen concentration is 20 times greater than tolerance limit established by law (20 mg L⁻¹). The Ba and Ni presented concentrations above those permitted by the legislation (CETESB Article 18 and CONAMA 357/05 Article 34). Those values of chemical oxygen demand (COD) and total organic carbon (TOC) were 1013 mg L⁻¹ and 286 mg L⁻¹, respectively. It was not possible to determine the biochemical oxygen demand (BOD) of slurry sample. In this sense, the biodegradability parameter for the slurry studied was Non-Determinable (ND), indicating that the organic matter of the slurry studied is recalcitrant. Recalcitrant humic substances of landfill leachate the present low polydispersity. These refractory acids play a detached role in carrying pollutants in the environment with regard to carrying toxic metals and pesticides. Finally, it was possible to verify that the humic acids' complexing capacity indicates that hydroxyl and carboxyl groups may exist in larger quantities than the nitrogen and sulfur groups. Further, the high content of metals may indicate that the waste was not properly separated.

Keywords: landfill leachate, leachate, physicochemical characterization, solid waste management, spectroscopic methods.

Caracterização do chorume proveniente do aterro controlado da cidade de Guaratinguetá – SP, Brasil

RESUMO

O objetivo deste trabalho foi avaliar os atributos físico-químicos do lixiviado de aterro controlado na cidade de Guaratinguetá-SP por métodos espectrométricos e espectrofotométricos para avaliar a formação de compostos persistentes. Além dos métodos de caracterização orgânica, como FTIR, RMN (RMN ^1H , RMN ^{13}C e APT), CG-MS, distribuição de massa molar e análise elementar (CHN), os parâmetros proporcionados no Artigo 18 da CETESB e no artigo 34 do CONAMA 357/05. A estabilidade química e física foi verificada medida que foi sendo feita a caracterização analítica. A concentração de nitrogênio amoniacal é 20 vezes maior que a fornecida (20 mg L $^{-1}$). Os Ba e Ni apresentaram concentrações acima das permitidas pela legislação (Artigo 18 da CETESB e Artigo 34 da CONAMA 357/05). Os valores de demanda química de oxigênio (DQO) e carbono orgânico total (TOC) foram de 1013 mg L $^{-1}$ e 286 mg L $^{-1}$, respectivamente. A demanda bioquímica de oxigênio não foi determinada. Não foi possível determinar a demanda bioquímica de oxigênio (DBO), indicando que a matéria orgânica da pasta estudada é recalcitrante. Substâncias húmicas recalcitrantes de aterros lixiviam a baixa polidispersidade presente. Estes ácidos refractários desempenham um papel destacado no transporte de poluentes no ambiente para ser capaz de transportar metais tóxicos e pesticidas. Por fim, foi possível verificar a capacidade de complexação de ácidos húmicos que indica que os grupos hidroxila e carboxila podem existir em maiores quantidades do que os grupos nitrogênio e enxofre. Além disso, o alto teor de metais pode indicar que os resíduos não foram adequadamente separados.

Palavras-chave: caracterização físico-química, chorume, gerenciamento de resíduo sólido, lixiviado de aterro, métodos espectroscópicos.

1. INTRODUCTION

Solid wastes are defined by standard NBR 10.004:2004 (ABNT, 2004) as wastes in the solid and semi-solid state resulting from industrial, domestic, hospital, commercial, agricultural, services and sweeping activities (Silva et al., 2016; 2017). Their physical, chemical and biological characteristics vary according to their source or generating activity (Klein et al., 2017; Zhang et al., 2017a). Economic, social, geographic, educational, cultural, technological and legal factors affect the solid-waste-generation process concerning the qualitative and quantitative attributes (Li et al., 2017; Peng, 2017). Once generated, the waste may have its characteristics altered due to the management employed, which may result in waste with great harmful potential to public health and to the environment (Mandal et al., 2017; Silva et al., 2016; 2017; Li et al., 2017).

The formerly controlled landfill in the city of Guaratinguetá, in the State of São Paulo, in the Paraíba Valley region, worked as a garbage disposal site for 30 years, being deactivated in 2006. The controlled landfill had a total area of 30,000 m 2 , located on Estrada Américo Ranieri, in the Santa Luzia Neighborhood. For many years, the landfill's major characteristics were stench, fly and insect proliferation, and a large number of garbage diggers with varying age ranges. According to information from the Secretariat of Urban Services of Guaratinguetá (Municipal Administration 2004/2007), the municipality landfill received about 60 tons of garbage a day, produced by around 110,000 inhabitants. This controlled landfill was used to dispose of solid urban waste (SUW) which was compacted after being deposited in the site. The

place is currently an Ecological Park, an initiative by the Guaratinguetá Autonomous Water and Sewage Services (SAAEG Municipal Company).

Although the controlled landfill has been deactivated, the slurry and wastewater keep being generated once the landfill keeps presenting decomposition reactions of the organic parcel until the wastes disposed of have been fully stabilized (Klein et al., 2017; Mandal et al., 2017; Van Turnhout, 2018). However, the liquid waste generated will be a polluting source of underground waters of the whole region circumscribed for a number of years, owing to the toxic character of the slurry gradually liberated with the decomposition of the organic matter and of the inorganic load leaching, since the effluent is not adequately collected by means of blanket and lateral ducts (Peng, 2017; Zhang et al, 2017a; 2017b). This occurs because this landfill does not meet some design requirements listed in the National Policy for Solid Wastes (Brazil) (Silva et al., 2016; 2017). It is therefore necessary to permanently characterize the physical-chemical parameters of the leachate material from the controlled landfill as a way of monitoring the landfill activity, and to propose solutions to possible remediation (Gomes et al., 2016; Peng, 2017; Mandal et al., 2017; Mohammad-Pajooch et al., 2017).

Nuclear Magnetic Resonance (NMR) is able to provide chemical structure information of whole organic matter, allowing the investigation of humus-containing samples without extraction and fractionation. Resonance regions can be assigned to lignin aromatic, alkyl, O-substituted alkyl, carboxyl- and carbonyl-C (Lü et al., 2018). The principle means to explain FTIR spectra is by identifying the bands relating to humus generation (e.g. unsaturated C=C, aromatic C=C) and organic matter degradation (e.g., aliphatic, hydroxyl phenols, carboxylic acids, N-H stretching, peptidic, C=O of carboxylic acids, ketones, and aldehydes, COO of carboxylic acids, polysaccharides, alcohols, amines, amide, alkenes, ethers, esters). Despite the amount of FTIR, and NMR data discussed in the literature, the mechanism of humification of municipal waste is not yet completely understood (Lü et al., 2018). Lenz et al. (2016) studied six different abandoned Austrian municipal landfills wherein different sections were sampled quarterly over a period of 15 months. Several functional groups were assigned such as primary amides, aliphatic methylene, thiole, aromatic ring modes, amines, aromatic compounds, carboxylic acids, carboxyl groups, etc. Xiaoli et al. (2013) studied elemental analysis, Fourier transform infrared spectroscopy (FTIR), and Carbon-13 Cross-Polarization Magic-Angle-Spinning Nuclear Magnetic Resonance (^{13}C CP/MAS NMR) were carried out to characterize the chemical and structural properties of humic acids (HA) extracted from the leachate of both semi-aerobic and anaerobic full-scale landfills. According to the study of Xiaoli et al. (2013), when the FTIR spectra of HA from the semi-aerobic and anaerobic landfills were compared, appreciable differences in resolution and strength of assigned peaks were found. The FTIR spectra for the semi-aerobic landfill HA displayed relatively higher adsorption intensity at 1560 cm^{-1} than the anaerobic HA, which suggested that it may have more aromatic ring or NH structures. By comparison, the relative adsorption intensity at 1120 cm^{-1} and 1046 cm^{-1} of the anaerobic landfill was stronger than that of the HA from the semi-aerobic landfill, which indicated that the anaerobic landfill HA contained more stabilized components, such as polysaccharides or polysaccharide-like substances. The FTIR spectra of peaks at $1560\text{--}1575\text{ cm}^{-1}$ and $1640\text{--}50\text{ cm}^{-1}$, which, associated with aromatic C=C, strongly increased with the extension of the stabilization process. The peaks eventually merged to become one adsorption band at $1601\text{--}1645\text{ cm}^{-1}$. This finding suggested that the aromatic group content in HA rose significantly over time. The FTIR spectra of intensive peaks at 1400 cm^{-1} relates to for the aliphatic group content in HA. It decreased as stabilization proceeded and ultimately disappeared, which indicates that the aliphatic group component decreased over time.

Gel Permeation Chromatography (GPC) and Elemental CHN analysis are able to complement the characterization information from NMR and FTIR. Xiao et al. (2013) investigated degradation of landfill leachate after its characterization (sanitary landfill from

Beijing, China). The chromatogram of raw leachate had a molecular weight (MW) distribution of UV₂₅₄ active components with a retention time between 11–15 min. According to the separation mechanism of GPC, higher MW compounds were eluted earlier. The raw leachate consisted of higher MW compounds ranging from 300 to 2000 Da. Morozesk et al. (2017) characterized humic acids, derived from landfill leachate (Brazil, 20° 27' 28" S 40° 23' 21" W) by elemental analysis. The authors found C content of 398.47 g kg⁻¹, H of 70.60 g kg⁻¹, N of 59.78 g kg⁻¹, and O of 471.15 g kg⁻¹. The C/N ratio of 56.50 in landfill HA was due to high nitrogen levels in these compounds, evidencing their potential as an important nitrogenous source.

In this sense, we here assessed the physical-chemical and microbiological attributes of the leachate of the controlled landfill in the city of Guaratinguetá-SP by spectrometric and spectrophotometric methods, according to the parameters provided in CETESB Article 18 (São Paulo, 1976) and CONAMA 357/05 Article 34 (CONAMA, 2005), and also employed organic characterization methods, such as FTIR, NMR (¹H-NMR, ¹³C-NMR and APT), GC-MS, molar mass distribution and elemental analysis (CHN); concurrently, chemical and physical stability was verified over time as a way of assessing the formation of compounds and complexes more refractory to those at the moment of sampling.

2. MATERIALS AND METHODS

2.1. Sampling, reagents and solutions

The landfill of the municipality of Guaratinguetá received about 60 tons of household waste per day, produced by about 110 thousand inhabitants. The leachate was collected in 2006 in channels arranged at the base of the municipal landfill (22° 48' 16.7" S 45° 13' 39.8" W). Initially, the slurry “*in natura*” (untreated landfill slurry) was homogenized by manual stirring in a plastic barrel, to ensure the reproducibility of the analytical results, seeing that the sample has complex physical-chemical characteristics (elements in the colloidal form or associated to the matter in suspension). The slurry was collected from the controlled landfill of Guaratinguetá a single time and homogenized by mechanical stirring, finally being stored at 4°C. The sampling was performed according to standard NBR 9898:1987 (ABNT, 1987).

All the chemical reagents were of the P.A. degree. The mineral acids used were of the Dinâmica brand. The metallic patterns used, with 1-mg mL⁻¹ concentration, were of the SpecSol brand with NIST traceability, Reagent organic solvents and other chemical reagents of the Vetec brand.

The solutions were prepared by employing analytical degree reagents, ultrapure water obtained from using Milli-Q (Millipore Corp, de Billerica, MA, EUA) water system at 18.2 MΩ cm resistivity, nitric and chloridric acid distilled in quartz sub-boiling (Milestone, Sorisole, Italy). To prevent contamination, the vials, glassware and polypropylene materials were washed and soaked in 10% v v⁻¹ HNO₃ and fully washed with deionized water.

2.2. Instrumentation

All the analytical determinations of the metallic elements of interest in the samples “*in natura*” were performed in an atomic absorption spectrometer (graphite flame and oven), using an Aanalyst 800 Model by PerkinElmer. The equipment presents a double-beam optical system (single beam for graphite oven operation); motorized monochrome of the Littrow type for automatically selecting wavelength, adjustment and alignment; work range from 185 to 870 nm, with 1800-line/mm diffraction grating and solid-state detector; background correction for flame, for deuterium lamp. The graphite oven has transversal heating, providing an even temperature profile, with background correction by longitudinal Zeeman effect.

Multi-elemental characterization constitutes of element determination at trace level ($\mu\text{g L}^{-1}$) (Ag, As, Cd, Cr, Hg, Pb and Se) and macroelements (mg L^{-1}) (B, Ba, Cu, Sn, Fe, Mn, Ni and Zn). The trace elements, macroelements and Hg were determined by employing GFAAS, FAAS and CVAAS, respectively.

2.2.1. Sample preparation for multi-element determination by AAS

To reduce the interference caused by the organic matter, and to convert metals associated to particles in a form capable of being atomized and characterized by atomic absorption spectrometry (AAS), the recommendation is to conduct an acid-digestion stage of the effluent (slurry) (APHA et al., 2012). Thus, the slurry acid digestion was carried out in closed system with reflux for later determining the elements of interest based on a procedure proposed by (Bianchi et al., 2012).

The metallic and semi-metallic elements determined in the slurry are provided by the CETESB Article 18 (São Paulo, 1976) and by CONAMA 430 (CONAMA, 2011), specifically dealing with characteristics of effluents to be discarded in receiving sources. The analytical characterization of the metals was performed by the atomic absorption spectrometry technique, with flame atomization and by graphite oven, according to the metal concentration in the sample. To assess the repeatability and reproducibility of the sample preparations by acid digestion, the analytical determination of the metallic elements was based on studies reporting the use of addition and recovery tests and the use of certified reference material for quantification by spectrometric techniques used for environmental samples (Salazar et al., 2011a; Bianchi et al., 2012; Gomes et al., 2016).

2.3. Analysis of Chemical Oxygen Demand (COD)

Due to the complex characteristics of the samples, adjustments of 5220 methodology *D. Closed Reflux, Colorimetric Method* from APHA Standard Methods were necessary to increase the reliability of analytical results (Peixoto et al., 2008; Salazar et al., 2011b).

In this procedure, the sample was heated for 2 hours with a strong oxidizing agent, potassium dichromate, in a closed system. The oxidation of organic compounds result from reducing the dichromate ion to green chromic ion. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to control chloride interferences. To determine the accuracy of the method, a standard solution of 850 mg L^{-1} potassium biphthalate was used as the sample, which should present a result of $1,060 \text{ mg L}^{-1} \text{ O}_2$ (Peixoto et al., 2008).

2.4. Analysis of Total Organic Carbon (TOC) of the dissolved fraction

The samples were filtered in $0.45 \mu\text{m}$ filter and injected in the equipment with a high temperature oven (680°C), containing platinum catalyst under an oxygen atmosphere. The CO_2 generated is analyzed by non-dispersive infrared (NDIR). For determining TOC, Shimadzu equipment was used, Model TOC 5000A.

2.5. Physical-chemical characterization of the slurry

The physical-chemical characterization of the slurry consisted in analyzing the following parameters: multi-elemental analysis (Ag, As, B, Ba, Cd, Co, Cr-total, Fe, Fe^{+2} , F^{-1} , Hg, Mn, Ni, Pb, Se, Sn and Zn), cyanide (CN^{-1}), phenol, odor, oils and (mineral) greases, oils and greases, pH (25°C), S^{-2} , sedimentable and surfactant solids. The procedures for the physical-chemical characterizations were extracted from *Standard Methods for Examination of Water and Wastewater* (APHA et al., 2012), as presented in Table 1.

Table 1. Methods and standards from *Standard Methods for Examination of Water and Wastewater 22nd Ed* (APHA et al., 2012) for characterizing the slurry samples.

Physical and physical-chemical Parameters	Protocol or analytical method
Arsenic (As)	3114C.
Total barium (total Ba)	3111D.
Boron (B)	4500-B C.
Total Cadmium (total Cd)	3111B.
Total lead (total Pb)	3111B.
Total cyanide (total CN)	4500 CN F.
Total copper (total Cu)	3111B.
Total chromium (total Cr)	3111D.
Biochemical oxygen demand (BOD)	5210 B and Lima et al. (2006)
Tin (Sn)	3111D.
Total phenols	5530D. (Direct)
Total iron (total Fe)	3111B.
Fluoride (F ⁻¹)	4500F. D
Ferrous ion (Fe ⁺²)	3500-Fe B
Manganese (Mn)	3111B.
Mercury (Hg)	3112B.
Total nickel (total Ni)	3111B.
Nitrogen total (mg L ⁻¹)	4500 N org B and 4500 NH ₃ B
Oils and greases	5520D.
pH a 25°C	NBR 9251:1986 (ABNT, 1986)
Silver (Ag)	3111B.
Selenium (Se)	3114C.
Sedimentable solids	2540F.
Sulfide (S ⁻²)	4500- S ² D.
Surfactants	5540C.
Temperature (°C)	APHA et al. (2012)
Total zinc (total Zn)	3111B.

2.6. Organic spectroscopy characterization

2.6.1. Sample pre-treatment: extraction in organic solvent

First, 100.00 mL of leachate “in natura” were acidified up to pH 1, employing HCl concentration. Next, the slurry was placed in a 500-mL separatory funnel. The organic matter extraction procedure was carried out by using 3 100.00-mL aliquots of the n-hexane solvent. After extraction for a period of 5 min each, the 3 solvent fractions were combined and the aqueous residue was removed with anhydrous Na₂SO₄. The organic phase was finally transferred to a 500-mL round-bottomed flask. After the extraction procedure stage, the organic solvent was evaporated in a rotary evaporator (vacuum system and 50°C bath temperature). The same former extraction procedure was also performed by using dichloromethane and ethyl acetate solvents. The residual matter was used for organic characterization by employing the following analytical techniques: infrared (FTIR), nuclear magnetic resonance (protons, carbon 13 and APT - Attached Proton Test) and CHN (carbon, hydrogen and nitrogen elemental analysis).

2.6.2. Nuclear magnetic resonance (NMR) analysis of protons, of carbon-13 and APT

NMR analyses of proton (NMR ¹H), carbon 13 (NMR ¹³C) and APT were performed in VARIAN equipment, Mercury Model. The sample (extraction residue) was dissolved in 0.6 mL of deuterated chloroform – CDCl₃ (99.98%) containing tetramethylsilane (TMS). The NMR

^1H analysis was performed at a 300 MHz frequency, with 32 accumulations (nt=32). Analysis by carbon resonance – NMR ^{13}C and APT - was performed at a 75-MHz frequency.

2.6.3. Analysis in the infrared region (FTIR)

The sample dissolved in volatile organic solvent (chloroform) was dispersed in a tablet of sodium chloride (NaCl), forming a film after the solvent evaporation. Spectra in the infrared region were obtained by Fourier transform (FTIR), from 4000 to 400 cm^{-1} , using Perkin-Elmer equipment, Spectrum One model.

2.6.4. Elemental analysis (CHN)

The analyses of the carbon, hydrogen and nitrogen elements present in the extraction residue (5.0 mg), were performed by the equipment Perkin-Elmer CHN 2400. The combustion process occurred at 925°C, using oxygen with 99.995% purity.

2.6.5. Analysis of molar mass distribution (GPC)

The molar mass distribution of the slurry was determined from the dissolved organic fraction, using the gel permeation chromatography technique. The slurry, previously homogenized, was filtered in 0.45 μm filter, and a 1.00 mL aliquot was diluted in a 10.0 mL volumetric flask with the eluent ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ at 50 mmol L^{-1} + NaCl 0.15 mol L^{-1} , in pH 12). The sample was then injected in the gel permeation chromatography instrument (GPC), keeping the mobile phase at a constant 0.7 mL min^{-1} flow. The absorbance measurements were made in three wavelength values: 210, 254 and 280 nm. GE equipment, Model ÄKTA 10 Purifier, was used with a Superose 12 column, 10/300 GL. The calibration curve was made with standard Blue Dextran (2000 kDa), albumin (66 kDa), carbonic anhydrase (29 kDa), cytochrome C (12.4 kDa), aprotinin (6.5 kDa) and acetone (58 Da), obtaining $R^2 = 0.998$.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization of the untreated landfill slurry

The physical, chemical and biological characteristics of the leachates depend on the type of waste, on the degree of decomposition, climate, season of the year, landfill age, depth of waste, type of landfill operation, among other things. It can thus be stated that the composition of leachates may considerably vary from one place to another, as well as in the same site and with the seasons of the year (MOHAMMAD-PAJOOH et al., 2017). It is therefore necessary to obtain the largest amount of information about a particular leachate under study, correlating its physical and chemical characteristics with the treatment processes involved. Among the major parameters used for characterizing leachate liquids are total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, nitrogen and ammoniacal total, solid series, and heavy metals, among other things. Table 2 shows the physical and chemical characterization of the slurry “in natura” of the former controlled landfill of the city of Guaratinguetá-SP, according to the CETESB Article 18 (São Paulo, 1976) and CONAMA 430 (CONAMA, 2011) parameters.

Table 2. Inorganic analytical parameters of the slurry “in natura”, according to the conditions and effluent discharge standards (CONAMA, 2011; São Paulo, 1976). Results of spectrometry analytical validation of atomic and spectrophotometry UV-Vi absorption.

Parameters	Average	Minimum	Maximum	Sp	Spike	Rec. (%)	N	Maximum content allowed (mg L ⁻¹)
As (µg L ⁻¹)	<10.0	<10.0	<10.0	-	50.0	95.0	2	0.5
Ba (mg L ⁻¹)	6.68	4.88	8.48	2.55	10.0	96.0	2	5.0
B (mg L ⁻¹)	0.03	0.03	0.03	0.01	5.0	93.0	2	5.0
Cd (µg L ⁻¹)	6.26	4.03	11.71	3.66	14.87	119.9	4	0.2
Pb (µg L ⁻¹)	9.51	7.51	12.82	2.89	10.20	107.5	3	0.5
CN ⁻¹ (mg L ⁻¹)	-	-	-	-	-	-	-	0.2
Cu (mg L ⁻¹)	0.14	0.08	0.21	0.05	0.49	96.0	7	1.0
Cr (µg L ⁻¹)	85.73	78.00	93.46	10.93	-	95.0	1	0.5
Sn (mg L ⁻¹)	<1.0	<1.0	<1.0	-	5.0	94.0	2	4.0
Fe (mg L ⁻¹)	6.84	3.71	10.88	2.38	20.73	102.0	7	-
Fe ²⁺ (mg L ⁻¹)	1.09	0.98	1.21	0.10	4.84	101.0	6	15.0
Fluoride (mg L ⁻¹)	0.17	0.17	0.17	0.01	2.0	99.0	-	10.0
Mn (mg L ⁻¹)	0.42	0.36	0.54	0.06	0.54	103.6	7	1.0
Hg (µg L ⁻¹)	< 11.0	< 11.0	< 11.0	-	50.0	95.0	2	0.01
Ni (mg L ⁻¹)	4.03	2.72	5.06	0.84	4.30	101.7	5	2.0
N-NH ₃ (mg L ⁻¹)	398.02	273.31	544.04	121.45	5.0	93.0	8	20.0
N-Org (mg L ⁻¹)	28.80	2.50	49.57	21.64	5.0	90.0	4	-
Ag (µg L ⁻¹)	68.22	4.67	110.00	55.94	50.0	97.1	3	0.1
Se	-	-	-	-	-	-	-	0.3
S ²⁻ (µg L ⁻¹)	< 0.002	< 0.002	< 0.002	-	5.0x 10 ³	95.7	2	1.0
Zn (mg L ⁻¹)	0.45	0.04	1.10	0.34	2.07	102.2	8	5.0
Sol. Hexane (mg L ⁻¹)	< 5.0	< 5.0	< 5.0	-	48.83	132.70	2	100.0
Phenols (mg L ⁻¹)	0.42	0.41	0.42	0.01	5.0	97.3	2	0.5
Phosphorus (mg L ⁻¹)	8.69	8.69	8.69	0.01	10.0	95.0	2	-
pH	8.05	7.90	8.20	0.21	-	-	2	5.00 to 9.00
Conductivity (mS cm ⁻¹)	7.074	6.683	7.464	0.552	-	-	2	-
COD (mg L ⁻¹)	1013	939	1105	51	-	-	12	-
BOD (mg L ⁻¹)	ND	ND	ND	-	-	-	6	-
TOC (mg L ⁻¹)	286	267	317	27	-	-	3	-
Total Fixed Solids (TFS)	3.669.50	3.653.00	3.686.00	23.33	-	-	2	-
Total Volatile Solids (TVS)	1.032.50	1.008.00	1.057.00	34.65	-	-	2	-
Fixed Suspended Solids (FSS)	22.33	10.00	37.00	13.65	-	-	3	-
Volatile Suspended Solids (VSS)	13.17	4.50	25.00	10.61	-	-	3	-
Total Suspended Solids (TSS)	38.75	36.00	41.50	3.89	-	-	2	-

(ND) Non-Determinable; Spike: known addition of analytical standard in pre-quantified sample; N: number of replicates.

Table 2 verifies that some slurry characterization parameters are above the concentrations allowed by the legislation in force (São Paulo, 1976; CONAMA, 2011). Barium presents a concentration 1.3 times as great as that permitted (5.0 mg L⁻¹). Nickel has twice the concentration allowed (2.0 mg L⁻¹). The ammoniacal nitrogen concentration is 20 times as great as that provided (20 mg L⁻¹). The addition and analyte recovery tests verify a minimum 90% recovery in all the analytical methodologies used, which therefore ensures the reliability of the spectrometric and spectrophotometric analytical results presented in Table 2. For being predominantly anaerobic environments, sanitary landfills produce effluents with considerably low nitrite and nitrate concentrations (Klein et al., 2017; Mandal et al., 2017; Van Turnhout, 2018). Conversely, the great biological activity found both in the waste mass and in the drainage system causes most of the organic nitrogen to be converted into ammoniacal nitrogen within the very landfill. Hence, there are great concentrations of ammonia and very little organic nitrogen in the leachate, which is evidenced in Table 2.

As stated by (Zhang et al., 2017b), ammonia is an important indicator of leachate contamination in water bodies. Most of the ammonia found in the leachate derives from organic

matter degradation. The major nitrogenous organic compounds which act as a source of ammonia are proteins. Proteins are organic macromolecules formed by the combination of a large number of amino acids. In biological decomposition, proteins are first broken into their amino acids, which then undergo deamination (removal of the amine group). Part of the ammonia produced is incorporated in the cell growth and its excess is released as ammonium ion (NH_4^+) (Van Turnhout, 2018).

Even though phosphorous is not provided by CETESB Article 18 (São Paulo, 1976) or by CONAMA 357/05 article 34 (CONAMA, 2005), its concentration in the slurry is considerable, and its high contents significantly influence the eutrophication processes of aquatic biota. The main chemical element used to control eutrophication is phosphorous, since the cyanobacteria are capable of fixing atmospheric nitrogen, not allowing the reduction in nitrogen concentration with the reduction in affluent load (Von Sperling, 2005; Peng, 2017). Practically the whole of the phosphorus found in leachates is in the form of orthophosphates (Van Turnhout, 2018). They act as an alkaline cover, contributing to the partial alkalinity ($\text{pH}=8.05$, Table 2). Phosphates derive mainly from organic matter (Li et al., 2017).

Table 2 shows the low results for COD ($1,013 \text{ mg L}^{-1}$), for BOD (ND) and for TOC (286 mg L^{-1}). The biodegradability parameter obtained for the slurry studied was Non-Determinable (ND), indicating that the organic matter of the slurry studied is recalcitrant (Fan et al., 2007). BOD_5/COD ratio values below 0.05 are characteristic of stabilized leachates, non-treatable by biological methods (Deng, 2007). The fraction of organic matter oxidizable by potassium dichromate, in the COD technique, was obtained by the TOC/COD ratio, with a 0.28 response (Li et al., 2017; Peng, 2017; Van Turnhout, 2018).

The BOD and COD concentrations tend to suffer reductions during the degradation of the landfill wastes over the years. However, BOD decreases faster in relation to COD, which remains in the leachate due to the organic matter, which is difficult to degrade. Theoretically, these stability stages of sanitary landfills can be divided in function of the BOD/COD ratio observed in the leachates; namely: $\text{BOD}/\text{COD} > 0.5 \text{ mg L}^{-1}$ indicates a new and unstable landfill; $0.1 < \text{BOD}/\text{COD} < 0.5$ indicates a moderately stable landfill; $\text{BOD}/\text{COD} < 0.1$ indicates an old and stable landfill. All this information justifies the low COD ($1,013 \text{ mg L}^{-1}$) value and the negligible value of BOD ($< 5.0 \text{ mg L}^{-1}$), once the former controlled landfill of Guaratinguetá - SP had been active for about 30 years, on the date the leachate studied was collected. Also verified were the concentrations of the total inorganic and organic solids, which, despite not considering specificity, the results help to analytically assess the untreated landfill slurry (Peng, 2017; Van Turnhout, 2018; Zhang et al., 2017b).

Table 2 includes the STF/STV ratio, which shows that the total inorganic fraction found in the leachate is 3.6 times as great as the total organic fraction. Part of the STF is indicated by the inorganic compounds shown in Table 2. The suspension matter, however, shows that the organic fraction, given by the SSV/SSF ratio, corresponds to about 59% of the total. Heavy metals do not originate in chemical reactions; they will only appear in the leachate if they have been introduced in the landfill. These metals are not necessarily a symptom that there are industrial wastes being illegally disposed of. Metals are present in all materials, including living beings. Domestic wastes, especially when not adequately separated at their origin, may be a significant source of metals. Moreover, another highly important metal source, especially iron, is the clayey soil used in cover layers and in waterproofing systems. The minerals found in the clay used in cover layers may be degraded by the carbonic acid found in rainwater, which derives from the atmosphere CO_2 . This process releases metals which infiltrate the landfill together with water, and may or not become a part of the leachate (Peng, 2017; Van Turnhout, 2018; Zhang et al., 2017a).

During the organic matter stabilization process, the biodegradable fraction of the compounds discharged in the municipal landfill is consumed, being replaced with refractory

organic compounds. It is therefore necessary to collect a larger amount of information about this class of compounds, which predominate in leachates, by means of different chemical characterization techniques, including FTIR and NMR (protons, carbon 13 and APT) spectroscopy analyses, besides the distribution of molecular mass and of elemental analysis.

Figure 1 shows the FTIR graph of the slurry “in natura” obtained after the liquid-liquid extraction procedure.

Figure 1. Infrared spectrum by Fourier transform (FTIR) of the slurry “in natura” residue obtained by extraction in ethyl acetate.

The spectrum in the infrared region by Fourier transform (FTIR) presented in Figure 1 is characterized by transmittance bands corresponding to the aromatic, aliphatic, carboxylic and hydroxyl groups (Christensen et al., 1998). A wide band is verified in the region between 2300 and 3600 cm^{-1} , characteristic of organic acids, as expected in slurry, the main group of organic compounds of which are humic and fulvic acids, with a marked presence of carboxylic groups and of weak acid groups, such as the phenolic ones (Christensen et al., 1998). In 3419 cm^{-1} , there is a characteristic band of hydroxyls. A 3047 cm^{-1} transmittance band is characteristic of aromatic rings in general, and may correspond, for example, to phenolic groups. 2961, 2927 and 2873 cm^{-1} bands correspond to carbon/hydrogen bonds of the CH, CH₂ and CH₃ types of organic aliphatic chains. At 1726 cm^{-1} , the carbonyl band (C=O) predominates and, at 1367 cm^{-1} , CH₃ groups bonded to carbonyl (Chai et al., 2007; Huo et al., 2008). The main mechanism for adsorbing pollutants (e.g. metals and pesticides) in organic matter dissolved in underground waters, including the class of humic acids, is ionic exchange involving the hydroxyl groups (3419 cm^{-1} transmittance band) and carbonyls from carboxylic acids (1,726 cm^{-1}) (Dia et al., 2017; Van Turnhout et al., 2018).

The analyses by nuclear magnetic resonance provide basic structural information on the organic matter found in the leachate under study, confirming and complementing the data presented by the FTIR technique. By analyzing NMR ¹H, relative quantitative mass information can be obtained, as opposed to the FTIR technique, which is essentially qualitative. Table 3 shows the results from the de NMR ¹H and ¹³C analyses, and Figure 2 shows the ATP spectrum of the slurry “in natura”.

Table 3. Regions of chemical displacement of ^1H and the respective relative contributions of the organic compounds extracted from the slurry “in natura”.

Regions δ (ppm) of chemical displacement	Attribution	Relative contribution (%)
I (0.4-1.7)	Protons of terminal CH_3 and protons of CH_2 , CH from methylene chains, etc.	72.3
II (1.7-3.3)	Protons of CH_3 , CH_2 and CH linked to aromatic or carboxylic groups, etc.	16.1
III (3.3-4.6)	Protons of carbon α linked to oxygen, carbohydrates, etc.	7.1
IV (6.5-8.1)	Aromatic protons (including quinone, phenol, etc.)	4.5

Characteristic peaks of aromatic protons were verified in the region between 8.1 and 7.5 ppm. The intense peak found in the 7.27 ppm region corresponds to the deuterated chloroform solvent used in the analysis. Peaks between 4.6 and 3.3 correspond to carbon protons linked to oxygen (e.g. carbohydrates). Peaks from 1.7 to 0.4 ppm, are characteristic of CH_3 , CH_2 and CH of aliphatic chains. In the proton spectrum, the different regions were quantified, according to (Kang et al., 2002).

Most of the protons analyzed (about 72%) derive from CH_3 , CH_2 and CH of aliphatic chains. Also found in large proportions (~16%) were CH_3 , CH_2 and CH protons linked to aromatic groups and/or carboxylic groups. Carbon protons linked to oxygen (~7%) and aromatic protons (4,5%) were found in small proportions.

Figure 2. NMR ^{13}C spectrum of the extraction residue of the slurry “in natura”.

NMR ^{13}C analyses indicated intense and well-defined peaks in the region of the chemical displacement from 0 to 50 ppm, corresponding to aliphatic carbons. In a region comprehended between 50 and 70 ppm, characteristic peaks of methyl and methylene groups close to heteroatoms were found, such as CH_3 of the acetyl group. Between 120 and 140 ppm, the presence of aromatic carbons was verified. Lastly, peaks between 160 and 180 ppm were

verified, corresponding to carboxylic carbons, carbons in aldehyde, ketones and quaternary carbons. The data from NMR are coherent with the information obtained by the FTIR technique.

The determination of molar mass distribution in the slurry “in natura” was performed in 254 and 280 nm (Figures 3a and 3b, respectively).

Figure 3. Chromatogram, at 254 nm (a) and at 280 nm (b), of the slurry “in natura” filtered at 45 μ m and diluted 10 times.

The analysis verified that the current effluent has a molar mass of 5.58 kDa, with 1.16 polydispersity. The soluble organic matter of the slurry collected from the controlled landfill of Guaratinguetá-SP is thus verified to be constituted by macromolecules with low polydispersity value, implying homogeneity of the carbonaceous matter molar mass. The low response from the 5.58 kDa molar mass (1.16 polydispersity) of that landfill leachate (landfill of about 30 years of age) is coherent with the literature values for stabilized cell leachates (Christensen et al., 1998; Pereira et al., 2007; Dia et al., 2017).

3.2. Elemental analysis (CHN) of the slurry “in natura”

To complement the chemical characterization of the municipal landfill leachate, elemental analysis of the sample was performed. Elemental analysis of organic compound provides information on its chemical composition, and in a way, on its chemical structure. For a natural substance, the elemental analysis can often provide information on the origin of the material and on the conditions under which it was formed. Table 4 shows the elemental analysis, in duplicate (N), of the slurry “in natura” of the former controlled landfill of the city of Guaratinguetá-SP.

Table 4. Results of the elemental analysis (CHN) of the slurry “in natura” of the former controlled landfill of the city of Guaratinguetá-SP.

Elements	Average	Minimum	Maximum	N
C (%)	57.21	57.19	57.23	2
H (%)	6.90	6.81	6.99	2
N (%)	1.89	1.78	2.00	2

A high percentage mass content of carbon is verified, with a 57.21% response. The C/H ratio of the slurry “in natura” is 8.29 and the C/N ratio is 30.27 (Table 4). Fulvic acids have molecular mass between 200 and 2 000 Da and humic acids, over 2 000 Da (Huo et al., 2008; Zhang et al., 2017a). Fulvic acids tend to be more difficult to degrade than humic acids (McBean et al., 1995). Humic acids are materials formed by the aggregation of small molecules resulting from the incomplete (chemical and biological) degradation from vegetal and animal wastes, and from synthesizing microorganisms (Silva et al., 2017). There is still no consensus regarding the spatial structure of humic substances, but the humic acid is believed to be constituted of two

main components: aromatic rings deriving from lignin and nitrogen from microorganism proteins (Dia et al., 2017). These rings are linked among them, be they condensed or not. The humic acids complexing capacity indicates that hydroxyl and carboxyl groups may exist in larger quantities than the nitrogen and sulfur groups. Carbon corresponds to 58% of the mass. This, added to the set of results presented for COD, BOD, FTIR, NMR, GPC and CHN, therefore indicates that the slurry of Guaratinguetá-SP is mainly constituted of humic acids, of difficult biodegradation, and able to form chelates with the metals present in aqueous medium (Table 2), solubilizing them even in basic medium (pH=8.05, Table 2).

These refractory acids play an important role by conveying pollutants to the environment by being able to form metallic chelates, for transporting pesticides in general and for being precursors of mutagenic products with supply-water chlorination (Wiszniewski et al., 2004). Humic substances have varied chemical composition. The variations in the degree of polymerization, in the number of lateral and radical chains that may be found in humic substances, account for there not being two identical humic molecules.

4. CONCLUSIONS

The leachate from the municipal landfill of Guaratinguetá (Sao Paulo, Brazil) is composed of a high content of salts, ammonia, and of recalcitrant humic substances. Ba and Ni with concentrations above those permitted by legislation is an indication that domestic wastes are not adequately separated in the households. Furthermore, the recalcitrant humic substances presented low polydispersity, with molecular mass characteristic of leachates from stabilized municipal landfills, with marked presence of aliphatic chains, aromatic rings in general, phenolic, and carboxylic groups. These refractory acids play a detached role in carrying pollutants in the environment by being able to carry toxic metals (forming metallic chelates even in basic medium) and pesticides in general; further, these substances are precursors of mutagenic products with the chlorination of supply water.

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The historical influence of tributaries on the water and sediment of Jacuí's Delta, Southern Brazil

ARTICLES doi:10.4136/ambi-agua.2150

Received: 15 Jun. 2017; Accepted: 07 Jan. 2018

Leonardo Capeleto de Andrade^{1*}; Rodrigo da Rocha Andrade²; Flávio Anastácio de Oliveira Camargo¹

¹Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brasil
Departamento de Solos. E-mail: eng.capeleto@gmail.com, fcamargo@ufrgs.br

²Departamento Municipal de Água e Esgotos (DMAE), Porto Alegre, RS, Brasil
E-mail: rodrigora@dmae.prefpoa.com.br

*Corresponding author

ABSTRACT

The high population density in a metropolis leads to socio-environmental impacts that directly affect local water resources. This work evaluated the historical data (between 2000 and 2014) of water and sediment monitoring in the Jacuí's Delta region and analyzed the relationship between these sites. Seven monitoring sites around the Jacuí's Delta were evaluated: the outflow of the rivers Jacuí, Caí, Sinos, and Gravataí; the channels Ilha da Pintada and Navegantes; and Lake Guaíba. Water data were evaluated for: air and water temperature; depth; pH; electrical conductivity; transparency; turbidity; dissolved oxygen; biochemical oxygen demand; phosphorus; nitrogen; total residues; and escherichia coli. Sediment were evaluated for pseudo-total concentrations of metals (Al, Fe, Ca, Mn, Ba, V, Zn, Cu, Pb, Cr, Ni, Co, Li, Be, Cd, Hg, As, and Ag). The quality of water and sediment in the Jacuí's Delta are linked with the tributaries and priority flows of the channels. The historical data of water and sediment around the Jacuí's Delta shows the influence of the tributaries with low quality in the downstream points. The pollution of the rivers Caí, Sinos, and Gravataí negatively affects the environmental quality of the channel Navegantes and Lake Guaíba (catchment points to water supply). The water in those sites presents reductions in dissolved oxygen and high values of coliforms, and the sediment shows high concentrations of metal Zn, Pb, Cr, and Hg. Despite the reduction in Pb and Hg values in the sediment over the past years, pollution from the tributary rivers still persists.

Keywords: monitoring, pollution, watershed.

A influência histórica dos afluentes na água e sedimento do Delta do Jacuí, RS, Brasil

RESUMO

A grande densidade populacional nas metrópoles gera impactos socioambientais que afetam diretamente os recursos hídricos locais. O objetivo deste trabalho foi avaliar os dados históricos (entre 2000 e 2014) de monitoramento de água e sedimentos na região Delta de Jacuí e analisar a relação entre esses locais. Foram avaliados sete locais de monitoramento entorno do Delta de Jacuí: foz dos rios Jacuí, Caí, Sinos e Gravataí; canais Ilha da Pintada e Navegantes; e Lago Guaíba. Os dados de água foram avaliados para: temperatura do ar e da água;

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profundidade; pH; condutividade elétrica; transparência; turbidez; oxigênio dissolvido; demanda bioquímica de oxigênio; fósforo; nitrogênio; resíduos totais; e escherichia coli. Os sedimentos foram avaliados para concentrações pseudo-totais de metais (Al, Fe, Ca, Mn, Ba, V, Zn, Cu, Pb, Cr, Ni, Co, Li, Be, Cd, Hg, As e Ag). A qualidade da água e dos sedimentos no delta de Jacuí está ligada aos afluentes e fluxos prioritários dos canais. Os dados históricos de água e sedimentos no Delta de Jacuí mostram a influência dos afluentes com baixa qualidade nos pontos a jusante. A poluição dos rios Caí, Sinos e Gravataí afeta negativamente a qualidade ambiental do canal Navegantes e do Lago Guaíba (pontos de captação para abastecimento hídrico). A água nesses locais apresenta reduções no oxigênio dissolvido e grandes valores de coliformes e o sedimento apresenta grandes concentrações dos metais Zn, Pb, Cr e Hg. Apesar da redução ao longo dos anos nos valores de Pb e Hg no sedimento, a poluição dos rios tributários ainda persiste.

Palavras-chave: bacia hidrográfica, monitoramento, poluição.

1. INTRODUCTION

The large expansion of big cities results in environmental impacts on local water resources, which often serve as a source of water for the same populations (Cavalcanti et al., 2014). Trace metals entering aquatic ecosystems through runoff or atmospheric deposition and eventually accumulate in sediments (Bing et al., 2016).

Lake Guaíba is the major source of water in the capital of the Rio Grande do Sul State. The lake has had historical, economic and cultural importance for the region since the 18th century. With almost 500 km² of shallow waters, Lake Guaíba is the final destination of the rivers Jacuí, Caí, dos Sinos, and Gravataí - accumulating potential liabilities generated in the drainage basin. Water pollution in Lake Guaíba's watershed has been noted since the end of 1950 (Freitas, 1962; Roessler, 2005), persisting for decades as a public perception. Nowadays, the waters have multiples uses: as water supply, sewage dilution, navigation, as well as fishing (Andrade et al., 2018).

The Jacuí's Delta (Figure 1) is an area of protection and great socio environmental interest, being the archipelago of a State Conservation Unit. This work evaluated the historical data (between 2000 and 2014) of water and sediments monitoring, developed by the Municipal Department of Water and Sewage (Dmae) of Porto Alegre in the Jacuí's Delta region. This work also analyzed the relationship between the sites.

Figure 1. Sampling sites (31 - Gravataí River; 36 – Navegantes Channel; 41B - Lake Guaíba; 57 - Jacuí River; 58 - Caí River; 59 - dos Sinos River; 86A – Ilha da Pintada Channel) of water and sediment in Jacuí's Delta. The darker area in the state map represents the lake's drainage basin.

Source: Google Maps.

2. MATERIALS AND METHODS

Analyses of water and sediment monitoring were carried out by the Municipal Department of Water and Sewage (Dmae) of Porto Alegre, RS, between 2000 and 2014. The seven sites evaluated around the Jacuí's Delta (Figure 1) were: 31 - Gravataí River outflow (29°58'12,6" S; 51°11'53,6" W); 36 – Navegantes Channel (30°00'52,1" S; 51°12'54,2" W); 41B - Lake Guaíba (30°03'32,7" S; 51°14'10,3" W); 57 - Jacuí River outflow (29°57'07,3" S; 51°19'21,2" W); 58 - Caí River outflow (29°55'51,7" S; 51°17'05,3" W); 59 - Sinos River outflow (29°55'49,0" S; 51°14'14,9" W); and 86A – Ilha da Pintada Channel (30°00'49,0" S; 51°15'34,2" W). Some of these sites are points of water catchment for Water Treatment Plants (WTP): 36 - São João and Moinhos de Ventos; 41B - Menino Deus; and 86A - Ilha da Pintada. Site numbers are standards codes defined by Dmae.

Water data, with monthly repetitions between the years 2000 and 2014, were evaluated for: air and water temperature; depth; pH; electrical conductivity (EC); transparency (secchi disk); turbidity (NTU); dissolved oxygen (DO - modified Winkler); biochemical oxygen demand (BOD₅ - manometric); total phosphorus (P - titulometric); total nitrogen (N - titulometric); total residues at 105°C (TR₁₀₅ - gravimetric); and escherichia coli (enzymatic substrate). Sediment (bulk) was oven-dried (50°C) and evaluated, with two annual repetitions in distinct seasons between the years of 2000 and 2011, to pseudo-total (USEPA, 2007) concentrations (dry basis) of metals (Al, Fe, Ca, Mn, Ba, V, Zn, Cu, Pb, Cr, Ni, Co, Li, Be, Cd, Hg, As, and Ag) and analyzed by atomic absorption spectrophotometry.

Data were submitted to analysis of variance (ANOVA) and, when significant, means were compared by Tukey test with a 95% confidence interval ($p < 0.05$). All graphs and statistical analyzes were developed in Statistica® v13 software.

3. RESULTS AND DISCUSSION

The quality of water and sediment in the Jacuí's Delta are linked with the tributaries and priority flows of the channels (Figure 1). Lake Guaíba has a historical mean water inflow of $780 \text{ m}^3 \text{ s}^{-1}$ (with occasional events exceeding $3000 \text{ m}^3 \text{ s}^{-1}$). This inflow is composed mostly (85%) of waters from Jacuí River (point 57) and the remaining by the Rivers Sinos, Caí, and Gravataí (flowing into the Jacuí's Delta), as well as small streams along the margins (Menegat et al., 2006; Andrade Neto et al., 2012; Porto Alegre, 2017b).

The relationship of the forming rivers with the Jacuí's Delta is observed in the cluster analysis (Figure 2a), such at Points 57 (Jacuí River outflow) and 86A (the channel of the Jacuí Delta - Ilha da Pintada). However, the greatest influence of the tributaries is verified by the accumulation of liabilities of the Rivers Caí (58), Sinos (59), and Gravataí (31) over the channel Navegantes (36) and Lake Guaíba (41B). The Rivers Caí and Sinos flow through regions with many industries, especially leather and footwear; and Gravataí River flows through the metropolitan region of Porto Alegre.

The pollution from tributaries can be verified by the increase in electrical conductivity (EC), biochemical oxygen demand (BOD5), P, N, TR105, and coliforms in water (Table 1), and metals (such as Zn, Cu, Pb, Cr, Ni, and Hg) in the surface sediment (Table 2) in the downstream points (such as 36 and 41B). Consequences of these changes are reductions in pH, dissolved oxygen (DO), and water transparency - which can result in damage to local biota.

These parameters have direct and indirect connections with the urban pollution commonly present in metropolitan regions (Figure 2b). Metals and other pollutants enter the aquatic environment by various ways and sources (natural and anthropogenic), such as runoff, sewage, atmospheric deposition, and vehicular traffic (Smol, 2008; Bing et al., 2016). High vehicular traffic has been reported around the world as a potential source of pollution by metals (Zhang et al., 2016; Sharley et al., 2016). Motor vehicles have a variety of emissions and releases involving many toxic metals (such as Zn, Cr, Cu, Hg, Ni, and Pb), which damage human health and the environment (Adamiec et al., 2016).

Figure 2. Analysis of (a) clusters for the sites and (b) principal components for water and sediment in Jacuí's Delta.

Table 1. Historical means (2000 to 2014) of water parameters around the Jacuí's Delta.

Parameters	31 Gravataí River	36 Navegantes	41B Lake Guaíba	57 Jacuí River	58 Caí River	59 Sinos River	86A Ilha da Pintada
air temperature (°C)	22.0±0.4 ^a	21.8±0.4 ^a	21.0±0.4 ^a	21.0±0.4 ^a	21.2±0.4 ^a	21.5±0.4 ^a	21.5±0.4 ^a
water temperature (°C)	21.6±0.4 ^a	21.2±0.4 ^a	21.2±0.4 ^a	21.1±0.4 ^a	20.8±0.4 ^a	20.9±0.4 ^a	21.1±0.4 ^a
depth (m)	4.5±0.1 ^{ed}	6.6±0.0 ^c	9.6±0.1 ^a	8.7±0.0 ^b	4.4±0.1 ^e	4.6±0.0 ^d	4.0±0.0 ^f
pH	6.9±0.0 ^d	7.0±0.0 ^{bc}	7.0±0.0 ^b	7.2±0.0 ^a	7.0±0.0 ^b	6.9±0.0 ^{cd}	7.2±0.0 ^a
EC (μS cm ⁻¹)	185.6±7.7 ^a	88.1±1.4 ^{cd}	80.8±1.1 ^d	54.0±0.6 ^e	97.6±2.7 ^c	132.8±3.9 ^b	54.4±0.7 ^e
Transparency (cm)	26.1±0.7 ^d	43.1±1.2 ^{bc}	44.6±1.3 ^{abc}	54.2±2.3 ^a	48.4±1.9 ^{abc}	39.2±1.1 ^c	51.3±2.7 ^{ab}
Turbidity (NTU)	38.9±1.6 ^a	31.1±1.1 ^a	32.5±1.4 ^a	36.4±2.6 ^a	36.6±2.5 ^a	33.2±1.5 ^a	36.7±2.3 ^a
DO (mg O ₂ L ⁻¹)	2.65±0.16 ^e	5.92±0.09 ^c	6.06±0.07 ^{bc}	7.93±0.08 ^a	6.54±0.09 ^b	3.86±0.12 ^d	7.76±0.08 ^a
BOD₅ (mg O ₂ L ⁻¹)	8.22±0.48 ^a	1.95±0.06 ^{bc}	1.77±0.06 ^{bcd}	0.77±0.04 ^e	1.22±0.06 ^{cde}	2.64±0.11 ^b	0.87±0.05 ^{de}
Phosphorus (mg L ⁻¹)	0.54±0.03 ^a	0.19±0.01 ^{bc}	0.16±0.00 ^{cd}	0.08±0.00 ^e	0.12±0.01 ^{de}	0.21±0.00 ^b	0.08±0.00 ^e
Nitrogen (mg L ⁻¹)	5.96±0.27 ^a	2.17±0.07 ^c	2.00±0.06 ^c	1.29±0.03 ^d	1.97±0.05 ^c	3.17±0.12 ^b	1.26±0.04 ^d
TR₁₀₅ (mg L ⁻¹)	161.1±4.4 ^a	104.5±2.2 ^d	99.8±1.8 ^d	93.8±3.2 ^d	118.3±2.9 ^c	131.9±2.9 ^b	92.8±2.7 ^d
Coliforms (NMP 100mL ⁻¹)	3.8x10 ⁴ ±2x10 ³ ^a	1.5x10 ⁴ ±1x10 ³ ^b	1.2x10 ⁴ ±690 ^b	210±46 ^c	446±117 ^c	2.9x10 ³ ±249 ^c	423±79 ^c
N	170	161	161	173	174	173	162

The means (±SE) followed by the same letter (in the comparative between sites) did not differ statistically from each other by the Tukey test at 95% confidence. EC - Electrical Conductivity; DO - Dissolved Oxygen; BOD₅ - Biochemical Oxygen Demand; TR₁₀₅ = Total solid residue at 105°C. N = average number of data per sampling site.

Table 2. Historical means (2000 to 2011) of metals in surface sediments around the Jacuí's Delta.

Parameters	31 Gravataí River	36 Navegantes	41B Lake Guaíba	57 Jacuí River	58 Caí River	59 Sinos River	86A Ilha da Pintada
Al (mg g ⁻¹)	45.9±3.2 ^{abc (1)}	54.3±4.3 ^a	44.5±5.5 ^{abc}	33.9±2.5 ^{bc}	47.7±3.5 ^{ab}	30.4±2.9 ^c	31.5±2.9 ^{bc}
Fe (mg g ⁻¹)	28.6±2.9 ^b	38.4±1.9 ^b	34.4±4.6 ^b	36.3±3.5 ^b	52.5±2.9 ^a	30.6±2.9 ^b	32.2±1.8 ^b
Ca (mg g ⁻¹)	-	3.6±0.2 ^a	1.9±0.3 ^b	-	-	-	2.3±0.2 ^b
Mn (mg kg ⁻¹)	276.4±12.4 ^d	484.7±36.0 ^{bc}	423.6±40.8 ^{cd}	661.7±48.6 ^b	929.2±42.4 ^a	438.6±31.8 ^{cd}	539.3±62.7 ^{bc}
Ba (mg kg ⁻¹)	179.1±11.5 ^{ab}	196.0±11.4 ^a	138.7±16.9 ^{bc}	196.9±11.2 ^a	229.0±9.4 ^a	121.9±9.1 ^c	187.5±14.7 ^{ab}
V (mg kg ⁻¹)	-	120.0±10.6 ^a	72.5±13.7 ^a	60.0 ⁽²⁾	-	-	110.4±11.4 ^a
Zn (mg kg ⁻¹)	295.8±19.8 ^a	347.7±16.7 ^a	131.3±16.4 ^b	79.3±5.1 ^c	141.1±8.4 ^b	172.5±15.0 ^b	74.5±4.6 ^c
Cu (mg kg ⁻¹)	64.3±4.7 ^b	103.5±6.2 ^a	41.0±6.7 ^c	52.4±5.0 ^{bc}	65.5±4.5 ^b	43.2±3.7 ^c	39.2±3.1 ^c
Pb (mg kg ⁻¹)	50.0±4.2 ^a	62.7±4.6 ^a	26.1±3.7 ^b	20.7±3.4 ^b	29.9±3.5 ^b	19.7±3.5 ^b	24.8±2.9 ^b
Cr (mg kg ⁻¹)	33.1±3.6 ^b	51.8±3.6 ^a	22.1±2.8 ^{bc}	21.6±1.7 ^{bc}	51.1±4.8 ^a	54.4±4.4 ^a	18.0±1.2 ^c
Ni (mg kg ⁻¹)	22.8±2.1 ^b	37.3±2.5 ^a	18.9±2.5 ^b	22.9±2.3 ^b	42.2±2.9 ^a	26.2±2.6 ^b	20.8±2.0 ^b
Co (mg kg ⁻¹)	-	28.5±1.8 ^a	15.3±2.0 ^b	15.0 ⁽²⁾	-	-	21.6±1.6 ^b
Li (mg kg ⁻¹)	-	14.8±1.1 ^a	8.2±1.5 ^b	-	-	-	8.3±0.7 ^b
Be (mg kg ⁻¹)	-	2.53±0.30 ^a	2.11±0.34 ^a	1.00 ⁽²⁾	-	-	2.26±0.33 ^a
Cd (mg kg ⁻¹)	0.22±0.02 ^a	0.25±0.04 ^a	0.21±0.03 ^a	0.25±0.03 ^a	0.29±0.04 ^a	0.20±0.03 ^a	0.23±0.03 ^a
Hg (mg kg ⁻¹)	0.16±0.01 ^b	0.43±0.04 ^a	0.12±0.02 ^{bc}	0.05±0.00 ^c	0.08±0.01 ^{bc}	0.16±0.02 ^b	0.06±0.00 ^c
As (mg kg ⁻¹)	ND	ND	ND	ND	ND	ND	ND
Ag (mg kg ⁻¹)	ND	ND	ND	ND	ND	ND	ND
N	16	16	17	17	16	17	16

⁽¹⁾ The means (±SE) followed by the same letter (in the comparative between sites) did not differ statistically from each other by the Tukey test at 95% confidence.

⁽²⁾ No repetitions. ND = not detected. N = average number of data per sampling site.

According to the Brazilian reference values for surface waters (Table 3), Conama No. 357 – Class 2 (Conama, 2005), Points 31 (Gravataí River) and 59 (dos Sinos River) surpass the mean values for DO and Coliforms (Table 1). However, self-purification re-establishes the DO levels in the Navegantes Channel (36), but does not reduce the coliform levels below the resolution limits.

According to the Brazilian reference values for dredged sediments (Level 1) of Conama No. 454 (Conama, 2012), the mean values were above the limits proposed in sediment for Zn (at Points 31, 36, 41B, 58, and 59), Pb (31 and 36), Cr (36, 58, and 59) and Hg (36). The site that presented the most values above the limits (besides the highest concentrations) was 36 (Navegantes Channel), where the water flow from all those rivers accumulate. Sites 57 (Jacuí River) and 86A (Ilha da Pintada Channel) did not present any values above the proposed limits. Site 41B (Lake Guaíba) only presents the concentrations of Zn above the limit.

The association of the analyzed parameters is corroborated by the correlation (r) of their attributes. The increase in P and N concentrations leads to an increase in BOD₅ (0.72 and 0.70, respectively; $p < 0.05$), which in turn reduces DO concentrations (-0.62 ; $p < 0.05$). This chain reaction occurs by the eutrophication of the water, consuming the oxygen available for the decomposition of the organic compounds from urban pollution (Andrade and Giroldo, 2014).

Previous studies in the Jacuí's Delta and Lake Guaíba show seasonal variations and the negative influence of pollution on river water quality and phytoplankton composition (Rodrigues et al., 2007; Andrade et al., 2012; Andrade and Giroldo, 2014). These studies point to the Gravataí River outflow (Point 31) as a highly degraded point relative to other points, as can be seen in the cluster analysis (Figure 2a).

Considering the historical values, the time (years) and the seasonality (months) had influence on the water parameters (Table 3) in Lake Guaíba (site 41B). Time (years) presents correlations (r) with the depth (-0.80), pH (-0.73), and electrical conductivity (0.73); and the air temperature (seasonal variation in the months) presents correlations (r) with the depth (-0.86), pH (0.83), dissolved oxygen (-0.85) and phosphorus (-0.80). The monthly variations (depth, pH, DO, and P) can be explained by the rainy seasons, with more rainfall in the winter (Aug - 140 mm) and less between the summer-autumn (Apr - 86 mm), influencing the water flow in the lake (Porto Alegre, 2017a). The reduction in the depth through the years (2000-2014) is natural, due to the deposition of sediments. However, the reduction of pH and increase of electrical conductivity (EC) probably occurred due to pollution.

Time (years) influenced the sediment (Table 4), reducing the concentration of some elements (Ca, Mn, Ba, V, Pb, Co, Li, Be, and Hg). The reduction in values of Pb ($r -0.90$; $R^2 0.80$) and Hg ($r -0.82$; $R^2 0.67$) is especially significant given the high toxicity of both metals. This decrease occurred throughout the world by the environmental pressure to control these priority metals (Bing et al., 2016).

The Rivers Caí, Gravataí, and Sinos are publicly known for their pollution, flowing through industrial areas in a metropolitan region, suffering many environmental impacts. Thus, the remediation and protection of Jacuí's Delta and Lake Guaíba are made even more complex by the liabilities upstream.

Table 3. Historic data (means) of water parameters in the site 41B - Lake Guaíba.

Parameters	air	water	depth	pH	EC	Secchi	Turbidity	DO	BOD ₅	P	N	TR ₁₀₅	Coliforms
dates	°C	°C	m	-	µS cm ⁻¹	cm	NTU	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	MPN
2000	20.7	21.2	10.5	7.4	79.9	27.9	47.0	6.19	1.72	-	2.15	112.2	12,575
2001	23.1	22.2	10.4	7.2	73.3	31.7	38.4	5.68	1.66	-	2.40	103.6	13,575
2002	21.7	21.0	10.8	7.2	72.1	35.8	32.6	6.32	1.63	0.14	1.58	97.4	10,191
2003	22.8	22.1	10.3	7.0	77.9	36.8	36.9	5.65	1.44	0.19	1.77	91.0	7,339
2004	20.4	21.1	9.8	6.9	80.5	48.8	27.7	6.37	2.01	0.15	1.66	92.0	9,591
2005	21.4	21.3	9.2	7.1	84.3	52.5	25.1	6.46	2.15	0.14	1.78	99.4	12,091
2006	21.3	21.5	9.5	7.1	82.3	53.3	27.2	6.24	2.01	0.15	2.40	90.7	11,308
2007	21.6	21.3	9.3	6.8	77.7	44.6	31.9	5.88	1.65	0.15	2.15	112.3	11,083
2008	19.5	21.2	9.4	7.0	79.8	46.7	29.4	5.95	1.87	0.19	1.95	104.3	14,854
2009	20.6	21.2	9.4	7.0	80.8	46.3	31.0	6.06	1.55	0.15	1.97	99.7	13,308
2010	19.6	20.3	9.5	7.1	80.4	40.0	32.0	6.38	1.48	0.17	1.84	93.7	13,366
2011	21.0	20.6	8.7	6.8	79.7	41.3	36.4	6.26	1.95	0.18	2.47	93.3	19,250
2012	22.0	22.0	8.7	7.0	92.9	53.8	28.6	5.72	2.28	0.15	2.56	104.7	9,336
2013	19.5	20.7	8.5	6.9	88.1	44.5	29.3	5.72	1.51	0.15	2.04	99.4	14,872
2014	17.3	17.8	9.7	6.9	88.6	36.7	40.4	5.60	1.05	0.14	2.08	113.5	6,750
r _{year}	-0.62	-0.57	-0.80	-0.73	0.73	0.41	-0.26	-0.29	-0.16	-0.01	0.29	0.10	0.14
Jan	27.2	27.1	9.3	7.2	75.5	48.2	25.9	5.79	1.59	0.14	1.82	92.3	9,743
Feb	26.5	27.2	9.3	7.2	81.4	49.3	22.3	5.84	1.82	0.12	1.76	82.7	10,057
Mar	26.2	25.7	9.3	7.1	76.2	50.0	24.4	5.64	1.63	0.13	1.54	96.1	10,621
Apr	22.0	22.6	9.2	7.1	84.3	54.6	25.2	6.02	1.72	0.14	1.58	86.7	10,909
May	18.0	18.3	9.7	6.9	84.1	51.3	25.1	6.33	1.48	0.15	1.85	100.1	12,260
Jun	17.0	16.0	9.9	7.0	85.3	43.5	30.8	6.69	1.70	0.18	2.10	101.6	16,115
Jul	13.3	14.8	9.8	6.9	86.9	37.5	47.3	6.86	2.35	0.20	2.48	110.4	13,564
Aug	16.7	15.8	9.7	6.9	81.1	37.9	35.0	6.56	1.70	0.17	2.30	108.4	11,179
Sep	17.1	17.7	9.9	7.0	78.3	32.5	41.0	6.23	1.91	0.17	1.96	105.4	13,254
Oct	20.6	20.7	9.8	6.9	76.6	34.7	45.0	5.57	1.69	0.18	2.19	111.2	13,847
Nov	23.9	23.7	9.4	7.1	80.6	33.9	41.2	5.53	1.82	0.17	2.30	101.9	11,577
Dez	23.5	24.9	9.5	7.1	79.6	43.2	26.4	5.71	1.90	0.16	1.82	99.9	14,700
r _{air °C}	-	0.99	-0.86	0.83	-0.62	0.45	-0.60	-0.85	-0.43	-0.80	-0.65	-0.71	-0.59
Conama No. 357	-	-	-	6 - 9	-	-	100	5	5	0.05	3.7	-	1,000

Table 4. Historic data (means) of metals in surface sediments in the site 41B - Lake Guaíba.

Year	Al	Fe	Ca	Mn	Ba	V	Zn	Cu	Pb	Cr	Ni	Co	Li	Be	Cd	Hg
	mg g ⁻¹			mg kg ⁻¹												
2000	45.8	57.0	2.7	680	275	130	218	81.0	49.0	38.5	23.0	23.0	18.0	4.0	0.30	0.25
2001	72.4	47.7	2.8	696	220	185	219	-	50.0	40.5	36.5	27.0	17.5	3.5	0.25	0.24
2002	69.5	47.1	2.8	695	-	130	209	-	30.0	39.0	42.0	33.0	13.0	4.0	0.10	0.21
2003	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2004	27.3	25.5	1.7	425	140	75	93.0	-	25.0	11.0	16.5	13.5	6.00	1.5	0.30	0.08
2005	13.6	15.3	1.3	281	85	35	83.0	28.0	30.0	9.5	11.0	11.5	2.00	1.0	0.10	0.08
2006	13.6	18.5	1.2	317	80	30	70.5	28.5	25.0	13.0	12.0	10.0	2.50	1.0	0.20	0.07
2007	33.6	28.3	1.0	505	175	70	125	49.0	10.0	22.0	19.5	14.0	9.50	2.0	0.10	0.06
2008	40.7	34.4	-	335	140	40	212	68.0	13.0	33.5	27.5	18.5	8.00	1.0	0.30	0.14
2009	84.9	-	-	313	93	24	65.5	27.1	11.4	14.5	9.19	5.50	4.50	-	0.16	0.08
2010	48.5	-	-	214	75	20	58.2	28.0	10.3	12.0	8.21	5.14	3.78	0.6	0.17	0.04
2011	60.1	-	-	249	70	20	78.0	23.0	16.0	14.0	9.00	6.00	4.00	1.0	0.10	0.07
R ²	0.00	0.54	0.92	0.76	0.66	0.76	0.47	0.44	0.80	0.42	0.47	0.67	0.59	0.72	0.15	0.67
r	0.02	-0.74	-0.96	-0.87	-0.81	-0.87	-0.69	-0.66	-0.90	-0.65	-0.69	-0.82	-0.77	-0.85	-0.39	-0.82
mean	46.4	34.2	1.93	428	135	69.0	130	41.6	24.5	22.5	19.5	15.2	8.07	1.96	0.19	0.12
±se	7.1	5.3	0.31	56	22	16.9	21	7.8	4.4	3.8	3.5	2.8	1.74	0.43	0.03	0.02

No detection for As and Ag. No differences between months. R² - coefficient of determination; r - correlation coefficient; ±se – standard error.

4. CONCLUSIONS

The historical data of water and sediment around the Jacuí's Delta shows the influence of the tributaries with low quality in the downstream points. The pollution of the Rivers Caí, Sinos, and Gravataí negatively affect the environmental quality of Navegantes Channel and Lake Guaíba (catchment points to water supply). The water in those sites present reductions in dissolved oxygen and high values of coliforms, and the sediment shows high concentrations of metal Zn, Pb, Cr, and Hg. Despite a reduction in past years in Pb and Hg values in the sediment, pollution from the tributary rivers persists.

5. ACKNOWLEDGEMENTS

We thank the Municipal Department of Water and Sewage (Dmae) of Porto Alegre for the data and the National Council for Scientific and Technological Development (CNPq) for the doctoral scholarship to the first author.

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Segregation of solid waste from a fish-processing industry: a sustainable action

ARTICLES doi:10.4136/ambi-agua.2155

Received: 07 Jul. 2017; Accepted: 17 Jan. 2018

Yeda dos Santos Silva¹; Liliana Pena Naval^{2*}

¹Universidade Federal do Tocantins (UFT), Palmas, TO, Brasil

Programa de Pós-Graduação em Ciências do Ambiente. E-mail: enga.yedasilva@gmail.com

²Universidade Federal do Tocantins (UFT), Palmas, TO, Brasil

Departamento de Engenharia Ambiental. E-mail: liliana@uft.edu.br

*Corresponding author

ABSTRACT

Segregation techniques represent a sustainable alternative to minimize wastes of raw material in processing industries. This study considered the premise; its purpose was to use segregation techniques to determine the theoretical removal rate of solid compounds present in processing effluents, in order to support the sustainable development of the fish industry. The removal rates obtained for different treatments were evaluated for the parameters: total solids, organic matter and oils and greases, and the efficiency of the segregation of the effluent streams in the different stages of fish processing was evaluated through descriptive statistical analysis. The segregation recovered from 31% to 70% of total solids; from 15% to 97.50% of organic matter, and from 10% to 63% of oils and greases. These results indicates that the raw material can be used in new products, leading to reduced final-effluent concentration.

Keywords: effluent streams, fish industry, separation processes.

Segregação dos resíduos sólidos na indústria processadora de pescado: uma ação sustentável

RESUMO

A segregação é uma alternativa para redução do desperdício de matéria-prima durante o processamento do pescado, uma vez que removem das correntes de efluentes, os resíduos sólidos. Considerando-se a premissa, objetivou-se neste estudo, determinar a taxa de remoção teórica de compostos sólidos presentes em efluentes do processamento, empregando técnicas de segregação, como ação voltada para o desenvolvimento sustentável da indústria do pescado. Foram avaliadas taxas de remoção alcançadas, por diferentes tratamentos, para os parâmetros: sólidos totais, matéria orgânica e óleos e graxas, e verificada a eficiência da segregação das correntes de efluente, nas diferentes etapas do processamento do pescado, por meio de análise estatística descritiva. A segregação recuperou de 31% a 70% de sólidos totais; de 15% a 97,50% de matéria orgânica, e de 10% a 63% de óleos e graxas, que poderão ser empregados como matéria prima para novos produtos, permitindo minimizar a concentração do efluente final.

Palavras-chave: correntes de efluente, indústria do pescado, processos de separação.

1. INTRODUCTION

Food waste is a current reality, from initial processing through distribution to the final consumer, part of the raw material that reaches the food-processing industries is wasted. This factor contributes to the generation of liquid and solid waste (ONU, 2012), which reduces food availability and increases the polluting potential of the food industry. The fish-processing industry is considered to be one of the industries that generate waste with maximum load (Chowdhury et al., 2010; Cristovão et al., 2012; 2015).

The effluent generated during the processing of this product includes soluble, colloidal and particulate forms of organic contaminants (Chowdhury et al., 2010), including proteins, nutrients, oils and greases (Muthukumaran and Baskaran, 2013). The main solid waste produced consists of scales, meat, bones, cartilage and viscera (Anh et al., 2011). In processing, the disposal of these residues is between 50 and 70% of the processed fish Hernández et al., 2013; Feltes et al., 2010, Herpandi et al., 2011; Monteiro, 2013; Rustad et al., 2011; Silva et al., 2014). Of this volume of generated waste, approximately half is equivalent to organic materials (Bugalo et al., 2012), and lacks a suitable site for disposal (Moraes et al., 2013). However, due to the high organic load, the potential pollutant of the final effluent is high, and should be considered (Cosmann et al., 2009; Hernández et al., 2013; Bugalo et al., 2012).

However, the search for sustainability generates goals such as the reduction of waste and the search for an increase in the efficiency of the production chain (Love et al., 2015; ONU, 2012), food availability and natural resources. Also, cleaner production, such as reuse, recycling, and other green technologies is encouraged instead of using the disposal and the end-of-pipe treatment for waste management (Wu et al., 2013). This necessitates the search for alternatives applicable to food processing, which reduce the volume of the waste generated, as well as economic valuation for the by-products produced (Lago, 2015; Lopes et al., 2015; FAO, 2014).

In this scenario, segregation presents itself as a management option for the waste generated, and can be applied during the processing of the food or later, in the pre-treatment phase, before the processing effluent comes into contact with the effluent generated in the pre-treatment phase, in order to reduce the risk of contamination, minimize the effluent flow, and reduce the cost of treatment and final disposal of the waste (Johanson, 2014; Alonso et al., 2010; Lopes et al., 2015; Mittal, 2006). Segregation is accomplished by adopting several techniques including: decantation, sieving, and filtration, which are unitary operations and can be used to recover part of the solid waste present in the effluent, the presence of which increases the pollutant load and requires more complex treatments (Bezama et al., 2012).

The segregation depends on the characteristics of the constituent material. Thus, for example, different operations are required when the sedimentation, sedimentation capacity and density difference of the material are preponderant, so that the process takes place efficiently. For sieving and filtration, which use the same principle of particle separation, one should consider the size of the material to be separated (Johanson, 2014; Sutherland, 2011; 2013). It is necessary to study the fish production process and the effluent generated in the different steps. The implementation of segregation depends on the type and volume of effluent produced and the chief generating points. This study analyzed the theoretical efficiency of segregation applied to the different streams of effluents produced in a fish warehouse to reduce solids, organic matter and oils and greases, in order to support the sustainable development for the fish-processing industry.

2. MATERIALS AND METHODS

2.1. Processing of raw material

The study was carried out in a fish warehouse located in the northern region of Brazil, which processes 1687.50 kg/month of fish. The species processed were *Colossoma macropomum* (tambaqui), *Brycon cephalus* (matrinxã), *Pseudoplatysto macrorruncans* (pintado) and *Leporinus freiderici* (piauí). The raw material was processed through evisceration and cooling in four steps: initial (I); Evisceration (II) cooling (III) and global (IV) (Figure 1).

Figure 1. Fish processing in the refrigerator under study with indication of collection points of effluent samples for physical and chemical characterization.

Step I was configured for receiving, weighing, sanitizing and transporting the raw material to the subsequent step, the processing. Step I was therefore characterized by the generation of liquid effluent with the presence of pieces of fish, oils and greases. Step II was evisceration, which employs a cutting or abdominal incision table and subsequent evisceration. The fish was placed on the evisceration table, the viscera was manually removed, the product weighed, cleaned, stored and subsequent routed to refrigeration. This stage is characterized by the generation of liquid effluent with pieces of fish, oils and greases, viscera, and blood.

Step III, the cooling room, is the storage location for the product and the waste. The product was conditioned and cooled in monoblocs until distribution to market and the waste goes to the treatment plant. This step was characterized by the washing of the monoblocs, with the generation of liquid effluent accompanied by blood and residues of the material used in the cleaning of the place. Step IV corresponds to the effluent created during fish processing and monobloc washing.

2.2. Sampling points, effluent characterization and evaluation of effluent segregation

Effluent samples were collected at the following points: I (Initial step), after the washing cylinder; II (Processing step), after the fish evisceration table; III (Cooling step); and IV, after

packing the product in refrigerated space monoblocs. The samples were taken at the effluent junction site (from processing and administrative area).

The analysis of the effluent was carried out as follows: total solids (ST) Ref. 2540-G Total, fixed, and volatile solids in solid and semisolid samples), biochemical oxygen demand (BOD), technique Ref. 5210 B. 5-Day BOD Test), chemical oxygen demand (COD) Ref. 5220 Closed reflux titrimetal method), and oils and greases (Ref. 5520-B Partition gravimetric method). The analyses were performed as described in the Standard methods for the examination of water and wastewater (APHA, 2005).

2.3. The segregation of effluent streams

In order to determine the rate of removal of the pollutants from the application of segregation in the effluent streams of each of the processing stages, the percentages of removal were determined for the studied compounds (total solids, organic matter, and oils and greases) obtained theoretically when employed in different unit operations and processes, namely:

- the percentage of theoretical removal for the separation of total solids was determined by the following techniques: screening; screen combined with filter and catch basin; screen, filter and catch basin with removal; screening with microfiltration, ultrafiltration, nanofiltration and reverse osmosis; flotation by dissolved air.

- the following techniques were used to determine the segregation of organic matter: screens; rotating filter; rotary sieve; ultrafiltration; prefiltration conjugated to nanofiltration.

- for the segregation of oils and greases, the membrane filtration processes associated with electrocoagulation were studied, specified by dynamic membrane and electrocoagulation, ceramic and electrocoagulation membrane, ceramic membrane, and dynamic membrane.

To determine the efficiency of the application of the segregation, descriptive statistical analysis was used, adopting the calculation of summary measures, taking into account the nature of the variables involved. For the inferential analysis of the results, parametric tests were used, taking into account the nature of the distributions of the values or the variability of the measurements made. This was accomplished using the Microsoft Office Excel 2007 statistical package.

3. RESULTS AND DISCUSSION

For the characterization of the effluent from Steps I, II, III and IV of the fish processing, the total solid parameters were analyzed, adopting the parameters: total solids, organic matter (BOD_{5, 20}, and COD) and oils and greases. For the total solids (Figure 2a) the following average concentrations were found: 1740 g L⁻¹ (Step I); 2714 g L⁻¹ (Step II); 444.1 g L⁻¹ (Step III), and 2094 g L⁻¹ (Step IV). The concentrations were similar to those found in other studies (Chowdhury et al., 2010; Garde, 2011). They presented the typical characteristics of the processing in the industry, whose final product is only gutted fish, not filleting, or preserving, for example, that increase solids in effluents.

Using the COD test, the organic matter showed a mean concentration of 1446 g L⁻¹ in Stage I, 1811 g L⁻¹ in Stage II, 167.6 g L⁻¹ in Stage III and 1592 g L⁻¹ in Stage IV (Figure 2b). A high content of organic matter was found in the steps that correspond to the processing itself and in the global effluent, due to the added load which originated in the processing. This is similar to the findings of other studies (Alexandre et al., 2014; Cristovão et al., 2012; 2015; Chowdhury et al., 2010; Garde, 2011; Anh, 2011; Queiroz et al., 2013).

When analyzing the BOD, the results were compatible with those obtained in the COD analysis and the concentrations were close to those obtained in other fish processing industries (Alexandre et al., 2014; Cristovão et al., 2012; 2015; Chowdhury et al., 2010; Garde, 2011; Anh, 2011; Queiroz et al., 2013). The mean BOD concentrations of 699.1 g L⁻¹ in Step I;

908 g L⁻¹ in Step II; 80.3 g L⁻¹, in Step III and 742.5 g L⁻¹ in Step IV were found in this study (Figure 2c). The highest concentration of organic matter in Step II was associated with evisceration and hygiene activities, which added solid waste to the effluent collection network, such as viscera, the residue most generated in the warehouse studied, besides blood and pieces of the fish, increasing the biodegradability of the effluent. It is observed that the reduction of the organic matter content is primordial, indicative of the necessity of the segregation of this effluent.

For the oils and greases, a concentration of 0.172 g L⁻¹ was obtained in Stage I, 0.837 g L⁻¹ in Stage II, 0.0316 g L⁻¹ in Stage III and 0.701 g L⁻¹ in Stage IV (Figure 2d). All steps studied presented upper and lower limits in relation to the quality standard recommended by the legislation CONAMA Resolution 357/2005 and complementary 430/2011 (CONAMA, 2006; 2011). As expected, Step II presents a higher concentration among the other stages studied due to the characteristics of the residues generated in this as a result of evisceration. This parameter differs greatly from industry to industry, since those that process preserves add oil to the product, so these data may be divergent from study to study, such as those performed by Mosquera-Corral et al. (2001), Cristovão et al. (2012; 2015), whose concentrations were between 156 g L⁻¹ and 2841 g L⁻¹ of oils and greases.

Figure 2. Concentration of total solids (a), Chemical demand for oxygen (b), biochemical oxygen demand (c), and oils and greases (d) found in the effluent generated during fish processing.

Based on the characterization of the effluent generated in the fish processing industry, a study can determine the concentrations of the parameters of interest. When applied to the segregation of effluent streams, this would aid in verifying the efficiency in reducing the concentration of these in the final effluent and in evaluating the possibility of recovery of co-products. This is especially important because the concentration of pollutants in effluent is equivalent to the concentration of final waste from the processing industry, even for different raw materials such as fish, seafood and crustaceans (Alexandre et al., 2014; Anh et al., 2011).

The implementation of technical segregation minimizes the final concentration of the pollutant, facilitating the operations involved in the treatment and also allowing the use of co-products, as previously mentioned. The theoretical percentages of removal obtained from the use of different segregation techniques for the studied compounds (total solids, organic matter, oils and greases) (Table 1) were used in the processing steps (I, III, II and IV) of the industry under study.

Table 1. Segregation techniques and percentages of removal achieved for the compounds studied.

Technician employed	Theoretical adopted	References
Total Solids (%)		
Screen	31 - 60	Bezama et al. (2012); Almandoz et al. (2015) FAO (2014)
Screen combined with filter and catch basin	40 - 70	
Screening combined with microfiltration, ultrafiltration, nanofiltration and reverse osmosis	100	Gebreyohannes et al. (2016)
Dissolved air flotation	80 - 90	Colic et al. (2007)
Organic matter (COD and BOD)		
Screens	25 - 60	Mittal (2006)
Rotary filter	15	Cowi (2008)
Rotary Sieve	25	Cowi (2008)
Nanofiltration conjugated pre-filtration	56	Gebreyohannes et al. (2016)
Ultrafiltration	36	Gebreyohannes et al. (2016)
Nanofiltration	60 - 80	Gebreyohannes et al. (2016)
Dissolved air flotation	30 - 90	Mittal, 2006; Bustillo-Lecompte e Mehrvar (2015)
Coagulation-flotation	90	Lefebvre e Moletta (2006)
Reverse osmosis	97.5	Gebreyohannes et al. (2016)
Oils and greases		
Membrane filtration associated with electrocoagulation	65	Yang et al. (2015)
Ceramic membrane and electrocoagulation	50	Yang et al. (2015)
Ceramic membrane	2	Yang et al. (2015)
Dynamic membrane	10	Yang et al. (2015)
Floating	37 - 63	Colic et al. (2007)
Screen	10 - 20	Colic et al. (2007)

The results when using the theoretical percentages of removal, related to the total solids found in the effluents from Steps I, II, III and IV according to the segregation techniques adopted. When simplified techniques are used, the reduction is from 25 to 60% (Figure 3a and b). However, reductions of up to 90% are achieved when the techniques are associated (Figure 3c).

For the techniques that considered the removal of total solids, using screening, the removal achieved was 31% (Figure 3a); the screen 40% to 60% (Figure 3b); filter screen and catch basin 40% to 70% (Figure 3c), and 80% to 90% dissolved air flotation (FAD) (Figure 3d).

For removal of organic matter, the highest theoretical percentages were associated with segregation techniques that operate through nanofiltration, dissolved air flotation, coagulation-flotation and reverse osmosis (Figure 4). These segregation techniques were able to remove up to 97.50% of the organic matter (Figure 4), that results in a quality effluent to be directly released into a water body, or to be reused or recycled in the processing, according to Brazilian legislation in force (Resolution CONAMA 430/2011 (CONAMA, 2011) and Resolution 54/2005 of the CNRH (2006). If the effluent from segregation is treated, a simplified system

will suffice. When the less efficient techniques are adopted, such as screens, it is still possible to achieve a 25 to 60% reduction, which is important, when the compound is to be minimized, as organic matter considered as one of the big problems for the treatment of effluents.

Figure 3. Estimation of total solids concentration in the processing effluent after application of segregation techniques.

Legends: (a) Screening; (b) Screen; (c) Screen combined with filter and catch basin; (d) Dissolved air flotation (DAF).

In general, the rate of removal of organic matter obtained when using screens was 25% to 60% (Figure 4a); rotary filters reached 15% (Figure 4b); rotating sieve reached 25% (Figure 4c); nanofiltration conjugated prefiltration reached 56% (Figure 4d); ultrafiltration reached 30% to 36% (Figure 4e); nanofiltration reached 60% to 80% (Figure 4f); dissolved air flotation reached 30% to 90% (Figure 4g); coagulation-flotation reached 90% (Figure 4h), and reverse osmosis 97.50% (Figure 4i).

The removal rates obtained for oils and greases, when theoretical removal is applied: membrane filtration associated with electrocoagulation, 65% (Figure 5ba); Ceramic membrane and electrocoagulation, 50% (Figure 5b); Ceramic membrane, 2% (Figure 5c); dynamic membrane, 10% (Figure 5d); flotation, 37% and 63% (Figure 5e); and screen, 10% to 20% (Figure 5f).

Oils and greases must be removed from fish-processing effluents, because they interfere with oxygen transfer, and cause operational problems in treatment systems (Alexandre et al., 2014); but primary treatments are sufficient to remove this contaminant, at least in part (Muthukumaran and Baskaran, 2013). In this study, when used at the theoretical removal rate achieved by the segregation techniques studied (Figure 5), it was possible to reduce up to 65% of the initial concentration when membrane filtration associated with electrocoagulation was adopted (Figure 5a).

Flotation reached from 37% to 63% removal for the parameter (Figure 5e). Due to the importance of this parameter, even the lowest rates of reduction contribute to both effluent treatment and disposal. It is also important to consider the possibility that this compound can be used to produce biofuels (Jayasinghe and Hawboldt, 2012; Alonso et al., 2010; Adeoti and Hawboldt, 2014).

Figure 4. Theoretical removal of organic matter from the studied effluent in concentrations (g L^{-1}) of (a) Biochemical Oxygen Demand and (b) Chemical Oxygen Demand of effluent from segregation.

Legend: (a) Screens; (b) Rotary filter; (c) Rotary sieve; (d) Nanofiltration conjugated prefiltration; (e), Ultrafiltration; (f) Nanofiltration; (g) Dissolved air flotation; (h) Coagulation-flotation; (i) Reverse Osmosis.

Figure 5. Oils and greases in mg/L per step after application of the rates of removal by segregation technique present in the effluent in fish-processing industry.

Legend: (a) Membrane filtration associated with electrocoagulation; (B) Ceramic membrane and electrocoagulation; (C) Ceramic membrane; (D) Dynamic membrane; (E) Flotation; (F) Screen.

Analyzing the results, segregation proved to be an efficient technique to minimize concentrations of the studied compounds: total solids, organic matter and oils and greases (Table 2). However, it does not exempt the final treatment effluent. The COD/BOD ratio below 2.5 indicates biodegradable matter, so there is an indication that it requires treatment for stabilization.

The segregation techniques have been shown to be effective in keeping waste out of the drain and reducing effluent treatment costs (Watson, 2003), as well as to be technologies used for the fish processing residues in order to foster development of the socioeconomic and environmental sustainability of the industry (Anbe, 2011). Studies of the valuation of by-products of fish processing conclude that the segregated material can be used in the creation of new products, with low raw material and production costs, increasing industry profit and reducing environmental impact (Arvanitoyannis and Kassaveti, 2008; Monteiro, 2013; Silva et al., 2015); with this favors the generation of new jobs.

The alternatives of reuse of fish-processing residues are available for animal and human consumption, which can contribute to the establishment of a fishing sector committed to environmental issues (Alonso et al, 2010). It is also possible to use the residues for the production of collagen and antioxidant isolation for cosmetics, biogas/biodiesel, fertilizers, dietary applications (chitosan), food packaging (gelatin), enzyme isolation (proteases) (Arvanitoyannis and Kassaveti, 2008; Oliveira et al., 2015) and fishmeal, as the most common reuse alternative (Jayasinghe and Hawboldt, 2012; Jayasinghe and Hawboldt, 2013; Adeoti and Hawboldt, 2014; Lin and Li, 2009). The purpose of this improvement in the production process is to improve the performance of the market in response to the demand for new food products or as required by governing legislation (Bar, 2015).

Table 2. Methods of segregation employed in-fish processing industry for the removal of total solids, organic matter and oils and greases, and maximum efficiency when applied in the following processing Steps: I (Initial stage) after the washing cylinder; II (Processing stage), after the fish-evisceration table; III (Cooling stage), after packing the product in monoblocs in refrigerated space; and IV (Processing effluent stage and administrative area).

Total Solids						
Techniques	Theoretical removal	[C]inicial (mg/L)	I (mg/L)	II (mg/L)	III (mg/L)	IV (mg/L)
Screening	31%	1740	1201	1873	306	1445
Screen	40% a 60%	1740	870	1357	222	1047
Screen combined with filter and catch basin	40% a 70%	1740	783	1221	200	942
Dissolved air flotation (FAD)	80% a 90%	1740	348	407	67	314
Organic matter						
Techniques	Theoretical removal	[C]inicial	I (mg/L)	II (mg/L)	III (mg/L)	IV (mg/L)
		DQO (mg/L) DBO (mg/L)				
Screens	25% a 60%	699	8314	1041,3	96,37	915,4
Rotary filter	15%	699.1	594.2	771.8	68.2	820..6
Rotary Sieve	25%	699.1	524.3	681	60.22	594
Nanofiltration conjugated prefiltration	56%	1446	636.2	796.8	73.74	628.7
Ultrafiltration	30% a 36%	1446	925.44	1159	107.2	859.7
Nanofiltration	60% a 80%	1446	433.8	543.3	50.3	658.0
Dissolved air flotation	30% a 90%	699.1	279.6	363.2	32.12	387.3
Coagulation-flotation	90%	699.1	69.9	90.8	8.03	222.7
Osmose Reversa	97,50%	1446	36	35	4	40
Oils and greases						
Techniques	Theoretical removal	[C]inicial	I (mg/L)	II (mg/L)	III (mg/L)	IV (mg/L)
Membrane filtration associated with electrocoagulation	65%	0.17	0.06	0.29	0.001	0.25
Ceramic membrane and electrocoagulation	50%	0.17	0.09	0.42	0.02	0.35
Ceramic membrane	2%	0.17	0.17	0.82	0.03	0.69
Dynamic membrane	10%	0.17	0.15	0.75	0.03	0.63
Floating	37% e 63%	0.17	0.09	0.42	0.02	0.35
Screen	10% a 20%	0.17	0.15	0.71	0.03	0.60

4. CONCLUSION

The segregation techniques studied showed that, for the effluent under study, higher rates of removal of solids, organic matter and oils and greases were reached when conjugated processes were adopted. The result is a final effluent with less polluting potential, thus requiring a more-simplified treatment.

Segregation of total solids, organic matter and oils and greases showed a better result in Step II (evisceration step) as a function of the solid waste load, such as pieces of fish, viscera and blood generated during processing.

Due to the low load of total solids, organic matter and oils and greases of Stage III (monobloc wash), the implementation of segregation techniques would result in an effluent in accordance with Brazilian legislation in force.

The introduction of segregation processes in the effluent streams not only allows the production of a better final effluent, but also the reduction of by-product loss.

5. ACKNOWLEDGEMENTS

The authors are grateful to the Brazilian governmental agency National Council for Scientific and Technological Development (CNPq) for the project funding (Process number: 407728/ 2012-0) and a scholarship (Process number: 312697/ 2014-7).

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Assessment of the water quality and trophic state of the Ribeirão Guaraçau Watershed, Guarulhos (SP): a comparative analysis between rural and urban areas

ARTICLES doi:10.4136/ambi-agua.2170

Received: 27 Jul. 2017; Accepted: 16 Jan. 2018

**Reinaldo Romero Vargas^{1*}; Márcia da Silva Barros²; Antonio Roberto Saad¹;
Regina de Oliveira Moraes Arruda¹; Fernanda Dall'Ara Azevedo³**

¹Universidade de Guarulhos (UNG), Guarulhos, SP, Brasil
Mestrado em Análise Geoambiental (MAG). E-mail: rei_vargas@terra.com.br,
asaad@prof.ung.br, rarruda@prof.ung.br

²Centro Universitário Anhanguera de São Paulo (UNIAN), São Paulo, SP, Brasil
Departamento de Ciências Exatas. E-mail: barros.r777@yahoo.com.br

³Universidade de Guarulhos (UNG), Guarulhos, SP, Brasil
Programa de Pós-Graduação em Análise Geoambiental
E-mail: fdallara.azevedo@gmail.com

*Corresponding author

ABSTRACT

The urbanization process through which large urban centers have been passing has affected drastically the availability and especially the quality of water. The Ribeirão Guaraçau Watershed, located in the northern part of the Guarulhos municipality, includes rural and urban areas of different land-use classes. The goal of this study is to assess the water quality and to diagnose the eutrophication stage of the surface waters of the Ribeirão Guaraçau, the main water course of the Ribeirão Guaraçau Watershed. To assess environmental quality, physical-chemical analyses (temperature, pH, turbidity, conductivity, and total phosphorus) and microbiological analyses (*E. coli*) were carried out during a period of 12 months. The Trophic State Index (TSI) was used to ascertain the environmental degradation conditions of lotic and lentic environments. The surface waters of the Ribeirão Guaraçau in the rural area are already compromised, with worsening of the water quality upstream indicated by high total phosphorus and *E. coli* caused by fecal contamination due to lack of basic sanitation in the region. Characteristic sites of the rural areas already present signs of degradation with trophic levels varying from oligotrophic to hypereutrophic. The need to provide sewage collectors and sewage treatment systems at the Bonsucesso Sewage Treatment Station, inaugurated in 2011, and the control of the occupation in areas that produce good quality water is paramount.

Keywords: eutrophication, São Paulo Metropolitan Region, urban waters, water pollution.

Avaliação da qualidade da água e do estado trófico da bacia de Ribeirão Guaraçau, Guarulhos (SP): uma análise comparativa entre áreas rurais e urbanas

RESUMO

O processo de urbanização pelo qual os grandes centros urbanos passaram afetou drasticamente a disponibilidade e, em especial, a qualidade da água. A bacia hidrográfica de

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Ribeirão Guaraçau, localizada na parte norte do município de Guarulhos, inclui áreas rurais e urbanas de diferentes classes de uso da terra. O objetivo deste estudo é avaliar a qualidade da água e diagnosticar o estágio de eutrofização das águas superficiais do Ribeirão Guaraçau, o principal curso de água da Bacia do Ribeirão Guaraçau. Para avaliar a qualidade ambiental, foram realizadas análises físico-químicas (temperatura, pH, turbidez, condutividade e fósforo total) e análises microbiológicas (*E. coli*) durante um período de 12 meses. O Índice de Estado Trófico (IET) foi utilizado para determinar as condições de degradação ambiental de ambientes lóticos e lênticos. As águas superficiais do Ribeirão Guaraçau na área rural já estão comprometidas, com o piora da qualidade da água a montante indicada pelo alto fósforo total e *E. coli* causada por contaminação fecal devido à falta de saneamento básico na região. Os locais característicos das áreas rurais já apresentam sinais de degradação com níveis tróficos que variam de oligotróficos a hipereutróficos. A necessidade de fornecer coletores de esgoto e sistemas de tratamento de esgoto na Estação de Tratamento de Esgoto de Bonsucesso, inaugurada em 2011, e o controle da ocupação em áreas que produzem água de boa qualidade é primordial.

Palavras-chave: águas urbanas, eutrofização, poluição das águas, Região Metropolitana de São Paulo.

1. INTRODUCTION

The development of modern society, mainly in the urban areas, has occurred in a disordered way, devoid of any planning, and with increasing levels of environmental degradation. As a result of this disequilibrium, significant impacts can be observed, which put environmental quality at risk, notably when it comes to great metropolises. The Guarulhos Municipality, located in the Metropolitan Region of São Paulo (MRSP), is considered the second greatest city of São Paulo State. It is in full urban expansion, characterized by planning problems induced by industrial development, road, airport, utilities operations and significant civil works, for example, the construction of the northern segment of the Mario Covas Ring Highway (Oliveira et al., 2009; Mesquita, 2011).

The environmental impacts caused by deforestation, agricultural, urban and industrial development, plus the lack of basic sanitation, lead to an increase of nutrient concentrations in the aquatic ecosystems. These nutrients, especially phosphorus and nitrogen, lead to the growth of algae, including potentially toxic cyanobacteria, which endangers the ecosystem, besides increasing water treatment costs (Esteves, 2011). Such a process, named eutrophication, can be quantified by means of the Trophic State Index (TSI), which is used to classify water bodies at different trophic degrees (Lamparelli, 2004). The index classifies the water body in six trophic classes, according to the total phosphorus concentrations in water. The conditions favorable to eutrophication are those of a lentic environment, characterized by the presence of nutrients, high temperatures, high radiation levels, low turbidity and high residence time of the water. Lotic environment water bodies classified as eutrophic, supereutrophic and hypereutrophic rarely present eutrophication due to the movement of their waters. However, it is through rivers and brooks that a great part of nutrient inflow to lakes and reservoirs takes place (ANA, 2013).

Depending on the land use and occupation, different trophic levels are observed in the water bodies. Cunha et al. (2010) studied three tropical rivers with different levels of anthropic interference. These authors observed that in more-preserved regions, with 70% of the area covered by forests, the trophic levels varied from oligotrophic to mesotrophic. On the other hand, in regions occupied by industry, trophic levels were hypereutrophic. In another study of a watershed with 65% of the urbanized area characterized by the presence of stilt houses, where domestic waste is disposed of *in natura* in the water bodies, trophic levels varied from supereutrophic to hypereutrophic. In the same study, in another river with the presence of

settlements and rural activity, the trophic levels varied from mesotrophic to supereutrophic (Silva et al., 2014).

Taking the concept of watershed as a study unit (Machado and Torres, 2012), the Ribeirão Guaraçau Watershed (RGW), mostly located in the northern part of the Guarulhos municipality, was selected for this study. Water producing areas are located in watershed zones (Andrade et al., 2008). Taking the municipal zoning into account, rural and urban zones are located in this watershed, each showing different forms of land use and representing foci of water quality change. The main objective of this study is the assessment of water quality and the diagnosis of the eutrophication stage of the Ribeirão Guaraçau surficial waters in rural and urban areas of the Ribeirão Guaraçau Watershed.

1.1. Geoenvironmental characteristics of the study area

The Guarulhos municipality is one of 39 municipalities located in the northeastern portion Metropolitan Region of São Paulo (MRSP), together with the neighboring Arujá, Itaquaquecetuba, Mairiporã, Nazaré Paulista, São Paulo and Santa Isabel municipalities (Figure 1). The municipality is characterized by a humid, subtropical climate with annual mean rainfall of 1470 mm. The annual rainfall indices were 1897 mm in 2015 and 1570 mm in 2016 (INMET, 2016). The mean annual temperatures in the coldest months reached 17-19°C, whereas in the summer they varied between 23°C and 24°C (Oliveira et al., 2009). The municipality is divided into five basins, the largest being the Baquirivu-Guaçu Watershed (BGW), 149 km² in area, encompassing the study area.

Figure 1. Location of the da Ribeirão Guaraçau Watershed (RGW), Guarulhos (SP).

Source: UnG Geoprocessing Laboratory.

The Ribeirão Guaraçau Watershed (RGW) is 20.5 km² in area, 8350 m long, maximum 5600 m wide, and 990 m of maximum and 750 m of minimum altitude (Ribeiro et al., 2013). RGW landforms and rock types are listed in Table 1.

Table 1. Characteristics of the Ribeirão Guaraçau Watershed (RGW) physical environment.

ZONE	CHARACTERISTICS DO PHYSICAL ENVIRONMENT	
	Landforms	Rock types
RURAL	Mountains and hills higher than 1000 m High hills higher than 900 m Hillocks Restricted fluvial plains	Predominant metamorphic rocks (phyllites; iron formation); igneous rocks (granites); local alluvial sediments.
	Low hills	Metasediments (phyllites).
URBAN	Hillocks Small mounds Ample and restricted alluvial plains	Clastic sediments (coarse to fine sandstones; argillites); alluvial sediments.

Source: Ribeiro et al. (2013).

2. MATERIALS AND METHODS

2.1. Land-use Map

The land-use map was prepared by upgrading the map produced by Ribeiro et al. (2013). The first step in this upgrade was to export the vector file (shapefile) of this base map to the format *Keyhole Markup Language* (kml) of the ArcGIS program – Version 10 (ESRI, 2013). The next step was to import from kml to *Google Earth*, which was overlain to an IKONOS II image, Sensor PSM, 1-m resolution, September 28, 2016, where the vertices of the vector were updated. The last step was to import the updated kml file to ArcGIS and export it to the shapefile format.

2.2. Water sampling and analysis

To assess the water quality along the Ribeirão Guaraçau, five points (P1 to P5) were selected, and six bi-monthly sampling campaigns were carried out from September 2015 to August 2016. The selection of the sampling points (Figure 2) was made considering the size of the drained surface and the different types of land use, so that points P1 to P4 are located in predominantly rural areas and point P5 in the urban zone. Point P1 (23°21'26.93'' S and 46°24'22.60'' W) is located in a more-preserved area, with the predominance of arboreal formations. Point P2 (23°21'42.98'' S and 46°24'16.55'' W) is located at the exit of Lago Azul. Point P3 (23°22'14.45'' S and 46°24'3.95'' W) is located in the northern portion of the watershed and receives the inflow of the households of the Água Azul neighborhood, including a high-density disordered urban occupation (slums) with no sewerage. Point P4 (23°22'50.74'' S and 46°23'44.67'' W), although located in an agricultural area surrounded by vegetated areas, it gathers the contributions from the upstream points. Point P5 (23°24'3.14'' S and 46°24'0.82'' W) is located in area characterized by high-density, ordered urban occupation.

Water analysis in the field was performed using properly calibrated analytical instruments and obtaining triplicate measurements for the following physico-chemical parameters: Temperature (Digimed DM-3 conductivity meter), pH (Digimed DM-2 pH meter), Conductivity (Digimed DM-3 conductivity meter), and Turbidity (Quimis Q279P turbidimeter). The other samples were collected following the National Guide for Collecting and Preservation of Samples (ANA, 2011) for Total Phosphorus and *Escherichia coli*, analyzed in triplicate, as recommended by the *Standard Methods for Examination of Water and Wastewater* (APHA et al., 2012).

Figure 2. Land-use and occupation map for 2016, with the location of the water-sampling points and land-use classes and their percentages (%) in the Ribeirão Guaraçau Watershed (RGW) in 2007 and 2016.

Source: UnG Geoprocessing Laboratory.

The results of these analyses were compared to standards established by CONAMA Resolution 357/2005 (CONAMA, 2005) and State Decree #10755, which assigns water bodies to the classification provided by the State Decree #8468, dated September 8, 1976. The Baquirivu-Guaçu River and all its tributaries up to the confluence with the Tietê River in the Guarulhos municipality belong to Class 3 (São Paulo, 1977). This class of water is destined for the supply for human consumption, after conventional or advanced treatment; irrigation of tree and forage crops; amateur fishing; secondary contact recreation; and animal watering.

2.3. Trophic State Index (TSI)

The calculation of TSI (TP), according to Lamparelli's (2004) methodology, took into account total phosphorus (TP) measured at points P1 to P5 ($\mu\text{g.L}^{-1}$).

The TSI values are distributed in the six trophic state classes as follows (CETESB, 2007; Lamparelli, 2004): $\text{TSI} \leq 47$ (ultraoligotrophic); $47 < \text{TSI} \leq 52$ (oligotrophic); $52 < \text{TSI} \leq 59$ (mesotrophic); $59 < \text{TSI} \leq 63$ (eutrophic); $63 < \text{TSI} \leq 67$ (supereutrophic), and $\text{TSI} > 67$ (hypereutrophic).

3. RESULTS AND DISCUSSION

The Ribeirão Guaraçau Watershed (RGW) contemplates zones with both rural and urban characteristics. From Point P1 to Point P4, arboreal formations, grassy vegetation and low-

density urban occupations predominate, which characterizes this region as a rural area (Figure 2). The consolidated urban zone predominantly occupies the southern portion of the basin. In the surroundings of Point P5, which is the last sampling point of the Ribeirão Guaraçau, there are high-density, ordered urban occupations, which are essentially of urban characteristics. During the last ten years, from 2007 to 2016, RGW has undergone little changes regarding occupation (Figure 2). A negative aspect is that in this period, despite the minor contribution of the high-density disordered occupations (slums), there has been an increase of approximately 108% of this type of occupation along RGW, from the rural to the urban area. The increase of these areas devoid of sewage collecting systems has led to the worsening of the quality of the watershed water bodies. Another relevant change regarding water quality was the 33% decrease in agricultural areas. The land-use and occupation map shows that the majority of the agricultural areas were replaced by grassy vegetation in 2007, as reported by Ribeiro et al. (2013). However, there was not an increase of grassy vegetation areas, due to the 10% increase of low-density urban occupations in the rural region.

Upstream Point P1, which is located in a low-density urban occupation area, a more preserved region is composed of arboreal formations. As a consequence, all the measured parameters indicate the very good quality of the surficial waters (Table 2). Only the mean value of the microbiological parameter (*E. coli*) is above the established in the CONAMA Resolution for Class 3 water bodies (CONAMA, 2005). This high value is explained by the fact that there are small animal farms surrounding Point 1. The total phosphorus analysis for this point, despite being below the limit established in the legislation, yielded a mean value close to the limit and a maximum value above the limit. Even though it is not high, this corroborates the fecal contamination of the water body, probably caused by animal feces.

Water temperature (Table 2) varied according to the occupation of the surroundings, the lowest mean value being obtained at Point P1 and corresponding to the most vegetated area, and the highest at Point P5, corresponding to the urban area. Several studies indicate that the presence of a vegetated area in the surroundings of a water body causes a decrease in water temperatures. Conversely, more urbanized areas with little vegetation significantly increase water temperature (Fia et al., 2015; Vargas et al., 2015; Pereira et al., 2016; Carvalho et al., 2016).

For all the analyzed points, pH did not vary significantly along the watershed, with low coefficient of variation and mean pH values within the limits established by CONAMA Resolution 357/05, even in areas characterized by industrial activity, agriculture and lack of basic sanitation.

Turbidity values for points P1 to P4 are below the maximum limit established by CONAMA 357/05. However, turbidity values for Point P5 exceeded the limit, due to the fact that domestic and chemical industrial wastes are discharged in the Ribeirão Guaraçau. The highest turbidity values were found in the rainy season, which was also observed by Sardinha et al. (2008), Ríos-Villamizar et al. (2011), Fia et al. (2015) and Andrietti et al. (2016). In this period the dragging of solids in suspension occurs by means of runoff processes, mainly in regions with exposed soil in the proximity of water bodies.

Many studies have reported the use of electric conductivity to assess the impact of pollutants in the aquatic environment, both rivers (Uwidia and Ukulu, 2013; Thompson et al., 2012; Vargas et al., 2015) and lakes (Das et al., 2006; Costa and Henry, 2010). The water of each region presents characteristic electric conductivity, which depends mainly on the rock types the water permeates (Tong and Chen, 2002). Mean conductivity values increased from Point P1 to Point P5 (Table 2), which indicates an increase of ion concentrations upstream to downstream. It is worth mentioning the high conductivity value (860 $\mu\text{S}/\text{cm}$) at Point P4, located in an agricultural area. The use of fertilizers, such as inorganic nitrogen and phosphorus salts, leads to an increase

in conductivity at P4. This can also be confirmed by the increase in total phosphorus (TP) at this Point P4 in relation to Point P3 (Table 2). The contribution of other water bodies between Points P4 and P5 causes the decrease of conductivity by dilution at Point P5 (671 $\mu\text{S}\cdot\text{cm}^{-1}$). Vargas et al. (2015) obtained similar results for the Córrego Taquara do Reino, which belongs to the homonymous watershed located north of the Guarulhos municipality. According to the authors, the lack of basic sanitation caused an increase in electric conductivity.

Table 2. Values of the physical-chemical and microbiologic parameters of Ribeirão Guaraçau Watershed waters from September 2015 to August 2016.

Parameter	Points	Mean	s.d.	Min.	Max.	CV (%)	CONAMA 357 Class 3
T ($^{\circ}\text{C}$)	P1	18.5	4.2	13.0	24.3	22.9	N.E.
	P2	20.9	4.3	14.5	26.0	20.7	
	P3	20.7	4.0	14.9	24.9	19.5	
	P4	19.5	4.2	13.6	23.9	21.6	
	P5	21.8	4.0	15.3	25.6	18.5	
pH (upH)	P1	6.1	0.4	5.6	6.6	5.8	6 to 9
	P2	6.9	0.4	6.5	7.5	5.8	
	P3	7.3	0.8	5.98	8.1	11.4	
	P4	7.5	0.6	6.9	8.4	7.7	
	P5	7.0	0.7	6.5	8.3	10.7	
TU (NTU)	P1	10	15	2	40	152	max. 100
	P2	22	20	2	55	88	
	P3	30	11	12	39	36	
	P4	14	10	2	30	68	
	P5	206	204	32	532	99	
CE ($\mu\text{S}\cdot\text{cm}^{-1}$)	P1	83	24	51	107	28.6	N.E.
	P2	138	23	115	172	16.5	
	P3	242	107	156	457	44.4	
	P4	860	415	446	1603	48.3	
	P5	671	235	421	956	35	
TP ($\text{mg}\cdot\text{L}^{-1}$)	P1	0.117	0.197	0.007	0.5	168	0.05 (lentic)
	P2	0.123	0.285	0.007	0.71	231	
	P3	1.88	2.1	0.007	5.14	112	
	P4	2.54	1.58	0.007	4.18	63	0.15 (lotic)
	P5	4.84	3.57	0.13	9.32	74	
<i>E. coli</i> (UFC.100 mL^{-1})	P1	4.7E+03	2.2E+03	2.5E+03	8.0E+03	47	max. 2400
	P2	6.3E+03	4.1E+03	2.4E+03	1.3E+04	65	
	P3	5.5E+05	1.1E+06	1.2E+04	2.8E+06	205	
	P4	7.9E+05	1.1E+06	1.2E+05	3.0E+06	145	
	P5	2.2E+07	2.3E+07	3.0E+06	5.4E+07	104	

P2 lentic body (Lago Azul). The other points: lotic body.

Abbreviations: s.d. (standard deviation); CV (coefficient of variation); T (temperature); TU (turbidity); CE (electric conductivity); TP (total phosphorus); *E. coli* (*Escherichia coli*); N.E (Not established).

Ribeirão Guaraçau reaches other water courses that flow towards the Lago Azul, which was an old open pit for sand exploitation (Mesquita, 2011). At present, the lake is used for recreation, such as swimming and fishing. At Point P2, total phosphorus values for lentic bodies and especially the microbiologic parameter exceeded the values established by the legislation. Fecal contamination from regular and irregular occupations, plus the lack of sewerage and farming lead to the values above those permitted by legislation and certainly this demands attention from municipal authorities, given that the use of Lago Azul for recreational activities is encouraged by them. Point P3, in the northern portion of the watershed, is the confluence of contributions from households of the Água Azul neighborhood, in particular the high-density

disordered urban occupation (slums) with no sewerage. Such a degradation scenario is confirmed when comparing Point P2 to Point P3. There is an increase of 15 times in total phosphorus mean concentration and 87 times in *E. coli* mean values. These values continuously increase along the basin, and the highest values are found at Point P5, which receives the inflow of urban area located in neighborhoods Chácara Recreio Rober and Vila Carmela.

The behavior of total phosphorus and *E. coli* was distinct during rainy periods. Total phosphorus values were higher during dry periods, with the exception of Point P4, indicating that in rainy periods dilution of phosphorus concentrations takes place in the surficial waters. The mean total phosphorus values and standard deviations for the dry and rainy periods were respectively at P1: 0.176 ± 0.281 and 0.059 ± 0.089 ; at P2: 0.240 ± 0.403 and 0.007 ± 0.000 ; at P3: 2.577 ± 2.335 and 1.175 ± 2.023 ; at P4: 2.463 ± 1.056 and 2.607 ± 2.268 , and at P5: 5.350 ± 3.838 and 4.329 ± 4.035 . The very close phosphorus values at Point P4 can be related to the constant use of fertilizers in the agricultural area (Figure 2). Saad et al. (2013) also observed the dilution effect in total phosphorus concentrations during rainy periods and, according to the authors, this effect was more pronounced in the consolidated urban area and impervious soil. Peláez-Rodríguez (2001) also observed an increase in the concentration of nutrients during the dry season and attributed this fact to the increase in nutrient concentration due to decrease in water flow. Similarly, Stacciarini (2002), when assessing the quality of the water resources in Paulínia (State of São Paulo), observed that in the majority of the points he analyzed phosphorus concentrations were higher in the dry period. Cruz (2003), assessing the quality of the Uberaba River waters (State of Minas Gerais), obtained the same trends regarding total phosphorus in rainy and dry periods.

Farage et al. (2010) observed in the region of the Pombas River (State of Minas Gerais) that during the rainy period, runoff in anthropized areas contributed to a higher discharge of phosphorus, increasing its concentration, even with higher river flows. The authors attributed this increase in total phosphorus to runoff occurring in the rainy periods mainly on soils devoid of vegetation or with predominant grassy cover, as on the margins of the Pomba River. According to Prada and Oliveira (2006), the increase in phosphorus in river waters during the rainy period can also be related to the re-suspension of bottom sediments as the river flow increases.

The amount of microorganisms present in surficial waters was higher in the rainy period, in special at the least-preserved points, as indicated by the *E. coli* logarithmic values during the rainy and dry periods, respectively for P3: 5.36 ± 1.20 and 4.46 ± 0.14 ; for P4: 5.96 ± 0.55 and 5.14 ± 0.10 , and for P5: 7.25 ± 0.41 and 6.92 ± 0.70 . Saad et al. (2013) obtained similar results for the Ribeirão Tanque Grande Watershed, which presents geomorphological characteristics similar to those of RGW. Due to the higher declivity, runoff takes place with the transport of microorganisms to the water bodies, preventing water infiltration in the soil (Chaves and Santos, 2009; De Azevedo Lopes and Magalhães Júnior, 2010; Andrietti et al., 2016).

The Trophic State Index was calculated using total phosphorus (TP) values. Figure 3 shows that TSI values increase from rural to urban zones.

Figure 3. Trophic State Index behavior along Ribeirão Guaraçau Watershed from September 2015 to August 2016.

In Points P1 and P2, which are the most-preserved, trophic state levels vary from oligotrophic to mesotrophic, indicating the presence of clean water bodies, in which unwanted interferences resulting from the presence of nutrients, in special phosphorus, do not occur. For the other points, progressive worsening of the water body trophic state is observed (Figure 3). In the rainy periods, TSI (TP) values were favorably lower, thanks to the dilution of the nutrients. For Point P3, the supereutrophic level predominates, but with ample variation from oligotrophic to hypereutrophic. The presence of small farms and the irregular occupation in the surroundings of Point P3, plus the temporal effect, besides the paving works during the sampling period, caused such variations in the trophic level. Similar results were obtained by Saad et al. (2013) and Vargas et al. (2015) for other watersheds of the Guarulhos municipality. The trophic levels at Point P4 got worse, varying from eutrophic to hypereutrophic. Agricultural activities close to this point cause the worsening of the trophic level, due to contamination by fertilizers used in plantations (Farage et al., 2010; Gonçalves and Rocha, 2016; Zhou et al., 2016). Point P5 reached hypereutrophic levels in all determinations, indicating a water body significantly affected by high organic matter and nutrient concentrations, compromising the use of the water at that point.

4. CONCLUSIONS

The recent hydric crisis that affected the southeastern region of Brazil from 2014 to 2016 and that still affects a large part of the Brazilian northeastern region calls attention to preservation policies and control of watershed areas. The expansion of urban areas towards these watershed areas directly affects the quality of surficial and underground waters, in particular in developing countries due mainly to the lack of sewage treatment, which is directly discharged in rivers, causing pollution and impacts on the environment. Urbanization favors impermeabilization of the soil, leading to flooding and making aquifer recharge difficult. Several areas in the northern part of the Guarulhos municipality produce water but unfortunately the studies of the watersheds, in particular of the Baquirivu-Guaçu River Watershed, have pointed to the degradation of the water bodies. The present study of the Ribeirão Guaraçau Watershed shows that the Ribeirão Guaraçau surficial waters in the rural area are already compromised in the surroundings of the Lago Azul (point P2). The other points,

P3 to P5, reveal the worsening of the water quality in respect to total phosphorus and *E. coli*, indicating fecal contamination due to the lack of basic sanitation. The increase of disordered developments close to Lago Azul has contributed to the worsening of the water quality. The values of both parameters at these sampling points exceeded the limit established by CONAMA Resolution 357/05 for Class 3 water bodies. Points P3 and P4 in the rural zone present signs of degradation, with trophic levels varying from oligotrophic to hypereutrophic and predominance of the supereutrophic level at Point P3, and worse conditions at Point P4, with the predominance of the hypereutrophic level and variations from eutrophic to hypereutrophic.

The Bonsucesso Sewage Treatment Station, located downstream from the Ribeirão Guaraçau Watershed, was inaugurated in December 2011 to attend to a sewage treatment demand for 260 thousand inhabitants (SAAE, 2013). The necessity to build a collecting net and sewage treatment installations in the Bonsucesso Station is herein emphasized (Vargas et al., 2017).

5. ACKNOWLEDGMENTS

To São Paulo Research Foundation for the financial support to Research Project Proc. 2015/07406-4.

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Effects of different operating conditions on total nitrogen removal routes and nitrous oxide emissions in a lab-scale activated sludge system

ARTICLES doi:10.4136/ambi-agua.2174

Received: 23 Aug. 2017; Accepted: 20 Jan. 2018

Renato Pereira Ribeiro¹; Débora Cynamon Kligerman²; William Zamboni de Mello³; Denise da Piedade Silva⁴; Renatah da Fonseca Correia²; Jaime Lopes da Mota Oliveira^{2*}

¹Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro (IFRJ), Nilópolis, RJ, Brasil
E-mail: renato.ribeiro@ifrj.edu.br

²Fundação Oswaldo Cruz (FIOCRUZ), Rio de Janeiro, RJ, Brasil
Departamento de Saneamento e Saúde Ambiental (DSSA). E-mail: deboracyklig@gmail.com,
renatah.correia@gmail.com, jaimel@ensp.fiocruz.br

³Universidade Federal Fluminense (UFF), Niterói, RJ, Brasil
Departamento de Geoquímica (GEO). E-mail: wzamboni@id.uff.br

⁴Universidade Federal do Rio de Janeiro (UFRJ), Rio de Janeiro, RJ, Brasil
Centro de Ciências da Saúde (CCS). E-mail: d.silv@yahoo.com.br

*Corresponding author

ABSTRACT

This study sought to determine the effects of different operating conditions, such as variable organic loading, different sludge retention times (SRTs) and airflow rates, limited dissolved oxygen (DO) concentrations and ammonium (NH_4^+) shock loading on total nitrogen (TN) removal routes and nitrous oxide (N_2O) emissions in a lab-scale activated sludge system. Short SRT (5 days) combined with very low DO levels (0.5 mg L^{-1}) were responsible for lower TKN oxidation efficiencies and, consequently, negligible NO_2^- accumulation rates. These results suggest that nitrification efficiency was hampered by the oxidation of organic matter, with a large part of TN removed by sludge waste process. As the SRT increased (from 5 to 10 days) and DO was set to 1.0 mg L^{-1} , TKN oxidation rates and NO_2^- accumulation reached their maxima, which are thought to be the optimal conditions for both organic matter oxidation and partial nitrification. Under these conditions, gas transfer to the atmosphere became the preferential route for TN removal instead of incorporation into the sludge waste. However, N_2O contribution is estimated as less than 5.6% (with respect to TN in the influent). Insufficient aeration and stress conditions (such as NH_4^+ shock loading) can cause limited DO conditions and NO_2^- accumulation, leading to higher amounts of emitted N_2O . Therefore, the adequate control of DO concentrations is a key factor to avoid NO_2^- accumulation and consequently high N_2O emissions.

Keywords: activated sludge, dissolved oxygen, nitrite accumulation rate, nitrogen removal routes, nitrous oxide emission.

Efeito das diferentes condições operacionais nas rotas de remoção do nitrogênio total e emissões de óxido nitroso em um sistema de lodos ativados em escala de bancada

RESUMO

O principal objetivo deste estudo foi determinar os efeitos das diferentes condições operacionais, tais como carga orgânica variável, diferentes idades do lodo e taxas de aeração, limitação das concentrações de oxigênio dissolvido (OD) e choque de carga de amônio (NH_4^+), nas rotas de remoção do nitrogênio total (NT) e nas emissões de óxido nitroso (N_2O) provenientes de um sistema de lodos ativados em escala de bancada. Idades do lodo reduzidas (5 dias) combinadas com baixas concentrações de OD ($0,5 \text{ mg L}^{-1}$) foram responsáveis por uma baixa eficiência de oxidação do NT Kjeldahl (NTK) e, conseqüentemente, negligenciáveis taxas de acúmulo de nitrito (NO_2^-). Esses resultados sugerem uma perda na eficiência da nitrificação completa em razão do maior comprometimento do OD com a oxidação da matéria orgânica, com a maior parcela do N removida pela incorporação ao lodo excedente. O aumento da idade do lodo (de 5 para 10 dias) combinada com o aumento da concentração de OD para $1,0 \text{ mg L}^{-1}$, levaram ao alcance das taxas máximas de oxidação do NTK e de acúmulo de NO_2^- , o que representou uma condição ótima para ambos os processos de oxidação da matéria orgânica e nitrificação incompleta. Sob essas condições, a transferência de gás para a atmosfera tornou-se a rota preferencial de remoção do NT. No entanto, a contribuição do N_2O foi estimada em até 5,6% da carga de NT afluente. Condições de stress (choque de carga de NH_4^+) e aeração insuficiente podem causar períodos de limitação de OD e acúmulo de NO_2^- , podendo levar assim à maiores emissões de N_2O . Portanto, o controle adequado das concentrações de OD é o fator chave para evitar o acúmulo de NO_2^- e, conseqüentemente, maiores emissões de N_2O .

Palavras-chave: emissão de óxido nitroso, lodo ativado, oxigênio dissolvido, rotas de remoção de nitrogênio, taxa de acúmulo de nitrito.

1. INTRODUCTION

The biological pathway for N removal in WWTPs is nitrification, followed by denitrification processes (Wrage et al., 2001; Law et al., 2012). The activated sludge process can provide optimal conditions for the conversion of ammonium (NH_4^+) to nitrate (NO_3^-) (complete nitrification: $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$), especially in tropical regions (Wrage et al., 2001). However, to combine both processes, the design and operation of a traditional WWTP must be altered (i.e. an anoxic zone and internal recirculation systems must be added) to allow for the complete denitrification process, the key process for the effective removal of N as molecular nitrogen (N_2) ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) (Wrage et al., 2001). Another route for N removal is by the sludge waste process (Lee et al., 2008; Bernat et al., 2011). Recently, several studies have addressed N removal processes under many controlled operating conditions, such as hydraulic retention time (HRT), sludge retention time (SRT), dissolved oxygen (DO) concentrations and organic loading rates, among others (Bernat et al., 2011; Rassol et al., 2014; Xiang et al., 2014; Lu et al., 2015). However, only some of these studies calculated the total N (TN) balance (Lee et al., 2008; Bernat et al., 2011).

WWTPs with biological N removal (BNR) are an effective way to decrease the discharge of oxidized N forms (as NO_3^-) into water bodies and thus prevent eutrophication. On the other hand, nitrous oxide (N_2O) emissions from WWTPs are an issue of international concern and should also be taken into account (Keller and Hartley, 2003; IPCC, 2006). Currently, wastewater treatment systems are thought to contribute with about 10% of total anthropogenic

N₂O emissions, when including both manure and sewage treatments (Desloover et al., 2012). N₂O is one of the most important substances from an environmental point of view, since it is linked to global warming and climate change. It is a greenhouse gas with a global warming potential 310 times that of carbon dioxide (CO₂), contributing approximately 7% to overall greenhouse gases (IPCC, 2013). In addition, N₂O is indirectly responsible for the depletion of stratospheric ozone (O₃) by its reaction with excited oxygen atoms and nitric oxide (NO) production: $\text{N}_2\text{O} + \text{O} (^1\text{D}) \rightarrow 2 \text{NO}$ and $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (Crutzen, 1979; Ravishankara et al., 2009). Ravishankara et al. (2009) believe that N₂O will become the major dominant ozone-depleting substance before the end of this century.

During nitrification and denitrification processes, respectively, N₂O is formed as a by-product of NH₄⁺ oxidation to nitrite (NO₂⁻) and as an intermediate of the reduction of oxidized N forms to N₂ (Wrage et al., 2001). Generally, there is no single N₂O emission mechanism from WWTPs and the pathways related to its production are dependent on the WWTP design and closely related to operating conditions (Ahn et al., 2011; Hu et al., 2013). Nitrification is reported as the main source of N₂O emission under DO limitations and, consequently, high NO₂⁻ concentrations. However, the denitrification process can contribute significantly to higher N₂O emissions under an insufficient organic carbon source (C/N ratio) with high NO₂⁻ concentrations (Kampschreur et al., 2009; Law et al., 2012). Thus, the operating conditions that lead to the accumulation of NO₂⁻ concentrations are subject to high N₂O emissions. Therefore, further studies are required to elucidate the importance of controlling operational conditions in order to reduce NO₂⁻ concentrations and thus mitigate N₂O emissions (Desloover et al., 2012).

In this context, this study sought to determine the effects of different operating conditions, such as variable organic loading, different SRTs and airflow rates, limited DO concentrations and NH₄⁺ shock loading, on TN removal routes and N₂O emissions in a lab-scale activated sludge system.

2. MATERIALS AND METHODS

2.1. Lab-scale system and regular operating condition

A continuous lab-scale reactor (total volume = 20 L) consisting of four adjacent and interconnected chambers (V = 5 L) was monitored over 212 days (Figure 1). For the first 135 days, the lab-scale system functioned with some small variations of load (denoted as regular operating condition) to promote the acclimatization of the biomass to the synthetic wastewater. These some small variations occurred as a function of the storage conditions of the synthetic sewage used to supply the reactor. The first chamber (C1; average DO < 0.1 mg L⁻¹) was used as a biological selector (with pre-denitrification) and a mixing zone of the synthetic wastewater and biological sludge that returns from the settler (V = 2 L). The other three chambers (V = 15 L) were aerated so as to maintain DO concentrations near 2.0 mg L⁻¹. During this period, HRT and SRT were maintained at 12 hours and 10 days, respectively. The continuous flow rate of synthetic wastewater was 1.7 L h⁻¹. Sludge recycling was performed by a peristaltic pump, pumping the biological sludge from the settler to the anoxic chamber (C1), at a flow of 1.7 L h⁻¹. Internal recirculation was present, in order to allow for the return of NO₂⁻ and NO₃⁻ to the reactor, at a flow rate of 3.7 L h⁻¹.

Figure 1. Schematic design of the lab-scale activated sludge system.

2.2. Operating conditions to determine the distribution of the routes of TN removal

To determine the relative distribution of the TN removal routes (sludge and atmosphere) under different operating conditions, the reactor was submitted to a two-phased experimental condition (Phases 1 and 2), between the 135th and the 212nd monitoring days, with different SRTs, limited DO concentrations (in C2-C4) and variable organic loading. Phase 1 was carried out between the 135th and the 169th day, under a SRT of 5 days and DO concentration of 0.5 mg L⁻¹, and Phase 2, between the 169th and the 212nd day, under a SRT of 10 days and DO concentration of 1.0 mg L⁻¹. The SRT was maintained for 5 or 10 days by controlling sludge wastage and monitoring the concentration of volatile suspended solids (VSS) in the reactor and the sludge recirculation line. In both phases, the HRT was maintained at 12 hours. The first 19 days of Phase 1 were considered an adaptation period (from the 135th to the 154th day), and the same was set for the first 21 days of Phase 2 (from the 170th to the 191st day). The process was performed at room temperature, at approximately 25°C.

2.3. Operating conditions to determine the magnitude of N₂O emissions

After conducting the experiment described previously (item 2.2.), the system was discontinued due to problems in its three peristaltic pumps used for the input of synthetic wastewater, sludge recirculation and internal recirculation. With the acquisition of new pumps (Masterflex), the continuous lab-scale system was restarted for a new 80-day experiment. The system was operated under the same operating condition as Phase 2 (SRT of 10 days and DO concentrations near 1.0 mg L⁻¹). The purpose was to achieve the accumulation of NO₂⁻ concentrations, and, after the 72nd monitoring day, to determine the magnitude of N₂O emissions (and the N₂O/N_{atmosphere} ratio) under different operating conditions, such as variable organic loading and different air flow rates applied to promote different DO levels (in C2-C4) (and NO₂⁻ concentrations) in the reactor. Four experimental conditions (EC) were performed varying the air flow rates, as follows, in chronological order: 200 mL min⁻¹ (EC 1: 74th day), 50 mL min⁻¹ (EC 2: 76th day), 300 mL min⁻¹ (EC 3: 78th day) and 400 mL min⁻¹ (EC 4: 80th day). The stabilization period for each EC was of 24 hours.

2.4. Biological sludge and wastewater composition

The biological sludge used in this work was collected from a WWTP and the reactor was fed with the synthetic wastewater. The synthetic wastewater was prepared mixing casein peptone (320 mg L⁻¹), meat extract (220 mg L⁻¹), urea (60 mg L⁻¹), potassium monohydrogen phosphate (56 mg L⁻¹), sodium chloride (14 mg L⁻¹), calcium chloride dihydrate (8 mg L⁻¹) and magnesium sulfate heptahydrate (4 mg L⁻¹) (Holler and Trösch, 2001). The pH of the synthetic wastewater ranged between 7 and 8. Variations in chemical oxygen demand (COD) and TN concentrations were obtained by increasing or decreasing the amount of substances, like casein peptone, meat extract and urea, in the synthetic wastewater.

2.5. Sampling and analytical procedures

Table 1 displays the sampling strategy used for the different operating conditions of the continuous lab-scale system. Liquid samples of synthetic and treated wastewaters were regularly collected to determine COD, TKN and TN concentrations. Liquid and gas samples from the four chambers were collected during the experimental operating conditions to determine the relative distribution of TN removal routes (Phases 1 and 2) and the magnitude of N₂O emissions (ECs 1-4). Liquid samples were filtered through 0.22 µm cellulose acetate membrane filters for the determination of dissolved inorganic nitrogen (DIN = NH₄⁺, NO₂⁻ and NO₃⁻) forms. In addition, VSS and TN sampling and analyses were carried out in the reactor and sludge recycler. The DO concentrations in the reactor were directly measured by a multiparameter Hanna portable meter (Model HI9828).

Gas samples were collected every 15 minutes, totaling 180 minutes per monitoring day (between the 74th and the 80th days), covering the four chambers of the lab-scale reactor for the determination of the N₂O emissions. A modified upturned funnel was used as the gas sampling technique (on a lab-scale). This same technique has been applied by our group in full-scale WWTP studies (Mello et al., 2013; Ribeiro et al., 2015; Brotto et al., 2015). The N₂O emission rate (ER) for the reactor was calculated by multiplying the ΔN₂O concentration, which is the difference between the upturned funnel headspace and the atmospheric N₂O concentrations, by the emerging airflow rate (Q_{air}), as displayed in Equation (1). The latter was measured at the surface of the reactor using the upturned funnel and a digital rotameter, and the result was scaled up for the entire reactor.

$$\text{N}_2\text{O ER (mg N h}^{-1}\text{)} = \Delta\text{N}_2\text{O concentration} \times Q_{\text{air}} \times (A_{\text{reactor}}/A_{\text{upturned funnel}}) \quad (1)$$

Table 1. Sampling strategy for the different operating conditions.

Samples	Items 2.1 and 2.2		Item 2.3	
	(0-135 th day) ^a	(135-212 nd day) ^b	(0-72 nd day) ^c	(74-80 th day) ^d
Synthetic wastewater	COD and TN	COD, TKN and TN	TKN and TN	TKN and TN
Lab-scale reactor	DO and VSS	DIN, DO and VSS	DIN, DO and VSS	DIN, N ₂ O, DO and VSS
Sludge excess	VSS	TN and VSS	VSS	TN and VSS
Treated wastewater	COD and TN	COD, TKN and TN	TKN and TN	TKN and TN

^aRegular operating condition (no experiments).

^bOperating conditions to determine the distribution of the TN removal routes (Phases 1 and 2).

^cSame operating condition as Phase 2.

^dOperating conditions to determine the magnitude of N₂O emissions (EC 1-4).

In the laboratory, N₂O determinations were performed on a Shimadzu gas chromatograph (Model GC-17) equipped with an electron capture detector with ⁶³Ni source. The limits of detection and quantification were of 30 and 300 ppb, respectively. All analytical procedures followed APHA et al. (2012) protocols. COD, TKN and TN were determined using the closed reflux colorimetric, block digestion and direct persulfate digestion methods, respectively. VSS concentrations were determined by the gravimetric method. NH₄⁺ concentrations were measured using an ammonia ion-selective electrode method coupled to an Orion pH-meter (Model Star 5). NO₂⁻ and NO₃⁻ concentrations were determined by ion chromatography with chemical suppression of eluent conductivity on a Methrohm ion chromatograph (Model 790 Personal). The limits of quantification were of 0.03 mg L⁻¹ for NH₄⁺, 0.1 mg L⁻¹ for NO₂⁻ and NO₃⁻, and 10 mg N L⁻¹ for TN. The analytical precision of the analyses performed in triplicate was within ± 5%.

3. RESULTS AND DISCUSSION

3.1. Regular operating condition

During the first 135 monitoring days, influent COD and TN concentrations (and volumetric COD and TN loads) varied from 447 to 1054 mg L⁻¹ (0.5 and 1.3 kg m⁻³ day⁻¹) and from 59 to 130 mg L⁻¹ (0.1 and 0.2 kg m⁻³ day⁻¹), respectively. The average COD and TN removal efficiencies ($\pm$ standard deviation) were 92% ($\pm$ 1.4%) and 57% ($\pm$ 6.6%), respectively. Using a lab-scale sequential batch reactor (SBR) system with fixed low volumetric COD load (0.4 kg m⁻³ day⁻¹), Lee et al. (2008) found COD and TN removal efficiencies of 92% and 65%, respectively. Similar values were reported by Vaiopoulou et al. (2007) for COD (74-97%), although their TN removal efficiency was somewhat higher, around 70%. They operated a differential lab-scale activated sludge system with a denitrification cascade and worked with a wide range of influent volumetric COD loads applied to the system (0.3 to 2.0 kg m⁻³ day⁻¹). Vaiopoulou et al. (2007) reported that the higher influent flow rate distribution to the reactor zones (denitrification cascade) explained the higher TN removal rates, in contrast to our study, that operated only with pre-denitrification.

The variability of the organic loading did not have any effect on COD removal efficiency, although lower TN removal efficiencies were related to lower influent TN concentrations. Between the 9th and the 21st monitoring day, influent TN concentrations dropped to about 30%, resulting in a decrease in TN removal efficiency, from 63 to 48% (Figure 2A). The same happened between the 55th and the 76th monitoring day, when the influent TN concentration dropped about 40% and TN removal efficiency decreased from 67 to 41%. These results indicate that significant decreases in influent TN concentrations result in decreasing TN removal efficiencies, given that TN concentrations and its removal efficiencies are positively correlated ($r = 0.68$; $n = 10$; $p < 0.01$) (Figure 2B). Liu et al. (2012) observed losses in TN removal efficiency when applying lower volumetric NH₄⁺ loads from a SBR using a completely autotrophic nitrogen-removal via nitrite (CANON) process. On the other hand, Zhang et al. (2014) demonstrated that maximal TN removal efficiency (90%) was obtained in a lab-scale sequencing batch biofilm reactor (SBBR) after 132 days of operation, where the volumetric TN load was gradually increased from 0.08 to 0.6 kg m⁻³ day⁻¹.

3.2. The relative distribution of TN removal routes

The fate of the removed TN was determined based on mass flow rates of the influent wastewater, liquid effluent and sludge waste. TN removal via mass transfer to the atmosphere was calculated by the difference between the influent TN load and TN removal via liquid effluent and sludge waste, as displayed in Equation 2.

$$TN_{atmosphere} = TN_{influent} - (TN_{liquid\ effluent} + TN_{sludge\ waste}) \quad (2)$$

Figure 3 shows the relative distribution of TN loss (and removal) calculated for the three different outlet routes from the 154th to the 169th day (Phase 1) and from the 191st to the 212nd day (Phase 2). The average TN removal efficiency of the system in the Phase 1 was of approximately 50%, of which about 40% was incorporated by the sludge waste and 10% released to the atmosphere. This result can be explained by the short SRT (5 days) and very low DO levels (DO = 0.5 mg L⁻¹). Short SRT can lead to an increased net sludge production rate and, consequently, higher TN removal by biomass production. During this phase, the net sludge production rate increased from 9 to 13 g VSS day⁻¹ under high volumetric COD (on average: 1 kg m⁻³ day⁻¹) and TN (on average: 0.1 kg m⁻³ day⁻¹) loading conditions. Bernat et al. (2011) reported that a high biomass production was responsible for 16-26% of the TN removed in a SBR at limited DO concentrations (< 0.7 mg L⁻¹) and that these values were the result of a low

specific biomass decay rate. In addition, Lee et al. (2008) reported that 50% of the influent TN in a SBR was removed by the sludge waste process.

Figure 2. (A) Influent TN concentrations (mg L⁻¹) and TN removal efficiencies (%) of the lab-scale activated sludge system. (B) Correlation between TN removal efficiencies and influent TN concentrations.

During Phase 2, the average TN removal efficiency was approximately 60% (Figure 3). Throughout this phase, TN removal via mass transfer to the sludge waste decreased from 40 to 15%. Concomitantly, the fraction transferred to the atmosphere increased from 10 to 50%. This can be explained by the increasing SRT (from 5 to 10 days) and DO levels (from 0.5 to 1.0 mg L⁻¹). Longer SRT can lead to decreases in the sludge mass by endogenous metabolism and, consequently, lower TN removal by biomass production. During this period, the net sludge production rate decreased from 13 to 6 g VSS day⁻¹ even under the same volumetric COD and TN loadings applied to Phase 1.

Figure 3. TN distribution (%) (regarding TN in the influent) in the different system lines (sludge waste, atmosphere and liquid effluent).

Figure 4 displays the effects of DO limitation on DIN concentrations during Phases 1 and 2. NH_4^+ was the predominant form of N in the reactor during Phase 1 (Figure 4A), due to lower TKN oxidation efficiencies (40-60%) (Figure 4B). Consequently, NO_2^- accumulation rates (NAR) were below 15% when the airflow rate was set to maintain DO levels close to 0.5 mg L^{-1} , with a SRT of 5 days. For the calculation of NAR the equation cited by Wei et al. (2014) was used. These results suggest loss of nitrification efficiency with no accumulation of NO_2^- , since DO was restricted by organic matter oxidation. Therefore, the operational condition applied in Phase 1 was characterized by loss of nitrification activity, which explains the highest TN removal efficiencies by the sludge waste (Figure 3).

During Phase 2, NH_4^+ concentrations dropped below 10 mg L^{-1} , with NO_2^- as the major form of DIN after the 200th monitoring day (Figure 4A). The NAR then began to prevail and increased up to 80%, with TKN oxidation reaching efficiencies above 80% (Figure 4B). At DO set near 1.0 mg L^{-1} with a SRT of 10 days, this phase showed optimal conditions for both organic matter oxidation and partial nitrification. Ruiz et al. (2003) reported that around 65% of the influent TN load was converted into NO_2^- in a lab-scale activated sludge reactor, operating at DO around 0.7 mg L^{-1} . These authors reported that when DO was below 0.5 mg L^{-1} , NH_4^+ accumulated in the system. The effect of increasing DO concentrations (from 0.5 to 1.0 mg L^{-1}) seems to explain the accumulation of NO_2^- , since Pollice et al. (2002) reported that NO_2^- accumulation took place regardless of the SRT during oxygen-limiting conditions ($\text{DO} < 2 \text{ mg L}^{-1}$) in a lab-scale activated sludge reactor. Therefore, in conditions that favor partial nitrification, it is probable that the priority route of nitrogen removal will be through the atmospheric path (Figure 3).

Figure 4. (A) Average DIN (NH_4^+ , NO_2^- and NO_3^-) concentrations (mg N L^{-1}) in the three aerobic chambers, (B) TKN oxidation (%), NO_2^- accumulation rates (NAR) (%) and DO concentrations (mg L^{-1}) during the 154th to 212th monitoring days in the lab-scale reactor.

3.3. Under the same operating condition as Phase 2

In order to achieve NO_2^- accumulation, the system was restarted and operated under the same conditions as Phase 2. During the first 37 days, NH_4^+ concentrations ranged from 5 to 10 mg N L^{-1} in the reactor (Figure 5A) with high TKN oxidation efficiencies (80-95%) (Figure 5B). These values are similar to those found in Phase 2, displayed in Figure 4. On the other hand, NO_3^- was the predominant form of N in the reactor, with low NO_2^- concentrations ($< 0.9 \text{ mg N L}^{-1}$) (Figure 5A). These results suggest favorable conditions for the completion of the nitrification process (and negligible NAR), since DO concentrations were above 1.0 mg L^{-1} (ranging from 0.9 to 1.8 mg L^{-1}) (Figure 5B). However, when DO concentrations dropped to $\leq 1 \text{ mg L}^{-1}$ (ranging from 0.7 to 1.1 mg L^{-1}), NO_2^- became the main form of oxidized N in the reactor, without loss of TKN oxidation efficiency. Interestingly, NH_4^+ concentrations were remained constant throughout the last monitoring days, especially between the 37th and the 72nd day. In addition, NAR increased from 0 to 90% and NO_3^- concentrations were low ($< 1 \text{ mg N L}^{-1}$). These results indicate the transition from complete to partial nitrification, and, thus, the greater fraction of N was transferred to the atmosphere, as observed previously in Phase 2 (Figure 3).

Figure 5. (A) Average DIN (NH_4^+ , NO_2^- and NO_3^-) concentrations in the three aerobic chambers; (B) TKN oxidation (%), NO_2^- accumulation rate (NAR) (%) and DO concentrations (mg L^{-1}) during 72 monitoring days.

3.4. Extent of N_2O emissions

Figure 6 displays the average DIN concentrations in the three aerobic chambers of the lab-scale reactor (Figure 6A), as well as TKN oxidation and NAR values (Figure 6B) under the different experimental conditions (EC 1-4). In addition, Figure 6C displays the N_2O emission variations and DO concentrations in the four experimental conditions. In EC 1 ($Q_{\text{air}} = 200 \text{ mL min}^{-1}$), NH_4^+ was the predominant form of N in the reactor, followed by NO_2^- and NO_3^- , respectively, 64% (11 mg N L^{-1}), 30% (5.2 mg N L^{-1}) and 6% (1.1 mg N L^{-1}) (Figure 6A). In addition, TKN oxidation and NAR were 76% and 84%, respectively (Figure 6B). More

of the influent TN was converted to NO_2^- (11%) than to NO_3^- (2%). In this experimental condition, DO concentrations varied from 0.9 to 1.1 mg L^{-1} (Figure 6C). These results are similar to those observed by Ruiz et al. (2003), that reported NO_2^- accumulation with DO concentrations close to 0.7 mg L^{-1} . Significant variations in N_2O emissions were observed within the range of 1.4 to 4.1 mg N h^{-1} , representing on average 2.6 mg N h^{-1} and 5.4% when normalized by influent TN load.

Similar NH_4^+ concentrations (9.6 mg N L^{-1}) and TKN oxidation rates (73%) were observed in EC 2 ($Q_{\text{air}} = 50 \text{ mL min}^{-1}$) operating at an airflow rate four-fold lower than EC 1 (Figures 6A and 6B). However, NO_3^- (0.6 mg N L^{-1}) and, especially, NO_2^- (0.1 mg N L^{-1}) concentrations were low, and, consequently, with NAR of 14%. In this condition, the DO concentrations were much lower (0.1-0.3 mg L^{-1}) due to the lower airflow rate applied to the system (Figure 6C). Therefore, under anoxic conditions, both NO_2^- and NO_3^- were probably reduced by complete denitrifying activity, without significant N_2O emissions ($< 0.5 \text{ mg N h}^{-1}$), which represented, on average, 0.1 mg N h^{-1} and 0.3% of the influent TN load. In a lab-scale system with activated sludge, Wunderlin et al. (2012) reported that N_2O emissions under anoxic conditions are likely to be of minor importance when operated without significant NO_2^- accumulation ($< 2 \text{ mg N L}^{-1}$).

Figure 6. (A) Average DIN (NH_4^+ , NO_2^- and NO_3^-) concentrations (mg N L^{-1}) in the three aerobic chambers, (B) TKN oxidation (%) and NO_2^- accumulation rate (NAR) (%) and (C) N_2O emissions (mg N h^{-1}) and DO concentrations (mg L^{-1}) in the lab-scale reactor for each of the four experimental conditions.

In EC 3 ($Q_{\text{air}} = 300 \text{ mL min}^{-1}$), as in EC 1, more of the influent TN was converted to NO_2^- (8%) than to NO_3^- (2%). Moreover, similar TKN oxidation rates (70%) and NO_2^- accumulation (83%) were observed (Figures 6A and 6B). However, unlike EC 1, the average values of NH_4^+ concentrations for the three aerobic chambers in EC 3 were much higher and linked to higher influent NH_4^+ concentrations (shock loading). Consequently, higher variations in N_2O emissions were observed, within the range of 1.2 to 6.1 mg N h^{-1} (Figure 6C). Nevertheless, this represents an average of 3.6 mg N h^{-1} and 5.6% of the influent TN load, very similar to what was found in EC 1. The NH_4^+ shock loading was responsible for reducing and maintaining DO concentrations close to 0.7 mg L^{-1} (Figure 6C) even under higher air flow rates when compared to EC 1 and EC 2. It could be argued that sudden changes, such as NH_4^+ shock loading, can lead to NO_2^- accumulation (partial nitrification) and higher N_2O emissions, as reported by other authors (Foley et al., 2010; Rodriguez-Caballero et al., 2013; Toor et al., 2015). Ahn et al (2010) suggested that the trigger for N_2O emissions from aerobic zones are simultaneous high NH_4^+ and NO_2^- concentrations, based on studies performed in full-scale BNR and non-BNR processes.

The highest airflow rate to the system was applied in EC 4 ($Q_{\text{air}} = 400 \text{ mL min}^{-1}$), and a different behavior was observed in relation to the other 3 ECs, since around 35% of the influent TN was converted into NO_3^- (the predominant form of DIN in the reactor). In addition, NH_4^+ (1.6 mg N L^{-1}) and NO_2^- (0.2 mg N L^{-1}) concentrations were low, with 96% TKN oxidation and negligible NAR (Figures 6A and 6B). In this condition, DO concentrations were above 1.5 mg L^{-1} and N_2O emissions varied from 0.6 to 1.8 mg N h^{-1} (on average 1.0 mg N h^{-1} and 2.3% of the influent TN load) (Figure 6C). This low N_2O emission can be attributed to complete nitrification. It could be argued that this experimental condition favors greater DO availability ($> 1.5 \text{ mg L}^{-1}$) for organic matter oxidation and complete nitrification and, consequently, low N_2O emissions. In studies performed both in the laboratory and in full-scale processing, Rodriguez-Caballero et al. (2013) and Song et al. (2014), respectively, reported lower N_2O emissions from complete nitrification compared to partial nitrification (with NO_2^- accumulation). Therefore, to reduce N_2O emissions, activated sludge systems should be operated at low NH_4^+ (without shock loading) and NO_2^- concentrations (without build-up) (Ahn et al., 2010; Foley et al., 2010; Wunderlin et al. 2012; Aboobakar et al., 2013). This condition can be achieved through longer SRT, equalization of organic loading and optimal control of airflow rates, depending on the DO concentrations in the reactor.

Figure 7 displays the relative distribution of TN loss (and removal) through three different system routes, (1) sludge waste, (2) atmosphere (via N_2 and N_2O separately) and (3) remaining in the liquid effluent for each of the four experimental conditions. The TN removal efficiencies of the system were high and ranged from 61 to 71%. A lower fraction of TN was removed by the sludge waste process and was similar in the four evaluated conditions (7-9%). Most of the TN was removed via gas transfer to the atmosphere (53-64%), with the highest efficiency associated to EC 2. Of the amount of TN transferred to the atmosphere, a significant $\text{N}_2\text{O}/\text{N}_{\text{atmosphere}}$ ratio was attributed to EC 1 (11%) and EC 3 (10%). On the other hand, the $\text{N}_2\text{O}/\text{N}_{\text{atmosphere}}$ ratio decreased from 10 to 5% due to transition from EC 3 (partial nitrification) to EC 4 (complete nitrification), as described previously and reported by other studies (Rodriguez-Caballero et al., 2013; Song et al., 2014). Therefore, the adequate control of DO concentrations is a key factor, in order to avoid the accumulation of NO_2^- and, therefore, achieve lower N_2O emissions.

Figure 7. TN distribution (%) (regarding TN in the influent) through three different system routes: sludge waste, atmosphere (via N₂ and N₂O separately) and liquid effluent for each of the four experimental conditions. In addition, TN removal (%) and N₂O/N_{atmosphere} ratio (%) are also displayed.

4. CONCLUSION

The effects of different operating conditions, such as variable organic loading, different SRTs and airflow rates, limited DO concentrations and NH₄⁺ shock loading on TN removal routes and N₂O emissions were studied in a lab-scale activated sludge system and the major conclusions are:

- The variable organic loading did not interfere with COD removal efficiency under the applied operating conditions. However, lower TN removal efficiencies were related to lower TN loads.
- Short SRT (5 days) resulted in a large part of TN removal in sludge waste. As the SRT increased from 5 to 10 days, TN removal decreased in the sludge waste and increased via the atmospheric route.
- Low DO levels (0.5 mg L⁻¹) were responsible for lower TKN oxidation efficiencies, suggesting that nitrification efficiency was hampered by the oxidation of organic matter. For DO set to 1 mg L⁻¹, TKN oxidation rates and NO₂⁻ accumulation reached their maxima, the best condition for both organic matter oxidation and partial nitrification.
- Part of the N transferred to the atmosphere is attributed to N₂O emissions (reaching a maximum N₂O/N_{atmosphere} ratio of 10%), which varied from 0.3 to 5.6% of the influent TN load.
- The presence of combined remnant NH₄⁺ and high NO₂⁻ concentrations due to partial nitrification strongly triggered N₂O emissions.
- Insufficient aeration and stress conditions (such as NH₄⁺ shock loading) can cause limited DO conditions, NO₂⁻ accumulation and, consequently, higher N₂O emissions.
- The adequate control of DO concentrations is a key factor to avoid NO₂⁻ accumulation and, consequently, high N₂O emissions.

5. ACKNOWLEDGMENTS

This work was supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes).

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Use of agricultural and agroindustrial residues as alternative adsorbents of manganese and iron in aqueous solution

ARTICLES doi:10.4136/ambi-agua.2181

Received: 13 Sep. 2017; Accepted: 17 Jan. 2018

**Fernanda Lansa Furlan¹; Nelson Consolin Filho^{2*};
Marcilene Ferrari Barriquello Consolin²; Morgana Suzsek Gonçalves³;
Patrícia Valderrama²; Aziza Kamal Genena¹**

¹Universidade Tecnológica Federal do Paraná (UTFPR), Medianeira, PR, Brasil
Programa de Pós-Graduação em Tecnologia de Alimentos. E-mail: fernanda.furlan.lansa@gmail.com,
azizakg@utfpr.edu.br

²Universidade Tecnológica Federal do Paraná (UTFPR), Campo Mourão, PR, Brasil
Departamento de Química. E-mail: consolin@utfpr.edu.br, marcilenef@utfpr.edu.br, patriciav@utfpr.edu.br

³Universidade Tecnológica Federal do Paraná (UTFPR), Campo Mourão, PR, Brasil
Departamento de Engenharia Ambiental. E-mail: morgana@utfpr.edu.br

*Corresponding author

ABSTRACT

The increase in the volume of agricultural and agroindustrial waste, associated with improper disposal, is a growing worldwide problem. The recovery of those residues is of crucial importance, since it reduces environmental impacts, protects public health, and allows the addition of value to the materials. One of the ways of exploiting adsorbents is related to the capacity of some wastes to be used as alternative adsorbents in the efficient removal of microcontaminants in aqueous systems. This work assessed the use of agricultural and agroindustrial residues: maize straw, wheat straw, soybean straw and soybean hulls for the production of alternative adsorbents to remove iron (Fe) and manganese (Mn) in water. For each residue investigated, two different polymers were obtained for use as adsorbents, a natural polymer (cellulose/lignin) and an EDTA-modified polymer (ethylenediaminetetraacetic acid). The adsorbents were characterized through FTIR (Fourier transform infrared spectroscopy) and nitrogen content. To evaluate the efficiency of the adsorbents, kinetic tests in batch mode and determination of Lagergren pseudo-first and pseudo-second order kinetic constants were performed. The results found that the modified polymer obtained from soybean hulls (SHE) showed increased Fe (96%) and Mn (88%) removal rate, in which the pseudo-second order kinetic model presented closer results between the experimental adsorption rates and the calculated ones for the two microcontaminants under study. In general, the modified soybean hulls proved to be a promising alternative adsorbent for the removal of iron and manganese in water treatment.

Keywords: adsorption, agribusiness, microcontaminants, waste recovery.

Uso de Resíduos Agrícolas e Agroindustriais como Adsorventes Alternativos de manganês e ferro em Sistema Aquoso

RESUMO

O aumento do volume de resíduos agrícolas e agroindustriais gerados, acompanhados do descarte inadequado dos mesmos é um problema mundial crescente. O aproveitamento desses resíduos é de extrema importância, já que resulta na redução de impactos ambientais, preservação da saúde da população, e permite agregar valor à esses materiais. Uma das formas de aproveitamento está relacionada à capacidade de alguns resíduos serem utilizados como adsorventes alternativos na remoção eficiente de micro-contaminantes em sistemas aquosos. Este trabalho teve como objetivo investigar o uso dos resíduos agrícolas e agroindustriais: palha de milho, palha de trigo, palha de soja e casca de soja para produção de adsorventes alternativos para remoção de ferro (Fe) e manganês (Mn) em água. Para cada resíduo investigado, dois diferentes polímeros foram obtidos para uso como adsorventes, um polímero natural (celulose/lignina) e um polímero modificado com EDTA (ácido etilenodiaminotetraacético). Os adsorventes foram caracterizados por FTIR (espectroscopia de infravermelho por transformada de Fourier) e teor de nitrogênio. Para a avaliação da eficiência dos adsorventes foram realizados testes cinéticos, em regime batelada, e determinação das constantes cinéticas de pseudo-primeira e pseudo-segunda ordem de Lagergren. Os resultados obtidos indicaram que o polímero modificado obtido da casca de soja apresentou maior remoção de Fe (96%) e Mn (88%), em que o modelo cinético de pseudo-segunda ordem apresentou resultados mais aproximados entre os valores de quantidade adsorvida experimentais e os calculados para os dois micro-contaminantes em estudo. De modo geral, a casca de soja modificada mostrou ser um adsorvente alternativo promissor para a remoção de ferro e manganês no tratamento de águas.

Palavras-chave: adsorção, agroindústria, aproveitamento de resíduos, micro-contaminantes.

1. INTRODUCTION

Water is a basic necessity worldwide and is of immeasurable environmental importance since it is the primitive requirement for human life (Bushra et al., 2017, Carolin et al., 2017). Inorganic and organic chemicals are major life-threatening factors of water pollution (Sharma et al., 2017). Metal ion pollution is a most concerning topic of investigation in the present era due to its alarming rate of increase (Naushad et al., 2016). Domestic and industrial wastewaters containing metal ions are increasingly discharged into the environment and these metal ions are of significant importance as they are not biodegradable and cannot be metabolized by the environment but tend to accumulate in living organisms, causing various diseases and disorders (Hasanzadeh et al., 2017). Most of the metals are carcinogenic and/or pose severe health problems, such as organ damage, reduced growth and development, oxidative stress, and nervous system impairments (Naushad et al., 2015).

The presence of micro contaminant compounds in groundwater, and eventually in drinking water, is a serious environmental problem which poses a substantial risk to local resource users and to the natural environment (Adekola et al., 2016). For example, iron overload in animal models and humans increases oxidative stress and induces cardiomyopathy that may contribute to increased cardiovascular risk (Marques et al., 2015). Manganese (Mn) might be toxic at excess exposure. Elevated concentrations of Mn in drinking water were associated with impaired child development and indicated an adverse effect on birth length in pregnant women (Rahman et al., 2015). In order to get safe drinking water, excessive iron and manganese must be removed (Rangreez et al., 2017).

The removal of toxic metals from water and wastewater has been achieved by several processes such as coagulation, electrochemical treatment, ion exchange, membrane separation, chemical precipitation and adsorption (Alqadami et al., 2016, Naushad et al., 2017, Reiad et al., 2012). In the last decade, the adsorption technique has been widely used for the removal of toxic metal from aqueous mediums (Ahamad et al., 2017) and has become one of the most preferred methods due to its high efficiency and low operational cost, making it a cost-effective method (Al-Othman et al., 2012). Furthermore, based on the regeneration, since adsorbents can be recreated by the desorption process, adsorption is also considered an environmentally acceptable method.

The selection of suitable precursors for the adsorption of metal ions from aqueous solutions is very important (Alqadami et al., 2017). The biosorption process using agricultural waste/plant material is an eco-friendly and easy method. Rapid industrialization associated with the population growth and intensive agricultural activities has prompted an increase in the amount and variety of agricultural and agroindustrial wastes produced (Asim et al., 2015). Most agricultural waste consists of three main structural components: lignin, cellulose and hemicellulose. These compounds possess adsorptive sites, such as ether, carbonyl, carboxyl, amine and hydroxyl groups, capable of absorbing metal species through ion exchange or complexation processes (Salleh et al., 2011).

Many agricultural wastes have directly or indirectly been used as sorbents for metal adsorption from water and wastewater which included rice husk, sunflower, potato, canola and walnut shell residues (Feizi and Jalili, 2015), peanut shell and orange peel (Surovka and Pertile, 2017).

In the light of the above, the present study investigated the use of agricultural and agroindustrial maize, soybean and wheat residues for producing alternative adsorbents, and their application in the removal of iron and manganese from aqueous solution.

2. MATERIALS AND METHODS

2.1. Agricultural and Agroindustrial Waste

Maize straw (MS), wheat straw (WT) and soybean straw (SS) soil residues were collected directly in the field after the harvest of the crops, respectively, in rural properties located in Campo Mourão, State of Paraná, Brazil and Peabiru, State of Paraná, Brazil, which use the no-tillage technique. Agroindustrial soybean hulls (SH) residues were provided by the COAMO – Agroindustrial Cooperativa warehouse located in the city of Araruna, PR, Brazil.

2.2. Preparation of Adsorbents

From each agricultural and agroindustrial residue, hemicelluloses were extracted to obtain a polymer composed of cellulose and lignin, known as a natural adsorbent of maize straw (MS), wheat straw (WT), soybean straw (SS) and soybean hull (SH). The stages of preparation and getting of a natural adsorbents followed the methodology described by Schafhauser et al. (2015).

For each residue, preparation of the adsorbent consisted of drying at 60°C in an oven for 24 h, grinding with a cutting mill and screening (10 mesh).

Subsequently, for hemicellulose removal, 30 g of the sample were weighed on an analytical balance and the extraction was carried out following an eluotropic series of solvents (n-hexane/alcohol/water) in Soxhlet-type extractors with a hot plate. After extraction using each solvent of the series, the residues were dried in an oven at 60°C for 24 h, weighed and returned to the Soxhlet system for further extraction with the other solvents. After extraction with water,

the material was dried and weighed and the hemicellulose-free natural polymer composed of cellulose and lignin, i.e., the natural adsorbent, was obtained.

Part of this product (natural adsorbent) was put aside and the other part was modified with EDTA (ethylenediaminetetraacetic acid) to obtain a modified polymer called modified maize straw (MSE), wheat straw (WTE), soybean straw (SSE) and soybean hulls (SHE) adsorbent, obtained from the natural adsorbent.

The introduction of EDTA into the cellulose fibers of the adsorbents was carried out in a 50 mL round-bottomed flask fitted with a ball condenser. Each flask contained 5 g of natural adsorbent, 15 g of disodium salt EDTA and 210 mL of DMF (dimethylformamide). The mixture was stirred and heated on a magnetic stirrer with a heating plate at 75°C for 24 h and then vacuum-filtered on a sintered plate funnel with porosity of 40-60 µm. The material trapped on the filter was subjected to sequential washing with solvents and then dried at 75°C for 24 h on a drying oven until constant mass, in order to obtain EDTA-modified natural polymer (Pereira et al., 2010).

2.3. Characterization of Adsorbents

In order to characterize the adsorbents, they were weighed in an analytical balance, followed by a FTIR analysis (Fourier transform infrared spectroscopy) and total nitrogen determination.

For the FTIR analysis performed on a FTIR (IRAffinity-1S, Shimadzu) spectrometer, the pellets were prepared using 1 mg of adsorbent and 100mg of spectroscopic grade KBr. The spectra were collected over the 4000 to 400 cm⁻¹ wavenumber range at a resolution of 4 cm⁻¹ and 32 scans.

The determination of total nitrogen was carried out using the Kjeldahl method.

The analyses of the elements C, H, N and O for SHE and SS were carried using an elemental analyzer Eurovector EA 3000-S.

2.4. Kinetic Study

Kinetic tests of Fe or Mn adsorption in aqueous solution, in batch mode, were performed for each of adsorbent obtained. For each test, 20 mL of metal (Fe or Mn) standard solution (1g.L⁻¹), 1980 mL of distilled water and 3 drops of nitric acid were added to 4 g of adsorbent, resulting in a solution of 10 mg.L⁻¹ for metal species and a concentration of 2 mg.mL⁻¹ of adsorbent material in solution. The solution was continuously stirred at 160 rpm, and kept at 25°C and pH of 6.8. The adsorption time ranged from 0 to 180 min, in which 20 mL-aliquots were collected at predetermined intervals, followed by sample filtration in a sintered glass filter and the analysis of the Fe or Mn concentration through atomic absorption spectrophotometry, using an Analytik Jena NOVAA300 spectrophotometer.

The amount of Fe and Mn adsorbed (q), in mg.g⁻¹, was calculated by Equation 1:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

in which C₀ and C_e correspond to the initial concentration of the micro-contaminant and the equilibrium concentration (mg.L⁻¹), respectively; V is the volume of solution (L) and m is the amount of adsorbent used (g).

The adsorption efficiency of Fe and Mn from the aqueous solution was calculated by Equation 2:

$$\% \text{Adsorbed} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

The results of the kinetic tests were fitted to Lagergren pseudo-first and pseudo-second order kinetic models (Equation 3 and 4):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \quad (3)$$

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

in which q_e and q_t are the adsorbed quantities (mg.g^{-1}) at equilibrium and time t , respectively; k_1 is the pseudo-first order adsorption constant (min^{-1}) and k_2 is the pseudo-second order adsorption constant ($\text{g.mg}^{-1}.\text{min}^{-1}$).

3. RESULTS AND DISCUSSION

3.1. Collection of Adsorbents

Table 1 shows the quantity and the respective percentage of extracts (hemicelluloses) removed in each extraction step using the elutropic series of different solvents for each waste assessed.

Table 1. Waste weight before and after extractions using the elutropic and total percentage rate of extractives removed.

Waste	Initial weight (g)	Weight after extraction (g)			Final weight (g)	Percentage of Removed Extracts (%)
		Extraction solvent				
		N-Hexane	Ethanol	Water		
MS	30.00	28.35	25.75	20.95	9.05	30.17
WT	30.00	28.00	26.15	21.00	9.00	30.00
SS	30.00	28.13	25.74	20.35	9.65	32.17
SH	30.00	26.00	24.10	19.25	10.75	35.83

The process of removing extractives from the adsorbent material is an extremely important step when one aims at performing adsorption in aqueous solution, since hemicellulose, which is the most soluble constituent among lignocellulosic biomass materials, must be completely removed from the medium in order to prevent its solubilization and, consequently, the complexation of microcontaminants and the impairment of the final adsorption result. This process also avoids fungal and bacterial attack, increasing the useful life of adsorbent materials.

At the end of the process, all agricultural byproducts showed a reduction in total weight, demonstrating their efficiency in the extraction process. The biggest extraction occurred with SS (35.83%).

Similar results were reported by Schafhauser et al. (2015) in extractions using the same solvents, in the same order, in maize straw. The authors observed that, at the end of the process, the total percentage of extractives removed was 30.15%.

In order to obtain modified adsorbents, part of the natural adsorbents (MS, WT, SS, SH) were subjected to chemical modification with EDTA, followed by filtration, washing and drying. After those steps, the weight gain of modified adsorbents (MSE, WTE, SSE, SHE) was assessed to verify the EDTA's inclusion in the adsorbent materials: 10.75% for MSE, 11.00% for WTE, 8.80% for SSE and 33.00% for SHE.

Weight gain was observed in the four types of adsorbent materials after modifications with EDTA, confirming the introduction of this chelating agent into the structures of the lignocellulosic fibers forming straws and hulls.

EDTA is a biodegradable and active agent containing two anhydride groups per molecule that can be used to introduce chelating abilities to the lignocellulosic materials through esterification reaction. This reaction allows introducing carboxylic and amine functional groups that present high ability to form stable complexes with heavy metal ions (Pereira et al., 2010). Therefore, the weight gain observed in modified adsorbent materials confirms that the carboxylate functions have been released and the amine functions have been conveyed into them.

3.2. Fourier Transform Infrared Spectroscopy

IR spectra for natural and modified adsorbents obtained are shown in Figures 1 (a) and (b), respectively. A comparison between the spectra revealed an increase and the appearance of strong bands in EDTA-modified straws and hulls at $1743\text{--}1747\text{ cm}^{-1}$, which can be attributed to the axial deformation $\text{C}=\text{O}$ of ester, at 1633 cm^{-1} due to the asymmetric axial deformation of the carboxylate, and at $1402\text{--}1408\text{ cm}^{-1}$ due to the symmetrical axial deformation of the carboxylate. This finding evidences the incorporation of two types of carbonyls, ester and carboxylate, and also confirms the introduction of EDTA into the modified adsorbents.

Figure 1. IR spectra for natural adsorbents (SH, SS, WT and MS) and modified adsorbents (SHE, SSE, WTE and MSE).

The results obtained in the present study are consistent with those reported by Pereira et al. (2010), who characterized through FTIR wood sawdust, EDTA-modified wood sawdust (SE), sugarcane bagasse (B) and EDTA-modified sugarcane bagasse (BE). When comparing the spectra of the modified materials with those of the starting materials, they observed the appearance of strong bands at 1742 cm^{-1} for SE and at 1741 cm^{-1} for BE, which correspond to stretching ester vibration. They also observed the presence of strong bands at 1634 cm^{-1} , 1596 cm^{-1} and 1403 cm^{-1} for SE and at 1633 cm^{-1} , 1602 cm^{-1} and 1406 cm^{-1} for BE, related to asymmetric and symmetrical stretch of the carboxylate ion, respectively. These bands indicate that EDTA was introduced via ester linkages accompanied by a release of carboxylic functional groups.

Gusmão et al. (2013) studied the adsorption of methylene blue (MB) and gentian violet (GV) in aqueous solution with unmodified sugarcane bagasse (B) and sugarcane bagasse modified with EDTA dianhydride (EB). When comparing the infrared spectra of EB with the unmodified bagasse spectrum, they observed the appearance of strong bands at 1741 cm^{-1} , which can be attributed to the axial deformation of the ester bond ($-\text{O}-\text{C}=\text{O}$), and bands at 1633 and 1406 cm^{-1} , which are probably due to axially asymmetric and symmetrical deformations of carboxylate ($-\text{COO}^-$). These bands confirmed the introduction of EDTA

dianhydride through the formation of ester bonds with the subsequent release of carboxylate functions.

3.3. Determination of Total Nitrogen

Data related to nitrogen analysis are presented in Table 2. A considerable increase in the nitrogen content after chemical modification with EDTA is observed. This finding also helps to confirm the introduction of EDTA in the materials through the incorporation of nitrogen in the modified adsorbents (WTE, MSE, SSE and SHE).

Table 2. Nitrogen content (%) of natural and modified adsorbents.

Adsorbents	Nitrogen (%)
WT	0.16
WTE	0.87
SS	0.16
SSE	2.46
MS	0.07
MSE	0.78
SH	1.36
SHE	3.75

Similar results were reported by Pereira et al. (2010) and Gusmão et al. (2013) with dianhydride of EDTA (EDTAD) modifications in sugarcane bagasse in the adsorption processes in aqueous solution. Both researchers verified that the nitrogen rate of sugarcane bagasse before EDTAD modification was 0.13% and after modification was 2.32%. They explain that this fact occurred due to the incorporation of amine functions in the bagasse after esterification of hydroxyl, proving the introduction of EDTAD into it.

3.4. Kinetics of Fe and Mn Adsorption

The kinetic curve of manganese (Figure 2a and 2b) showed that the optimum adsorption time was approximately 15 min for SHE and 60 min for WT, SS, SH, MSE, WTE and SSE. In relation to the natural adsorbent of maize straw (MS), equilibrium was not reached up to 180 min.

Overall, natural adsorbents showed reduced efficiency in the removal of manganese (Figure 2a). The maximum adsorbed amount was 16% for MS, 19% for WT, 13% for SS and 6% for SH.

Among modified adsorbents, the amounts of manganese removed were higher than that observed with natural adsorbents, except for the MSE, which showed a removal rate below 5%. The maximum removal was achieved using the modified soybean hulls adsorbent (SHE), with 88%.

Tavlieva et al. (2015) used rice husk ash to remove Mn ions in aqueous solutions. The results showed that the Mn removal rate was 26.62%, much lower than that obtained in the present study with modified soybean hulls (SHH).

Regarding the kinetic tests for iron removal with the natural adsorbents, the kinetic curve (Figure 2c) shows that the optimum adsorption time was approximately 30 min for MS and WT, 60 min for SS and 180 min for SH. The maximum iron removal level achieved with natural adsorbents was 78%, using soybean hulls (SH).

Figure 2. Adsorption kinetics of manganese and iron by the following materials (a) MS, WT, SS and SH and (b) MSE, WTE, SSE and SHE.

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The adsorption of Fe with modified adsorbents (Figure 2d) revealed that the time required for the system to balance is approximately 15 min for MSE, WTE and SHE. There was no equilibrium for SSE up to 180 min.

It was also observed that the modified adsorption systems were more efficient in the removal of iron in comparison with the natural ones, reaching values 77% for MSE, 93% for SSE, 85% for WTE and 96% for SHE.

Considering only the modified soybean adsorbent (SHE), which showed the best results in Fe and Mn adsorption, the pseudo-second order kinetic model evidenced results that more closely match the experimental and calculated q_e values (Table 3), with higher coefficients of determination (R^2) in comparison with the pseudo-first order kinetic model, describing better the adsorption process.

According to Feng et al. (2011), the pseudo-second order model assumes that the velocity-limiting factor may be the chemical adsorption involving valence forces, through the sharing or exchange of electrons between heavy metal ions and the adsorbent. It is a model that describes well the processes of chemical adsorption that involve donation or exchange of electrons between the adsorbate and the adsorbent, as covalent forces and ionic exchanges (Ho and Mckay, 2000).

Table 3. Parameters of the pseudo-first order and pseudo-second order kinetic models for Mn and Fe adsorption in SHE.

Metal	qe (exp) (mg. g ⁻¹)	Pseudo-first order			Pseudo-second order		
		qe (calc) (mg. g ⁻¹)	k ₁ (min ⁻¹)	R ²	qe (calc) (mg.g ⁻¹)	k ₂ (g.mg ⁻¹ .min ⁻¹)	R ²
Mn	1.00	0.41	0.021	0.735	1.00	0.359	0.999
Fe	2.60	0.95	0.021	0.701	2.59	0.168	0.999

In the present study, the pseudo-second order adsorption rate (k₂) for Mn and Fe in SHE was 0.359 and 0.168 g.mg⁻¹.min⁻¹, respectively.

4. CONCLUSION

Agricultural and agroindustrial wastes are high-abundance and low-cost materials that can be used as alternative adsorbents for the removal of microcontaminants in water treatment systems.

All the adsorbents produced from maize, wheat and soybean residues were able to adsorb iron and manganese in aqueous solution. However, the soybean hulls modified adsorbent (SHE) showed the best results in the removal process, displaying an adsorption rate of 96% for iron and 88% for manganese. The pseudo-second order kinetic model presented a better description of the adsorption process of Fe and Mn in SHE adsorbent.

It is concluded that this material has proved promising for use in the adsorption of metal microcontaminants in aqueous solution, creating added value to waste and economic and environmental advantages.

5. ACKNOWLEDGEMENTS

We would like to thank Fundação Araucária for the financial support (scholarships and grants) from Agreement 043/2015, and Federal Technological University of Paraná (UTFPR), Campus Campo Mourão and Medianeira, for providing all structure and facilities.

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Determination of carbamazepine and diazepam by SPE-HPLC-DAD in Belém River water, Curitiba-PR/Brazil

ARTICLES doi:10.4136/ambi-agua.2196

Received: 05 Oct. 2017; Accepted: 05 Jan. 2018

**Beatriz Böger^{1*}; Bianca do Amaral²; Priscila Lagner da Silveira Estevão²;
Ricardo Wagner¹; Patricio Guillermo Peralta-Zamora²; Eliane Carneiro Gomes¹**

¹Universidade Federal do Paraná (UFPR), Curitiba, PR, Brasil
Programa de Pós-Graduação em Ciências Farmacêuticas (PPGCF). E-mail: beatrizboger@gmail.com,
sorw2003@yahoo.com.br, ecarneirogomes@gmail.com

²Universidade Federal do Paraná (UFPR), Curitiba, PR, Brasil
Programa de Pós-Graduação em Química (PPGQ). E-mail: biancadoamaral_@hotmail.com,
priscilalagner@hotmail.com, zamora@ufpr.br

*Corresponding author

ABSTRACT

This work sought to determine the two psychotropic drugs most commonly released by Psychosocial Care Centers (CAPS) into urban river waters (Belém sub-basin, Curitiba, PR, Brazil). A simple analytical method using SPE followed by a HPLC–DAD was developed and validated. Strata-X® cartridges were used to extract (carbamazepine) CZ and diazepam (DZ) from water and SPE conditions were optimized by 2³ factorial design. The validated method was specific for target compounds; correlation coefficients were above 0.9998, recovery between 85.8 and 98.4% and precision below 6.60% (RSD, n=3). This method was successfully applied to analyze river samples and pollution hotspots were identified. The CZ and DZ concentrations found ranged from 0.670 to 0.856 µg L⁻¹ and from LOQ to 0.763 µg L⁻¹, respectively, and confirmed that drug consumption is directly related to river pollution in the studied region.

Keywords: carbamazepine, diazepam, emerging pollutants.

Determinação de carbamazepina e diazepam por SPE-HPLC-DAD nas águas do rio Belém em Curitiba-PR/ Brasil

RESUMO

Este trabalho teve como objetivo determinar duas drogas psicotrópicas mais dispensadas pelos Centros de Atenção Psicossocial (CAPS) nas águas de um rio urbano (sub-bacia do rio Belém, Curitiba - PR, Brasil). Foi desenvolvido e validado um método analítico SPE seguido de HPLC-DAD. Os cartuchos Strata-X® foram utilizados para extrair carbamezepina (CZ) e diazepam (DZ) das águas e as condições de SPE foram otimizadas por um planejamento fatorial 2³. O método validado foi específico para compostos alvo. Os coeficientes de correlação foram superiores a 0,9998, a recuperação entre 85,8 e 98,4% e a precisão abaixo de 6,60% (RSD, n = 3). Este método foi aplicado com sucesso para analisar amostras de rios e pontos críticos de poluição foram reconhecidos. A CZ e DZ foram encontradas em concentrações variando de

0,670 a 0,856 $\mu\text{g L}^{-1}$ e de LOQ a 0,763 $\mu\text{g L}^{-1}$, respectivamente, confirmam que o consumo de drogas está diretamente relacionado à poluição do rio na região estudada.

Palavras-chave: carbamazepina, diazepam, poluentes emergentes.

1. INTRODUCTION

About 450 billion people worldwide have some mental or behavioral disorder, and this number is expected to grow significantly up until 2020 (Menken et al., 2000). Psychiatric drugs are of particular concern because of their toxicity, persistence and the increased consumption in the last decade (Stuart et al., 2012; Subedi and Kannan, 2015; FENAFAR, 2015). Diazepam (DZ) is a psychotropic medication of the benzodiazepine class that are selective central nervous system modifiers and can be classified as anxiolytic. They are the most commonly used in the world (Sebastião and Pelá, 2004). About 1-3% of the Western population has already consumed diazepam regularly for over a year and in Brazil about 10% of adults have been prescribed these drugs (Huf et al., 2000; CREMESP, 2002). Carbamazepine (CZ) is a controlled drug in Brazil and is considered a mood stabilizer (Rang et al., 2003). In 2008, carbamazepine, with anticonvulsant action, was among the five active ingredients most consumed in Brazil (Mota, 2011). Carbamazepine has been detected in the surface of drinking water in more than 29 countries (Ebert et al., 2014). Diazepam was found in 8 of 20 wastewater treatment plants at relatively low concentrations ($< 0.04 \text{ mg L}^{-1}$) with a high frequency of detection in these treatment plants (Cabeza, 2012).

Although the present knowledge in the occurrence and behavior of these compounds in rivers is well documented in the world (Li, 2014; Pal et al., 2013; Patrolecco et al., 2013; Camacho-Muñoz et al., 2009; Madureira et al., 2010), in Brazil it is still very limited (Montagner and Jardim, 2011; Campanha et al., 2015; Almeida et al., 2013). Only eight quantification studies of emerging pollutants of pharmaceutical origin were performed between 2000-2015 in Brazil. Among these studies, only three psychoactive drugs were investigated in aqueous matrices. Also, the southern region has only one study on hospital sewage and none on rivers (Böger et al., 2015).

Pharmaceuticals are released into the environment through excretions via feces and urine in a conjugated or unmetabolized way, and through disposal of outdated medicines in household sewage and effluents of wastewater treatment plants (WWTPs) (Subedi and Kannan, 2015; Alygizakis et al., 2016). While the toxic effects related to the disposition of these compounds are not fully known, recent studies demonstrate some interference in the metabolism and behavior of aquatic organisms (Fent et al., 2006; Morley, 2009), crossing all biological hierarchy, from cells and organs, and even ecosystems (Jorgensen and Halling-Sorensen, 2000). A recent study showed that exposure of fish and benthic invertebrates to psychoactive drugs altered their behavioral responses (Brodin et al., 2014; Rosi-Marshall et al., 2015).

Due to the matrix complexity and the low concentration of the target analytes, the direct analysis of these drugs is not feasible. Also, sample pretreatment is necessary to eliminate the interferences and to achieve desirable limits of detection and quantification. Solid phase extraction (SPE) has been applied to trace analysis to obtain significant preconcentration factors, with the use of smaller volumes of solvent (Madureira et al., 2010; Huntscha et al., 2012; Amaral et al., 2014).

Recently, the emerging organic pollutants have been investigated worldwide; nevertheless, there is no legislation that considers pharmaceuticals as micropollutants. The analytical techniques for medicine quantification and identification are well-established in governmental agencies such as ANVISA in Brazil. Despite this, conventional methodologies are used for raw material and commercial product quality (Anvisa, 2003). Hence, the development of rapid,

cheap, sensitive and accurate methods for monitoring pharmaceuticals at trace level have represented an analytical challenge in the last years. Further, the simultaneous determination of compounds with different chemical nature, from various therapeutic classes (Gros et al., 2006; Gomez et al., 2007) and also track pharmaceuticals in highly polluted aquatic environments, decreased time, and reduced overall cost is still a challenge. Most of these new methodologies are based on liquid chromatography-tandem mass spectrometry (LC-MS/MS) due to its high sensitivity and ability to confirm the compound's identity; however, the application of this sophisticated and expensive technology is not yet available in all laboratories. Taking into account the previously mentioned concerns, the purpose of this work was to develop an analytical method based on a single and efficient preconcentration procedure based on solid-phase extraction (SPE) followed by high-performance liquid chromatography with diode array detection (HPLC-DAD) analysis, demonstrating that this methodology is very useful for detecting levels of carbamazepine and diazepam in polluted water samples. These analytes were chosen based on survey of the most prescribed drug by Psychosocial Care Center (CAPS) in Curitiba, Paraná- BR performed in this work.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

Carbamazepine (CZ, 5*H*-Dibenz[*b,f*]azepine-5-carboxamide) and Diazepam (DZ, 7-Chloro-1-methyl-5-phenyl-3*H*-1,4-benzodiazepin-2(1*H*)-one) were purchased from USP (Rockville, MD, USA).

All the other solvents used were HPLC grade and supplied by J. T. Baker (Philipsburg, NJ, USA). Ultrapure water was obtained using Milli-Q system coupled with a UV lamp (18.2 MΩ cm, Bedford, MA, USA). 0.45-μm glass fiber filters were purchased from Millipore (Macherey Nagel). Stock solutions for individual standards (1000 mg L⁻¹) were prepared in methanol and stored in the dark at -6°C. Stock solutions were stable, and no evidence of degradation of the analytes was observed on the chromatograms during the six-month study period. Working solutions were prepared daily by diluting the stock solution with a suitable solvent. The pH of the solutions was measured by OHAUS Starter 2100 pH-meter.

2.2. Sample collection

The river studied was chosen according to the geographical location of the CAPS evaluated. These two CAPS are located on the watershed of Belém. Therefore, the river selected for the study was the sub-basin of Belém River (tributary of the Iguaçu River, which is one of the basins used for water supply in other cities in Paraná), considered a contaminated hotspot. Several samples were collected at three distinct areas of the Belém River: two considered highly polluted since most waste generated in this region is not suitably treated and is directly discharged into the Belém River (the mouth and about 7 km from the headspring of the river) and the other with low levels of pollution as it was near the headspring. The samples were fortified with 2.56 μg L⁻¹ of DZ and 2.26 μg L⁻¹ of CZ to monitor retention time (*T_R*) of drug. The water samples were collected during May, June, July and October. Two liters of river water samples were collected into 2.5 L pre-rinsed amber glass bottles. Upon collection, all samples were immediately transported at 4°C to the laboratory and vacuum-filtered through a 0.45-μm glass fiber filter with a 47 mm diameter (Millipore). The pH of filtered samples was adjusted to 4.00. Each sample was divided into different volumetric flasks, then stored in darkness at 4°C and extracted within a maximum of 24 h after collection.

2.3. Solid-phase extraction

SPE was performed on a PrepSep 20-port vacuum manifold (Waters, Milford, MA, USA) with Strata-X[®] cartridges (Phenomenex, 200 mg/ 3 mL). The SPE operational variables such as conditioning and elution solvent, analytes concentration and sample volume, were optimized by a two-level factorial design (2^3 with triplicate of center point) according to Table 1. The assays were carried out in a randomized mode. The response evaluated was the recovery of psychoactive drugs.

In the optimized SPE procedure, cartridges were conditioned with two aliquots of acetonitrile (2.50 mL) and two aliquots of ultrapure water pH 4 (2.50 mL) before each run. Sequentially, water samples at 4.00 pH were percolated through the cartridges at a constant flow rate of 3 mL min⁻¹. Afterward, elution was performed with 5.00 mL of acetonitrile. The extracts were evaporated to dryness in a thermostatic bath at 30°C under a gentle nitrogen stream. The residues were dissolved in 1.00 mL of water, and 15 µL was injected into the HPLC system. The pH and reconstitution volume were evaluated separately.

Table 1. Factors and levels analyzed in two-level full factorial design.

Factor	Level		
	-1	0	+1
Concentration	1.28 µg L ⁻¹ DZ	2.56 µg L ⁻¹ DZ	3.84 µg L ⁻¹ DZ
	1.13 µg L ⁻¹ CZ	2.26 µg L ⁻¹ CZ	3.39 µg L ⁻¹ CZ
Sample volume	100 mL	200 mL	300 mL
Conditioning/elution solvent	Acetonitrila (ACN)	ACN:MetOH (1:1)	Metanol (MetOH)

2.4. HPLC–DAD analysis

Chromatographic analyses were performed with the Agilent 1260 Infinity Quaternary LC system (Agilent Technologies, Waldbronn, Germany) equipped with an autosampler, quaternary gradient pump, and diode array detector (DAD) system. Separation was achieved in a 100 mm × 2.1 mm, 5 µm particle size Waters XBridge BEH C18 column. The data were collected with OpenLab EZChrom Elite software. The chromatographic conditions were optimized based on previous information in literature (INMETRO, 2010; Madureira et al., 2010). Hence, an isocratic elution mode was selected for simultaneous determination of carbamazepine and diazepam with methanol and ultrapure water (60:40 v/v) as mobile phase at a flow rate of 0.4 mL min⁻¹. Separations were performed at a 30°C. The following wavelengths were monitored: 254 nm (DZ) and 286 nm (CZ), which allowed a selective analysis with a suitable absorption of the studied compounds. The optimized chromatographic condition had 8.0 minutes of total run time.

2.5. Method validation

The method validation for the determination of pharmaceuticals in river water was performed with the following parameters: linearity, detection and quantification limits, precision and accuracy (n=3 for all assays) according to guidelines described by the National Agency of Health Surveillance (Agência Nacional de Vigilância Sanitária – ANVISA) (Anvisa, 2003). All procedures were performed with preconcentration step.

3. RESULTS AND DISCUSSION

3.1. Psychotropic drugs studied

This study aims to analyze the most commonly used psychotropic drugs in the Psychosocial Network, the Psychosocial Care Center (CAPS) in Curitiba, Paraná, BR, assisted

by Unified Health System (SUS), which consists of healthcare venues for people suffering from mental disorders and needs arising from the use of crack, alcohol, and other drugs.

A transverse quantitative analysis was performed to search for information in the Specific Registration Books of controlled drugs in CAPS for the years 2011 to 2014. There were 10,897 drugs dispensed for emergency use in mental disorders. The Brazilian Common Denomination (DCB), pharmaceutical forms and concentrations that are exempted from the following drug classes was considered: antidepressants, anxiolytics, antiepileptics, antipsychotics, anticholinergics, and hypnotic/sedative. Based on this survey, carbamazepine and diazepam were among the most prescribed antipsychotics (Diazepam 5 mg pill (11.86%) and Carbamazepine 200 mg (9.08%)). Hence, the both psychotropic drugs were selected for further investigation.

3.2. Solid phase extraction

Pre-concentration methods are essential to environmental analysis since the target analytes are at low concentrations (the trace levels – $\mu\text{g L}^{-1}$) (Amaral et al., 2014). Initially, the selection of pH included different values of 4.00, 6.50 and 8.00 ($n = 3$). Water acidified to pH 4.00 showed better recovery results to both analytes because CZ ensures the prevalence of the neutral form of compounds in the solution (around pK_a) and DZ is undissociated; however the best recoveries were obtained in acidic media compared with neutral and basic pH recoveries.

To determine the influence of conditioning and elution solvent, analytes concentration and sample volume on the preconcentration system, a two-level full factorial design, 2^3 with 8 runs was employed. Based on central point standard deviation (CZ: 0.38; DZ: 0.15), 3-way interactions were statistically significant (95% of confidence level) for both analytes. Hence, the factors can not be evaluated individually. As shown in Figure 1, this higher-order effect means there are several conditions which provide proper psychoactive drug recovery.

The optimized SPE conditions were in the low level for all variables (5.00 mL of ACN followed by 5.00 mL of ultrapure water pH 4.00 as conditioning solvents, 5.00 mL of ACN as an elution solvent, 100 mL of sample volume and $1.13 \mu\text{g L}^{-1}$ to CZ and $1.28 \mu\text{g L}^{-1}$ to DZ) and were employed in further experiments. Similar recoveries were estimated by Patrolecco et al. (2013) employing Strata X cartridge (80 to 93% to CZ) and by Madureira et al. (2010) using Oasis HLB cartridges (81 to 91% to CZ and 86 to 91% to DZ).

Reconstitution volume was also investigated. Recoveries of around 80% with RSD below 3.7% were obtained for CZ and DZ at 1.00 mL of ultrapure water. Meanwhile, volumes of 0.500 and 0.250 mL recovered less than 70% of both analytes. Moreover, an enrichment factor of 100 times was achieved.

Figure 1. Graphical representation of SPE optimization by 2^3 factorial design. Recovery observed in each assay appears in the boxes.

3.3. Method validation

Figure 2 shows the chromatograms obtained for the proposed method. Well-resolved peaks were observed, for which the retention times were 1.47 minutes and 3.07 minutes for CZ and DZ, respectively.

The linearity of the method was studied in ten different concentrations of analyte in triplicate in the range between 10.0 e 1500 $\mu\text{g L}^{-1}$. The proposed method showed good linear range between 20 - 1500 $\mu\text{g L}^{-1}$ to CZ and 40 - 1500 $\mu\text{g L}^{-1}$ to DZ, with excellent coefficients of determination ($R > 0.999$) for both analytes, as recommended by ANVISA (2003). Angular coefficients were used to evaluate method sensitivity, which showed slightly more sensitivity to carbamazepine (Figure 2C).

Selectivity was observed by the association of the T_R and DAD spectra, standards in a pure solvent and standards in matrix ensures that the signal measured is not influenced by matrix interferences. This observation guarantees that the method is selective for the pharmaceuticals and can be used for monitoring purposes in river water samples. The RSD values were obtained as a result of a precision estimation of the t_R between the standard in solvent solutions, and spiked matrix were below 2.45% ($n = 18$). The difference in the baseline shift observed at the beginning of chromatograms is entirely related to the absorption of humic substances commonly present in river water samples, which due to its high conjugated system caused this characteristic band (Moffat et al. 2004). However, in our study, this fact did not interfere with the determination of the studied compounds.

The instrumental precision was estimated by repeatability and intermediate precision assays and was expressed as percent relative standard deviation (%RSD) of replicate measurements using the peak areas for calculation. Table 2 summarizes the precision results from replicate measurements at three different concentration levels (50.0 $\mu\text{g L}^{-1}$, 500 $\mu\text{g L}^{-1}$, and 1000 $\mu\text{g L}^{-1}$, $n=3$) for each studied psychoactive compound.

Repeatability of replicate measurements was satisfactory, with RSD values below 6.06% and 3.64% for CZ and DZ, respectively. The intermediate precision showed RSD values below 3.87% for CZ and 6.61% for DZ (Table 2). The Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO, 2010) determines a maximum RSD value of up to 20%. ANVISA (2003) recommends that the coefficients of variation should not exceed 5% for the determination of drugs in medicine and more complex matrices, such as serum, blood or plasma, but accepts a value of up to 15%. Hence, the method's precision was satisfactory within the maximum value permitted by applicable Brazilian legislation.

Table 2. Repeatability, intermediate precision RSD (%) and recovery values (%) at three different concentration levels.

	Concentration levels ($\mu\text{g L}^{-1}$)					
	50.0 (n=3)		500 (n=3)		1000 (n=3)	
	CZ	DZ	CZ	DZ	CZ	DZ
Repeatability (%)	6.06	1.34	0.640	3.64	0.420	2.15
Intermediate precision (%)	3.87	6.61	0.820	0.240	1.56	0.210
Recovery $\pm$ RSD (%)	98.3 $\pm$ 4.46	98.4 $\pm$ 5.32	89.7 $\pm$ 2.25	92.7 $\pm$ 10.7	85.8 $\pm$ 3.86	89.7 $\pm$ 9.07

Accuracy was established based on CZ and DZ recovery, which was performed by extracting and analyzing triplicate ultrapure water samples spiked with analytes (50.0 $\mu\text{g L}^{-1}$, 500 $\mu\text{g L}^{-1}$ and 1000 $\mu\text{g L}^{-1}$). The results of recovery experiments are reported in Table 2, which shows that the method is accurate within the desired recovery range. Similar recoveries were found in real samples (Patrolecco et al., 2013, Madureira et al., 2010)

Figure 2. HPLC-DAD chromatograms of a standard mixture of the psychoactive at 10 to 1500 µg L⁻¹ performed under the optimized conditions: A) DZ and B) CZ. C) Analytical curves for CZ at 286 nm and DZ at 254 nm.

Limits of detection and quantification of the developed method were estimated by the relation of the intercept standard deviation (s) and the value of the calibration curve slope (S), according to Equations 1 and 2:

$$LOD = \frac{3,3s}{S} \quad (1)$$

$$LOQ = \frac{10s}{S} \quad (2)$$

The LODs and LOQs were 0.0670 µg L⁻¹ and 0.209 µg L⁻¹ to CZ and 0.130 µg L⁻¹ and 0.435 µg L⁻¹ to DZ. These results were close to those described in the literature (Madureira et al. 2010; Ebert et al. 2014).

The LOD and LOQ obtained in this work were lower than Madureira et al. (2010) have found with the SPE method (LOD and LOQ to CZ of 3.8 and 15 $\mu\text{g L}^{-1}$, respectively, and to DZ 10.3 and 40 $\mu\text{g L}^{-1}$, respectively). Ebert et al. (2014) related that the global mean concentration in surface water to CZ is between 0.187 and 8.05 $\mu\text{g L}^{-1}$. Based on that, the proposed method would be able to detect CZ in concentrations lower than this minimum limit.

The evaluation of robustness was made by analyses of the influence of variations in column temperature at 20°C, 25°C and 30°C, respectively, and in flow rates of 0.3, 0.4 and 0.5 mL min^{-1} . This data allowed us to correlate each area of peak to the corresponding chromatographic retention time. For robustness evaluation, small changes in flow rate ($\pm 10\%$) and column temperature ($\pm 5^\circ\text{C}$) did not make significant changes to resolution or recovery.

3.4. Psychoactive pharmaceuticals in the Belém River water

To demonstrate the applicability of the developed method, three sampling locations in the Belém River were selected according to the level of pollution in each area (low, medium and high pollution). Water samples were collected in May, June, July and October 2015 (Table 3).

The mouth of the river is the most-polluted site. It is fully inserted in the city of Curitiba; there are many irregular houses on its margins. Many of these houses are not connected to the city's sewage network, thus discarding their sewage into the river.

Table 3. The average concentration of residues found in different locations in the river in each collection.

Locations	Analytes	Average concentration ($\mu\text{g L}^{-1}$)			
		May	June	July	October
Headspring	CZ	<LOQs	<LOQs	0.371	nd*
	DZ	<LOQs	nd*	nd*	nd*
Middle of river	CZ	<LOQs	<LOQs	<LOQs	nd*
	DZ	nd*	nd*	nd*	nd*
Mouth	CZ	nd*	0.856	<LOQs	nd*
	DZ	nd*	0.763	nd*	nd*

*nd: not detected.

Carbamazepine was found higher than LOQ in headspring (July-CZ = 0.371 $\mu\text{g L}^{-1}$) and the both at the Belém River mouth (June-CZ = 0.856 $\mu\text{g L}^{-1}$, DZ = 0.763 $\mu\text{g L}^{-1}$) in the second and third collections, which are consistent with the results that similar work reported (Ebert et al., 2014, Patrolecco et al., 2013). These collections were performed during a dry period (winter), which increases the analytes concentration and lowers degradation rates. Further, during the spring (October), the increase of rain volume and warm weather (INMET, 2015) promotes the dilution of analytes and increases degradation rates. Therefore, CZ and DZ were not detected at any of the collection points. The highest frequency of CZ detection is indicative of inadequate sewage disposal along the river localized in the region that this drug is widely distributed by CAPS, as early mentioned.

CZ were found in the Tiber River (Italy) at the concentration level of 0.063 $\mu\text{g L}^{-1}$ (Patrolecco et al., 2013). Madureira et al. (2010) found CZ at 0.0327 $\mu\text{g L}^{-1}$ and did not detect DZ in the Douro River estuary (Portugal). Campanha et al. (2015) found CZ in 71% of analyzed samples between 0.50 and 0.215 $\mu\text{g L}^{-1}$ in the Monjolinho River, São Carlos, SP. According Clara et al. (2004), CZ could be considered a qualified parameter for detecting wastewater in aquatic environments due to its high persistence.

Carbamazepine and diazepam were found to be ubiquitous (present in 58.3% of samples collected) and persistent in river water. Here again, a strong correlation was observed between the amount of pharmaceuticals dispensed in the CAPS and their excretion as an unchanged drug

and their concentration levels in the surface water (the amount of CZ that would go to the Belém River would be 19.7 g – estimating that 10% is excreted as unchanged drug, and the amount of DZ would be 0.194 g – calculating that 3% is excreted as unchanged drug) (Moffat et al., 2004). CAPS provide a regionalized service, implying the delineation of specific geographical areas. These two CAPS studied delimited the region on the sub-basin of the Belém River, where houses not connected to the sewage system properly end up discarding their waste into rivers or streams of this subbasin.

Despite diazepam being the most commonly dispensed medication in the community between 2011-2014, carbamazepine was found at much higher concentrations in both the mouth and headspring of the river than diazepam (a maximum concentration of $0.763 \mu\text{g L}^{-1}$ determined in the mouth of the river during dry weather conditions). This can be explained by the fact that carbamazepine is excreted by the human body in approximately 10% unchanged form, while diazepam is excreted approximately 3% as an unchanged compound. Therefore, CZ environmental concentrations are much higher. Other similar observations about carbamazepine are reported (Glassmeyer et al., 2009; Subedi and Kannan, 2015). To date, diazepam has not been extensively reported.

Because of the importance of these substances to public health, according to the ecotoxicological point of view (Alonso et al., 2010; Brodin et al., 2014; Petersen et al., 2014; Rosi-Marshall et al., 2015), it is essential to ascertain their occurrence in surface water systems, even though it is not contemplated in Brazilian environmental legislation. Further studies of this are extremely necessary to support the establishment of legal parameters of drug residues in aqueous matrices.

The proposed HPLC-DAD method showed specificity, accuracy and sensitivity, good linearity for both analytes ($R > 0.9998$) and LOD and LOQ were found to be suitable for environmental analysis with a preconcentration step (micrograms per liter or parts per billion). This paper provided a useful and expressive guidance on HPLC-DAD that is in accordance with validation requirements for pharmaceutical analysis in water samples. To our knowledge, this is the first study reporting the method validation of the psychoactive drugs by SPE-HPLC-DAD for river water, especially in developing countries such as Brazil.

4. ACKNOWLEDGMENTS

We gratefully acknowledge the Federal University of Paraná (UFPR) and the financial support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Araucária and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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Determinação de hormônios estrogênicos em esgoto bruto e efluente de uma estação descentralizada de tratamento por lodos ativados

ARTICLES doi:10.4136/ambi-agua.2059

Received: 05 Dec. 2016; Accepted: 19 Dec. 2017

Rossana Borges Teixeira^{*}; Carolina Alves Marques; Natália Rodrigues de Carvalho; Luiz Eduardo Thans Gomes; Flávio Teixeira da Silva; Teresa Cristina Brazil de Paiva

Escola de Engenharia de Lorena (EEL-USP), Lorena, SP, Brasil

Departamento de Biotecnologia. E-mail: rossanabt@hotmail.com, carolina.4545@hotmail.com, nataliadecarvalho@gmail.com, luizeduardo.gomes@hotmail.com, flavio@debiq.eel.usp.br,

teresa@debiq.eel.usp.br

^{*}Autor correspondente

RESUMO

Hormônios estrogênicos, provenientes dos esgotos, atingem os corpos hídricos e podem causar perturbações aos organismos aquáticos. Os tratamentos secundários das estações de tratamento de esgoto (ETE) possibilitam alguma remoção destes compostos, mesmo em ETEs descentralizadas, apesar de ainda haver poucos estudos sobre elas. Em sistemas por lodos ativados, a eficiência tem sido relacionada ao tempo de detenção hidráulica (TDH), à idade de lodo, à desnitrificação biológica e à carga de alimentação. O objetivo deste trabalho foi quantificar os hormônios estrona (E1), 17- β -estradiol (E2), estriol (E3) e 17- α -etinilestradiol (EE2) no esgoto e no efluente de uma ETE descentralizada por lodos ativados, além de caracterizar a ETE do Campus Universitário da EEL-USP quanto à matéria orgânica recebida, ao tempo de detenção hidráulica e a remoção de nitrogênio. Cromatografia líquida com detecção UV foi utilizada na determinação dos hormônios. Os resultados mostraram concentrações dos hormônios superiores às encontradas na literatura, em ambos: esgoto ($5,158 \pm 2,747$; $7,434 \pm 4,356$; $5,200 \pm 3,331$ e $5,638 \pm 4,312$ $\mu\text{g L}^{-1}$ de E1, E2, E3 e EE2) e efluente ($5,062 \pm 3,366$; $4,191 \pm 3,527$; $7,743 \pm 3,951$, $2,550 \pm 2,162$ de E1, E2, E3 e EE2). No esgoto, as altas concentrações podem ser relacionadas à maior predominância de urina, visto os altos níveis de nitrogênio detectados, à menor geração de esgoto e a amostragem em período seco causando reduzida diluição dos hormônios. Remoção insuficiente dos hormônios devido a menor TDH (2h05) e irregularidade na desnitrificação (-54 a 61%) pode ser o motivo das altas concentrações de estrógenos no efluente. Ademais, a desconjugação dos hormônios pode ter ocorrido durante o tratamento.

Palavras-chave: cromatografia líquida com detecção UV, esgoto de Campus universitário, estrógenos, ETE batelada, remoção de hormônios estrogênicos.

Determination of estrogenic hormones in sewage and effluent of a decentralized sewage treatment plant by activated sludge

ABSTRACT

Estrogenic hormones from sewers reach water bodies and can disrupt aquatic organisms. Secondary treatment of sewage treatment plants (STP) can remove some of those hormones,

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even in decentralized STPs, although there are few studies regarding this. In activated sludge systems, efficient removal has been attributed to hydraulic retention time (HRT), sludge age, biological denitrification and organic load. This study sought to quantify the hormones estrone (E1), 17 β -estradiol (E2), estriol (E3) and 17 α -ethynylestradiol (EE2) in the sewage and effluent of a decentralized STP with activated sludge, and also to characterize this college campus STP regarding received organic matter, hydraulic retention time and nitrogen removal. Hormone levels were determined by liquid chromatography with UV detection. The results showed hormone concentrations far superior to those found in the literature in both the sewage (5.158 ± 2.747 ; 7.434 ± 4.356 ; 5.200 ± 3.331 e 5.638 ± 4.312 $\mu\text{g L}^{-1}$ of E1, E2, E3 and EE2) and the effluent (5.062 ± 3.366 ; 4.191 ± 3.527 ; 7.743 ± 3.951 , 2.550 ± 2.162 of E1, E2, E3 and EE2). In the sewage, the high concentration could be related to a large predominance of urine, given the high level of nitrogen detected, or to low generation of sewage and to sample collection in dry periods causing decreased dilution of hormones. Insufficient removal of estrogens due to short HRT (2h05) and irregular denitrification (-54 to 61%) can be the reason for high concentrations of estrogens found in the effluent. Furthermore, deconjugation of hormones may have occurred during treatment.

Keywords: batch WWTP, estrogens, liquid chromatography with UV detection, removal of estrogenic hormones, wastewater of College Campus.

1. INTRODUÇÃO

Os hormônios estrogênicos, inclusive os naturais, têm sido apontados como os responsáveis por grande parte das perturbações endócrinas em organismos aquáticos identificadas nos últimos anos. A relevância dos hormônios estrogênicos na perturbação endócrina se deve: à alta afinidade dos estrógenos aos receptores presentes nos organismos de outras espécies permitindo a ação, mesmo em baixíssimas concentrações (ng L^{-1}); à ampla excreção destes hormônios por seres humanos e por outros animais nas fezes e urina; e ao posterior despejo dos esgotos, tratados ou não, nos ecossistemas aquáticos (Carballa et al., 2004; Fonseca et al., 2013).

Diversos estudos realizados ao redor do mundo demonstraram que os esgotos municipais têm apresentado concentrações dos hormônios estrogênicos na faixa de ng L^{-1} e detecção dos hormônios pesquisados em quase todas as amostras. Já os hormônios artificiais têm sido determinados menos frequentemente, visto que a sua presença depende da prescrição e regulamentação para uso (Carballa et al., 2004; Janex-Habibi et al., 2009; Stanford e Weinberg, 2010; Fonseca et al., 2013; Ferreira, 2013).

Diferente dos esgotos domésticos, os efluentes de estações de tratamento de esgoto (ETE) apresentam menor concentração e menor frequência de detecção dos hormônios estrogênicos, inclusive os naturais. Estas reduções foram atribuídas, principalmente, à remoção destes compostos pelos tratamentos secundários adotados nas ETES. A remoção dos hormônios engloba os processos de biotransformação conduzido pelos micro-organismos e a sorção dos compostos ao lodo, assim como ocorre com os constituintes majoritários dos esgotos (Carballa et al., 2004; Servos et al., 2005; Janex-Habibi et al., 2009; Stanford e Weinberg, 2010; Fonseca et al., 2013).

Estima-se que o sistema de lodos ativados seja o tratamento biológico mais utilizado no mundo e com isto, trabalhos sob a remoção de hormônios estrogênicos vêm sendo investigados neste tipo de tratamento (D'Ascenzo et al., 2003). Diferentes eficiências de remoção têm sido obtidas e os melhores resultados foram atribuídos a maior tempo de detenção hidráulica (TDH), prolongadas idade de lodo, baixa carga de alimentação e melhor remoção biológica de nutrientes, principalmente, o nitrogênio (Johnson et al., 2005; Ferreira, 2013).

As ETEs descentralizadas, atendendo pequenas comunidades ou negócios, podem ser uma alternativa para a redução da poluição hídrica, porém podem apresentar riscos à qualidade da água se não forem efetivamente monitoradas. Nos Estados Unidos (USA), a participação das ETEs descentralizadas no tratamento de esgotos foi estimada em 25% (Stanford e Weinberg, 2010). Apesar da relevância deste modelo de tratamento de esgotos, grande parte das publicações a respeito da presença e remoção de hormônios estrogênicos foi realizada em ETEs centralizadas. Uma exceção é o trabalho de Stanford e Weinberg (2010). Estes quantificaram e avaliaram a remoção dos hormônios estrogênicos em tratamentos descentralizados comumente utilizados nos USA: tanques sépticos, alagados aeróbios e anaeróbios e filtros de areia. Mesmo nestes tratamentos de operação mais simplificada, foram obtidas remoções dos hormônios superiores a 80%.

O objetivo deste trabalho foi quantificar os hormônios estrogênicos naturais, E1, E2 e E3, e o hormônio artificial EE2, no esgoto e no efluente da ETE descentralizada com operação em batelada que atende a Escola de Engenharia de Lorena (EEL-USP), além de caracterizar a ETE quanto ao tempo de detenção hidráulica (TDH), carga orgânica de alimentação e desempenho na remoção de nitrogênio, visto o impacto destes fatores na remoção dos hormônios estrogênicos.

2. MATERIAL E MÉTODOS

2.1. Local de estudo

A ETE da EEL-USP utiliza lodos ativados em bateladas sequencias (SBR) para tratar todo o esgoto gerado no Campus I, em média 85 m³ por dia. O esgoto é proveniente de laboratórios, sanitários, vestiários, da limpeza de edifícios e da lavagem de utensílios do serviço de alimentação. Não há moradias no Campus e nem há preparo dos alimentos servidos no Restaurante Universitário.

A ETE em estudo foi, primeiramente, projetada para operar de forma contínua, porém o aumento na geração de esgoto, consequência do aumento do número de alunos, fez com que o regime de operação em bateladas fosse adotado. O modo SBR permitiu utilizar o decantador secundário também como tanque de reação/aeração, aumentando a capacidade da ETE. A ETE possui duas particularidades: (i) não possui tratamento preliminar como outras ETEs sanitárias instaladas na região, que possuem ao menos caixa para a remoção de areia e possuem grades para a remoção de sólidos grosseiros; (ii) não opera com os tanques de aeração (15 e 25 m³) alternadamente, dado que possui um tanque pulmão (50 m³) para o recebimento do esgoto enquanto o processo de depuração biológica ocorre. A ETE opera com tempo de detenção hidráulica de 02h05 (intervalo de tempo medido entre a finalização do enchimento e início do descarte) e ciclo total de aeração de 01h20 divididos em baterias de aeração intermitentes (50% do tempo aerando a cada 5 minutos). Na operação regular da ETE não são controlados os parâmetros oxigênio dissolvido (OD), idade do lodo e série de sólidos, porém, mesmo com estas deficiências, a ETE apresenta a eficiência necessária para atendimento das legislações aplicáveis.

2.2. Caracterização da ETE e do esgoto

Informações sobre o desempenho da ETE na remoção de matéria orgânica, nitrogênio e fósforo e carga de alimentação foram obtidas pela realização de análises químicas utilizando os procedimentos descritos em APHA et al. (1998) para a determinação de DBO, DQO, nitrogênio total Kjeldahl (NTK) e fósforo total.

2.3. Amostragem

Foram realizadas sete campanhas de amostragem entre junho de 2014 e outubro de 2015 em dias de semana e em horário comercial (entre 08 e 18 horas). A cada campanha de

amostragem, foram coletados 3 litros de esgoto na entrada do tanque de aeração e 3 litros de efluente na linha de descarte.

As coletas foram pontuais, visto a retenção anterior ao tratamento pelo tanque pulmão e a operação do tratamento em ciclos (batelada) que equaliza os conteúdos.

2.4. Determinação dos hormônios

2.4.1. Reagentes e insumos

Foram utilizados cartuchos de extração em fase sólida (EFS) C18 (500 mg e 3 mL), metanol e acetonitrila grau HPLC, água ultra-pura produzida em sistema de purificação Milli-Q, estrona (E1, 99% pureza), 17- β -estradiol (E2, 98% pureza), 17- α -etinilestradiol (EE2, 98% pureza) e estriol (E3, 98% pureza) e filtros em fibra de vidro de 1,2 μ m, 0,7 μ m e 0,45 μ m.

Foram preparadas soluções estoque, 1000 mg L⁻¹, de cada um dos padrões pela pesagem dos padrões e adição de acetonitrila em balões de 25,00 mL. Estas soluções foram armazenadas sob refrigeração e ao abrigo da luz.

Soluções de trabalho, 10 mg L⁻¹, contendo os 4 hormônios (E1, E2, E3 e EE2) foram preparadas a partir das soluções estoque no dia de uso utilizando micropipetador, balão volumétrico de 10,00 mL e acetonitrila.

2.4.2. Preparo das amostras

As amostras de esgoto (750 mL) e de efluente (1000 mL) foram filtradas a vácuo em filtros de fibra de vidro de 1,2 μ m e depois de 0,7 μ m e armazenadas sob refrigeração por no máximo 12 horas. O pH foi corrigido para 3,0 com solução de HCl 0,1 M após atingir a temperatura ambiente.

Os cartuchos C18 foram colocados no manifold para EFS e condicionados pela aplicação de 7,00 mL de acetonitrila, 5,00 mL de metanol e 5,00 mL de água ultra-pura sob vácuo.

As amostras foram aplicadas nos cartuchos utilizando vácuo. Após a passagem de todo o volume de amostras, parte das impurezas foram removidas com a adição de 10,00 mL de solução 1:10 de metanol em água ultra-pura sem vácuo, os cartuchos foram secos por 10 minutos à vácuo e estocados sob refrigeração e ao abrigo da luz.

Utilizando o manifold de EFS, os cartuchos foram eluídos com 4,00 mL de acetonitrila e o eluato foi recolhido em balões de 5,00 mL. A eluição foi realizada após os cartuchos terem sido aclimatados a temperatura ambiente.

O eluato foi avolumado com acetonitrila para 5,00 mL em balão volumétrico e fracionado em alíquotas de 0,850 mL com o uso de micropipetador em 5 balões de 1,00 mL. A cada um dos balões foi adicionado uma quantidade predeterminada da solução 10 mg L⁻¹ dos hormônios e avolumado para 1,00 mL com acetonitrila. O método de adição de padrão ao eluato foi necessário para minimizar o efeito matriz.

2.4.3. Análise Cromatográfica

As análises cromatográficas foram realizadas em Cromatógrafo Profissional IC 850 Metrohm com detector Profissional UV-VIS 887, utilizando coluna C18 ProntoSil 120-5-C18-AQ-150/4.0 mm a 30°C e fase móvel isocrática 50% água ultra-pura e 50% acetonitrila em fluxo de 1 mL min⁻¹. O volume de injeção foi 90 μ L e a detecção foi a 230 nm.

O uso de cromatografia líquida acoplada a detector UV na separação e quantificação dos hormônios foi a alternativa adotada que possibilitou menores custos operacional e de implantação e a realização deste trabalho. Para contornar o problema de menor detecção deste tipo de equipamento, quando comparado a outros tipos de detectores, como os detectores por

fluorescência ou por espectrometria de massa, foram utilizados volumes maiores de amostras (750 mL de esgoto e 1000 mL de efluente).

Os métodos de preparo da amostra e cromatográfico foram validados previamente por Teixeira (2016).

3. RESULTADOS E DISCUSSÃO

3.1. Caracterização do esgoto

Ao longo das sete coletas realizadas foi verificado que, em média, o esgoto da EEL/USP se apresentou menos concentrado em matéria orgânica (DQO e DBO5) e fósforo total que a média de 166 esgotos recebidos em ETES municipais instaladas nos estados de Minas Gerais e São Paulo consolidados por Oliveira e Von Sperling (2011). Por outro lado, a concentração de nitrogênio total Kjeldahl (NTK) é superior ao relatado para esgotos sanitários. Os resultados médios destes parâmetros podem ser verificados na Tabela 1.

Os resultados analíticos encontrados (menor concentração de DQO, DBO5 e fósforo e elevada concentração de nitrogênio), podem ser consequência do perfil do campus (sem moradia e preparo de refeições) e podem sugerir uma maior participação da urina neste esgoto em relação aos esgotos municipais avaliados por Oliveira e Von Sperling (2011) e podem interferir na quantidade dos hormônios estrogênicos visto que estes são descartados principalmente na urina (D'Ascenzo et al., 2003).

Tabela 1. Comparativo entre o esgoto da EEL/USP e os resultados médios para alguns parâmetros de caracterização do esgoto recebidos em ETES municipais.

Parâmetros	Esgoto EEL/USP	*Média de 166 ETES
DBO5 (mg L ⁻¹)	123±5	339±135
DQO (mg L ⁻¹)	194±92	639±326
Fósforo (mg L ⁻¹)	3,1±1,9	3,9±3,0
NTK (mg L ⁻¹)	55±30	50±17

*Fonte: Oliveira e Von Sperling (2011).

3.2. Caracterização da ETE EEL/USP

A ETE apresentou bom desempenho na remoção de DQO, entre 65 e 95%, e desempenhos irregulares para a remoção dos nutrientes: entre -54 e 61% de NTK e entre -18 e 99% de fósforo total.

As eficiências médias de remoção de DQO e fósforo, obtidas nesse trabalho, estão em faixas similares às relatadas (81 e 46%, respectivamente) por Oliveira e Von Sperling (2011), quando avaliado o desempenho de 13 ETES com tratamento por lodos ativados, em operação no sudeste brasileiro. Ao passo que, quando avaliado a remoção de nitrogênio total Kjeldahl (NTK), a média de remoção relatada por Oliveira e Von Sperling (2001) (entre 54 a 61%) é superior ao do corrente trabalho. Esses autores, porém não detalham a operação das ETES avaliadas para que possam ser comparadas ao desempenho da ETE deste trabalho para a remoção de NTK.

A remoção de nitrogênio pode ser melhorada, com impacto positivo na remoção de hormônios, com melhor controle nas etapas sequencias (anóxico/aeróbio) e na idade de lodo (Carballa et al., 2004). Porém, não há na ETE estudada controles que verifiquem o atendimento a estas condições, medidores de potencial de oxi-redução (POR) e de oxigênio dissolvido (OD), podendo ser a causa para o desempenho insatisfatório.

3.3. Presença dos hormônios estrogênicos livres no esgoto bruto

As concentrações médias e as frequências de determinação de cada um dos hormônios são apresentadas na Tabela 2, onde se constata que neste estudo os hormônios E1, E2, E3 e EE2 foram determinados em concentrações superiores aos relatados na literatura consultada, usualmente na faixa de ng L^{-1} (Carballa et al., 2004; Janex-Habibi et al., 2009; Fonseca et al., 2013).

As concentrações de hormônios estrogênicos também foram superiores aos relatados por Stanford e Weinberg (2010) em 5 diferentes ETEs descentralizadas dos EUA, na faixa de ng L^{-1} . O esgoto das ETEs avaliadas por estes autores atendiam também escolas, universidades e escritórios, todos com ocupação em parte do dia.

Tabela 2. Concentrações médias em $\mu\text{g L}^{-1}$, desvio padrão e frequência de determinação dos hormônios em esgoto bruto.

	E1	E2	E3	EE2
Média ($\mu\text{g L}^{-1}$)	5,148	7,434	5,200	5,688
Desvio padrão	2,747	4,356	3,331	4,312
Frequência	100%	100%	75%	100%

As concentrações dos hormônios em esgoto determinadas por Ruchiraset e Chinwetkitvanich (2014), em estudo realizado na Tailândia, também foram determinadas na faixa de $\mu\text{g L}^{-1}$, porém com uma menor frequência de detecção. Os picos de concentrações foram associados a períodos climáticos secos, visto que as amostras sem detecção dos hormônios foram coletadas em períodos chuvosos, o que mostraria o efeito do aumento da precipitação pluviométrica como fator de diluição de esgotos sanitários e dos hormônios.

No Brasil, também foram encontradas maiores concentrações dos hormônios em regiões de seca, o que pode ser exemplificado pelo trabalho de Pessoa et al. (2014), realizado no Ceará, região seca, que encontrou concentrações máximas dos hormônios estrogênicos entre $0,776 \mu\text{g L}^{-1}$ de E2 a $3,180 \mu\text{g L}^{-1}$ de EE2. Já as concentrações encontradas de E1 e E2 por Ferreira (2013) em esgoto do Rio de Janeiro estiveram na faixa de ng L^{-1} . No corrente trabalho, além das amostras terem sido coletadas em período climático de seca, também foram provenientes de um campus universitário com reduzido consumo de água e geração de esgoto (estimado em $47 \text{ L pessoa}^{-1} \text{ dia}^{-1}$). Estas considerações reforçam o impacto da diluição, por chuva e outros consumos de água, na concentração destes compostos.

Concentrações ainda maiores foram relatadas por Kvanli et al. (2008) para os hormônios em esgoto: até $36,1 \mu\text{g L}^{-1}$ de E1, até $40,3 \mu\text{g L}^{-1}$ de E2 e abaixo de $20,0 \mu\text{g L}^{-1}$ de E3 e de EE2. Este estudo utilizou urina coletada de grupos de jovens para compor duas amostras de esgoto a ser aplicado em duas diferentes estações de reciclagem de água em escala de laboratório, similares às utilizadas em ônibus espaciais. Os autores acreditam que a utilização apenas de urina, sem outras fontes de água para diluição e a faixa etária dos doadores foram os motivos para as elevadas concentrações. Isto porque os estrogênios são descartados majoritariamente pela urina.

Neste trabalho, o elevado teor de NTK nas amostras de esgoto em relação a outros esgotos municipais, a baixa geração de esgoto per capita e a utilização diferenciada de água no Campus podem indicar um peso maior da urina no esgoto gerado, de forma semelhante ao estudo de Kvanli et al. (2008), e deve ser a causa principal da elevada concentração dos hormônios estrogênicos determinada.

3.4. Presença dos hormônios estrogênicos livres no efluente

Os hormônios estrogênicos foram detectados em concentrações tão elevadas no efluente quanto as determinadas no esgoto e nas mesmas frequências de detecção, como pode ser verificado na Tabela 3. A desconjugação às formas livres, a perda dos grupamentos sulfato ou glicuronídeos com os quais os hormônios estão ligados a serem excretados durante o tratamento biológico e a remoção insuficiente pelo tratamento são as possíveis causas destes altos valores.

O percurso da rede de esgoto, entre os sanitários e a entrada do tratamento biológico no campus da EEL/USP, pode ter sido insuficiente para que os hormônios fossem desconjugados às formas livres. Isso porque os glucorohormônios excretados na urina são desconjugados às formas livres dos hormônios ao entrar em contato com os micro-organismos do trato intestinal, principalmente a *E. coli*, proveniente das fezes. Por outro lado, os sulfatohormônios, outra forma dos hormônios excretados na urina, são mais persistentes. O que pode ser verificado pelo trabalho de D'Ascenzo et al. (2003), no qual foram necessárias 60 horas para a redução dos sulfatohormônios a 50% da concentração inicial quando em contato com o esgoto e 5 horas para atingir a mesma redução dos glucorohormônios. Durante o tratamento biológico, os sulfatohormônios sofreram desconjugação sendo reduzidos a 26% da concentração inicial e os glucorohormônios foram reduzidos a 2%. Ambas as desconjugações, de glucorohormônios e de sulfatohormônios, ocorrendo durante o tratamento podem ter produzido hormônios livres encobrendo parte do que foi removido, visto que as formas conjugadas não foram quantificadas neste trabalho. Fenômeno semelhante, aumento ou pequena redução dos hormônios livres, foi identificado no trabalho de Kvanli et al. (2008), no qual os autores associaram a baixa remoção dos hormônios ao curto tempo entre a coleta da urina para composição do esgoto e a aplicação nos tratamentos estudados.

Tabela 3. Concentrações médias em $\mu\text{g L}^{-1}$, desvios-padrão e frequências de detecção por hormônio no efluente.

	E1	E2	E3	EE2
Média	5,062	4,191	7,743	2,550
Desvio padrão	3,365	3,526	3,951	2,162
Frequência	100%	100%	75%	100%

Além da desconjugação durante a etapa biológica, a remoção dos hormônios pode ter sido insuficiente, haja visto que as condições relacionadas à eficiente biodegradação destes compostos em tratamento por lodos ativados (idade do lodo) não foram aferidas ou não foram alcançadas (tempo de detenção hidráulica maior e remoção de nitrogênio) neste trabalho. Apenas a baixa carga de alimentação foi constatada dentre os fatores que promoveriam a melhor biodegradação (Johnson et al., 2005; Li et al., 2008; Pessoa et al., 2014).

No estudo de Servos et al. (2005) com 18 ETEs em operação no Canadá, duas destas, operando com sistema de lodos ativados convencional apresentaram condições semelhantes entre si de TDH (aproximadamente 7 horas) e remoção de E2 distintas (40 e 76%). A ETE de melhor remoção de E2, apesar de não operar com elevada idade de lodo, obteve melhor remoção parcial de nitrogênio (85% contra 45% da ETE que não obteve bom desempenho).

Uma das 17 ETEs utilizadas no estudo de Johnson et al. (2005), Eindhoven (Ei), possuía sistema de tratamento de lodos ativados com TDH menor do que deste trabalho (1,3 horas). Porém, apresentou remoção de E1 de 94%, o que pode ser atribuído à existência de zona anóxica e à elevada idade de lodo (25 dias) condições necessária para a desnitrificação. Boas remoções, com médias acima de 85% de E1 e de E2, também foram determinadas por Janex-Habibi et al.

(2009) em 9 ETEs por lodos ativados operando na Europa e Estados Unidos. Além do maior TDH, entre 5 e 30 horas, estas possuíam etapas para remoção biológica de nitrogênio.

A baixa carga orgânica alimentada, similar ou inferior aos valores citados nos estudos de Carballa et al. (2004) e Ferreira (2013), pode ter sido o fator determinante para a remoção parcial dos hormônios, E2 e EE2, mesmo em condições adversas de TDH, de desnitrificação e sem acompanhamento da idade de lodo. Fato que é corroborado pelo trabalho de Li et al. (2008) que determinaram taxas de biodegradação dos hormônios E1, E2 e EE2 inversamente proporcionais à concentração de glicose (usada como matéria orgânica) no meio reativo.

Em relação ao hormônio E1, além da desconjugação e da baixa capacidade do tratamento biológico para a remoção dos hormônios estudados, a conversão por oxidação microbiana de outros hormônios estrogênicos a E1 pode ser fundamento adicional para as altas concentrações detectadas no efluente. Carballa et al. (2004) e Servos et al. (2005) também relataram menor remoção do E1 em relação aos outros hormônios estrogênico ou até o surgimento destes em meios nos quais não foram inoculados.

4. CONCLUSÕES

O esgoto gerado na EEL-USP e o efluente tratado na estação por lodos ativados em bateladas sequenciais apresentaram altas concentrações dos hormônios estrogênicos ($5,158 \pm 2,747$; $7,434 \pm 4,356$; $5,200 \pm 3,331$ e $5,638 \pm 4,312 \mu\text{g L}^{-1}$ de E1, E2, E3 e EE2 no esgoto bruto e $5,062 \pm 3,366$; $4,191 \pm 3,527$; $7,743 \pm 3,951$, $2,550 \pm 2,162$ de E1, E2, E3 e EE2 no efluente) e com frequência de detecção próxima a 100%. Ambos os parâmetros diferem da maioria dos resultados publicados em trabalhos semelhantes que apresentaram concentrações na faixa de ng L^{-1} .

As características químicas do esgoto avaliado (elevada concentração de NTK e menores concentrações de matéria orgânica, DBO5 e DQO, e de fósforo em comparação ao esgoto doméstico) e as particularidades do Campus (sem preparo de refeições, sem moradias e com geração per capita de esgoto reduzida, $47 \text{ L pessoa}^{-1} \text{ dia}^{-1}$) associadas à condição climática nos períodos de coleta (clima seco) podem indicar uma maior participação da urina no esgoto e, consequentemente, justificar as elevadas concentrações dos hormônios estrogênicos determinadas neste trabalho, visto que os hormônios estrogênicos são excretados principalmente pela urina.

As concentrações dos hormônios estrogênicos no efluente, após o tratamento biológico, também foram superiores às encontradas na literatura pesquisada. Isto pode ter acontecido devido às elevadas concentrações de entrada (no esgoto bruto), mas também podem estar associadas à baixa eficiência de remoção dos hormônios. Em sistemas de lodos ativados, as melhores eficiências de remoção dos hormônios estrogênicos têm sido relacionadas ao prolongado TDH, elevada idade do lodo, baixa carga orgânica e caráter desnitrificante do tratamento. Porém, apenas a baixa carga orgânica foi atingida neste trabalho, a remoção de nitrogênio foi insatisfatória e inconstante e a idade do lodo não pode ser medida.

Ademais, os hormônios estrogênicos são excretados pelo corpo humano conjugados a grupamentos sulfatos e glicuronídeos. Grande parte dos grupamentos glicuronídeos pode ser removida pela ação das bactérias do trato intestinal presentes no esgoto demandando tempo de contato e de reação, já os grupamentos sulfatos e o glicuronídeos restante podem ser removidos pelos micro-organismos do lodo ativado durante o tratamento. Visto que a ETE estudada é interna ao Campus, o esgoto é tratado próximo aos pontos de geração, assim o tempo de trânsito pode não ter sido suficiente para a remoção dos grupamentos conjugados antes do tratamento. Desta maneira, os hormônios conjugados não foram quantificados no esgoto bruto, mas passaram a ser quantificados no efluente se a desconjugação ocorreu durante o tratamento por

lodos ativados, mascarando a remoção dos hormônios livres, que foram os quantificados neste trabalho.

Recomenda-se que novos estudos sejam realizados no qual se determine também as concentrações dos hormônios estrogênicos conjugados para que possa ser aferido o impacto da desconjugação durante o tratamento.

Ademais, a redução nas concentrações dos hormônios no efluente pode ser melhorada com implantação de condições necessárias para a remoção biológica de nitrogênio, como a adoção de acompanhamento da idade de lodo e o controle da aeração por ORP.

Deve ser ressaltado que a ETE em estudo, da mesma maneira que outras ETEs com processo de tratamento convencionais, foi projetada e posteriormente adaptada para reduzir a carga de poluentes orgânicos e não visava especificamente a remoção de contaminantes emergentes presentes no esgoto sanitário, como os hormônios estrogênicos. Assim, qualquer remoção que possa ocorrer desses compostos é eventual e não específica ao processo de tratamento convencional. Os dados determinados nesse estudo mostram a necessidade de se rever o modelo de tratamento de esgoto em uso no campus, com vistas de se estabelecer um novo paradigma para lançamento de seus efluentes na bacia do Rio Paraíba do Sul.

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Combined use of O_3/H_2O_2 and O_3/Mn^{2+} in flotation of dairy wastewater

ARTICLES doi:10.4136/ambi-agua.2078

Received: 27 Jan. 2017; Accepted: 21 Jan. 2018

Marta Cristina Silva Carvalho¹; Alisson Carraro Borges^{1*}; Magno dos Santos Pereira¹; Fernanda Fernandes Heleno¹; Leda Rita D'Antonino Faroni¹; Luiza Cintra Campos²

¹Universidade Federal de Viçosa (UFV), Viçosa, MG, Brasil

Departamento de Engenharia Agrícola. E-mail: marta.carvalho@ufv.br, borges@ufv.br, magno.pereira@ufv.br, fernanda.heleno@ufv.br, lfaroni@ufv.br

²University College London (UCL), London, United Kingdom

Department of Civil, Environmental and Geomatic Engineering. E-mail: l.campos@ucl.ac.uk

*Corresponding author

ABSTRACT

This work investigated the degradation of organic matter present in synthetic dairy wastewater by the combination of ozonation (ozone (O_3)/hydrogen peroxide (H_2O_2)) and catalytic ozonation (ozone (O_3)/manganese (Mn^{2+})) associated with dispersed air flotation process. The effect of independent factors such as O_3 concentration, pH and H_2O_2 and Mn^{2+} concentration was evaluated. For the flotation/ O_3/H_2O_2 treatment, the significant variables ($p \leq 0.05$) were: O_3 concentration (linear and quadratic effect), H_2O_2 concentration linear and quadratic effect, pH values (linear and quadratic effect) and interaction O_3 concentration versus pH. For catalytic ozonation, it was observed that the significant variable was the linear effect of O_3 concentration. According to the desirability function, it was concluded that the optimal condition for the treatment of flotation/ O_3/H_2O_2 can be obtained in acidic solution using O_3 concentrations greater than 42.9 mg L^{-1} combined with higher concentrations of H_2O_2 to 1071.5 mg L^{-1} . On other hand, at pH values higher than 9.0, the addition of O_3 may be neglected when using higher concentrations than 1071.5 mg L^{-1} of H_2O_2 . For flotation/ozonation catalyzed by Mn^{2+} , it was observed that metal addition did not affect treatment, resulting in an optimum condition: 53.8 mg L^{-1} of O_3 and pH 3.6.

Keywords: advanced oxidation processes, catalytic ozonation, physico-chemical treatment.

Uso combinado de O_3/H_2O_2 e O_3/Mn^{2+} para flotação de águas residuárias de laticínio

RESUMO

Neste trabalho, estudou-se a degradação da matéria orgânica presente no efluente de laticínio sintético por ozonização combinada (ozônio (O_3)/peróxido de hidrogênio (H_2O_2)) e a ozonização catalítica (ozônio (O_3)/manganês (Mn^{2+})) associada com o processo de flotação por ar disperso para obter o ponto ótimo de tratamento. Foi avaliado o efeito dos fatores independentes concentração de O_3 , pH e concentração de H_2O_2 e Mn^{2+} . Para o tratamento flotação/ O_3/H_2O_2 os parâmetros significativos ($p \leq 0,05$) do modelo foram: concentração de O_3 (efeito linear e quadrático), concentração de H_2O_2 (efeito linear e quadrático), valores de pH

(linear e quadrático) e interação concentração de O_3 versus pH. Para a ozonização catalítica, observou-se que houve diferença significativa no tratamento apenas para o efeito linear da concentração de O_3 . De acordo com a função de desejabilidade, concluiu-se que a condição ótima para o tratamento de flotação/ O_3/H_2O_2 pode ser obtida em meio ácido utilizando concentrações de O_3 superiores a $42,9 \text{ mg L}^{-1}$ associada com concentrações de H_2O_2 mais elevadas que $1071,5 \text{ mg L}^{-1}$. No entanto, em valores de pH maiores do que 9,0, a utilização de O_3 pode ser negligenciada quando se usam concentrações mais elevadas do que $1071,5 \text{ mg L}^{-1}$ de H_2O_2 . Observou-se também que a flotação/ozonização catalisada pela adição do metal Mn^{2+} não afetou o tratamento, obtendo-se como condição ótima de $53,8 \text{ mg L}^{-1} O_3$ e pH 3,6.

Palavras-chave: ozonização catalítica, processos oxidativos avançados, tratamento físico-químico.

1. INTRODUCTION

Brazil is a major milk-producer, ranking fourth in the world, with the production of 35 billion liters in 2013 (FAO, 2013). The generation of wastewater from dairy products and derivatives is growing, so the management, recycling and treatment of these effluents have become a growing concern in Brazil and worldwide (Leal et al., 2006).

In the dairy industry, according to Matos et al. (2011), a relationship of about 1 to 5 can be observed between volumes of wastewater and milk processed, depending on the final product and the technological level of the industry. The polluting organic load that these effluents present is high, and in the case of inappropriate treatment or disposal, major environmental impacts can be seen in the areas near this type of industry.

Because biological treatment is economically viable, it is one of the most-used options for the removal of organic matter in dairy effluent. However, the so-called biological reactors may present some practical limitations. Biodegradation depends on a stable and diverse microbial population, the interaction between the various microorganisms present in the treatment system, pH, and temperature, among other factors, which are not always easily controlled. Furthermore, the long treatment time and space required for the implementation of the treatment plants may hamper the application of biological processes. Another common problem of this treatment is the oscillation of organic load in the effluents of dairy products, which may affect the balance of the microbial community present in the reactor and compromise the efficiency of biological processes (Villa et al., 2007).

Among physico-chemical treatments, the flotation used as primary treatment can be highlighted, where the separation of particles present in the effluent occurs through their adhesion to gas bubbles. The bubble-particle aggregate rises in the aqueous phase, thereby allowing separation of the particle.

To complement the treatment of dairy effluent, advanced oxidation processes (AOPs) have been a widely studied alternative because they are less selective, have an electrophilic property, and the kinetics of the reaction can be controlled. These processes generate hydroxyl radicals ($\bullet OH$) that are capable of oxidizing a wide variety of organic compounds into carbon dioxide (CO_2), water (H_2O), and inorganic ions (Oliveira and Leão, 2009). The hydroxyl radicals originate from combinations between oxidants, such as ozone (O_3), hydrogen peroxide (H_2O_2), and ultraviolet (UV) irradiation, with catalysts, such as metal ions or semiconductors (Glaze et al. 1987 apud Melo et al., 2009).

Among the AOPs, ozone gas has been widely used in water and wastewater treatment. This gas is able to react with a wide range of organic compounds, mainly due to its high oxidative potential ($E_0 = 2.07 \text{ V}$), greater than $KMnO_4$ and Cl_2 . Under certain conditions, ozone leads to the formation of hydroxyl radicals ($\bullet OH$), the oxidation potential of which is even higher

($E_0 = 2.80$ V) and tends to be more effective in treating certain recalcitrant compounds (Mahmoud and Freire, 2007).

The stability of the ozone depends on several factors, especially pH, because hydroxyl ions initiate the ozone decomposition process (Von Gunten, 2003). In an acidic environment, ozone will react with compounds that have specific functional groups, such as electrophilic, nucleophilic, or dipole addition (direct reaction with O₃). However, at high pH (basic medium), ozone decomposes into radicals •OH, which react with organic compounds unselectively.

H₂O₂ combined with ozone gas is widely used as a good source of radicals •OH, as it is easily found, highly adaptable to existing ozonation equipment, and has the lowest cost of AOP systems based on the radical •OH.

Another way to increase the ozonation efficiency is with the use of catalysts. Several studies have reported the use of several metal salts in ozonation of effluents. Hewes and Davinson (1972) showed that the effluent ozonation in the presence of Fe²⁺, Mn²⁺, Ni²⁺, and Co²⁺ resulted in an increase of total organic carbon removal efficiency compared to conventional ozonation process (without addition of a catalyst).

This study aimed to determine the optimal conditions for the degradation of organic matter present in synthetic dairy effluent, using flotation concomitantly with AOPs.

2. MATERIALS AND METHODS

Synthetic dairy wastewater (SDW) was prepared by adding 10.0 mL of Type A supplemented whole milk to distilled water to make 1.0 L of solution with COD concentrations close to 2000 mg L⁻¹ (Brião and Tavares, 2007). After preparing the synthetic solution, the alkalinity of the sample was measured, having an average value of 75.56 mg L⁻¹ CaCO₃.

The ozone gas was obtained using an ozone generator (Model O&G 10.0 MRI, Ozone & Life, São José dos Campos, Brazil). Oxygen used as feedstock was obtained from a hub installed on the ozone generator body. The concentration of ozone gas in the air that was injected in the bottle washer during treatment was quantified as recommended by the International Ozone Association, using the iodometric method by indirect titration (APHA et al., 2012).

The ozonation was performed at a flow rate of 1.0 L min⁻¹ in a bottle washer with a capacity of 1.0 L. A porous diffuser was placed inside the bottle close to the bottom from which the gas was introduced. Based on preliminary analysis, the ozonation period was set at 180 min.

The experimental design used was the central composite rotational design (CCRD), because this method allows for easier, more economical, and faster analysis of several variables (factors) with a variety of levels. The CCRD is an evolution of factorial experiments with 2 levels and n factors composed of three parts: Vertex points (complete or fractional factorial), axial points ($\alpha = n^{1/2}$; allows tests of significance for quadratic or cubic curvature effects) and central points (executed with replicas allowing the estimation of the pure error and a lack of fit test of the model).

The resident concentration divided by the influent concentration or relative concentration of COD, denoted by COD (C/C_0), was used as the dependent variable, applied at the startup of the batch, determined by the colorimetric method (APHA et al., 2012). The “C” represents the COD of the samples measured at the end of the treatment and “C₀” the COD of the samples at the start. The C/C_0 parameter was chosen for its capacity to represent treatment efficiency and due to its mathematical advantages during statistical analysis. COD removal (%) = $(1 - C/C_0) \times 100$.

The independent variables were the concentration of ozone gas (O₃), the concentration of catalyst (i.e. H₂O₂ or Mn²⁺) and the initial pH of SDW.

Tables 1 and 2 present the level values used in the CCRD for the ozonation experiments with H_2O_2 and Mn^{2+} , respectively.

Table 1. Values used in the CCRD to three factors, using H_2O_2 as an aide to the ozonation.

Variables	Units	Levels				
		$-\alpha = -1,68$	-1	0	+1	$\alpha = +1.68$
O_3 (X_1)	mg L^{-1}	0.0	10.9	26.9	42.9	53.8
H_2O_2 (X_2)	mg L^{-1}	0.0	272.1	673.5	1071.5	1343.6
pH (X_3)	-	3.6	5.0	7.0	9.0	10.4

Table 2. Values used in the CCRD to three factors, using Mn^{2+} as catalyst in the ozonation.

Variables	Units	Levels				
		$-\alpha = -1,68$	-1	0	+1	$\alpha = +1.68$
O_3 (X_1)	mg L^{-1}	0.0	10.9	26.9	42.9	53.8
Mn^{2+} (X_2)	mg L^{-1}	0.0	0.008	0.020	0.032	0.040
pH (X_3)	-	3.6	5.0	7.0	9.0	10.4

The variation ranges between the lower limit and the top of each independent variable were assumed based on literature (Assalin et al., 2006; Mahmoud and Freire, 2007) and preliminary tests.

The hydrogen peroxide solutions were prepared using H_2O_2 solution with 30% w/w, $[\text{H}_2\text{O}_2] = 9.007 \text{ mol L}^{-1}$ and density of 1.1 g mL^{-1} . The manganese source was the monohydrate manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$).

Interference caused by H_2O_2 in COD analysis was eliminated by determining its concentration in the sample by the iodometric method and subsequent determination of its COD according to Equation 1 (Oliveira and Leão, 2009):

$$\text{COD}_{\text{peroxide}} = -4.06 \times 10^{-5} [\text{H}_2\text{O}_2]^2 + 0.4706 [\text{H}_2\text{O}_2] \quad (1)$$

To calculate the main effects of the factor, their interactions on the response variable (C/C_0), as well as to obtain data relating to the analysis of variance (ANOVA), Statistica 10 (StatSoft, Inc., Tulsa, USA) and Minitab 17 (Minitab Inc., State College, PA, USA) software were used.

3. RESULTS AND DISCUSSION

Tables 3 and 4 present, for H_2O_2 and Mn^{2+} respectively, the values of COD removal and the C/C_0 obtained for each trial suggested by the CCRD design.

It was noticed that among all the tests, the best results were in trial number 13 (Tables 3 and 4), where the ozone central points and the catalyst/auxiliary $-\alpha$ were used with $-\alpha$ pH of 3.6, obtaining close values for the relative concentration of COD (C/C_0) independent of the catalyst/auxiliary used.

Table 3. Array of values to the concentrations of ozone, H₂O₂ and the pH of the samples in the delineation of the CCRD.

Trial	O ₃	H ₂ O ₂	pH	COD Removal (%)	(C/C ₀)
1	10.9	272.1	5.0	62.5	0.37
2	10.9	272.1	9.0	15.2	0.85
3	10.9	1071.5	5.0	65.3	0.35
4	10.9	1071.5	9.0	24.9	0.75
5	42.9	272.1	5.0	59.6	0.40
6	42.9	272.1	9.0	43.3	0.57
7	42.9	1071.5	5.0	62.7	0.37
8	42.9	1071.5	9.0	64.5	0.35
9	0.0	673.5	7.0	6.5	0.93
10	53.8	673.5	7.0	43.9	0.56
11	26.9	0.0	7.0	15.5	0.84
12	26.9	1343.6	7.0	50.5	0.49
13	26.9	673.5	3.6	74.4	0.26
14	26.9	673.5	10.4	23.7	0.76
15	26.9	673.5	7.0	12.4	0.88
16	26.9	673.5	7.0	17.1	0.83
17	26.9	673.5	7.0	12.1	0.88
18	26.9	673.5	7.0	14.6	0.85
19	26.9	673.5	7.0	7.6	0.92
20	26.9	673.5	7.0	13.3	0.87

Table 4. Array of values to the concentrations of ozone, Mn²⁺ and the pH of the samples in the delineation of the CCRD.

Trial	O ₃	H ₂ O ₂	pH	COD Removal (%)	(C/C ₀)
1	10.9	0.008	5.0	12.9	0.89
2	10.9	0.008	9.0	14.7	0.87
3	10.9	0.032	5.0	4.3	0.98
4	10.9	0.032	9.0	17.9	0.84
5	42.9	0.008	5.0	28.7	0.73
6	42.9	0.008	9.0	39.9	0.61
7	42.9	0.032	5.0	45.9	0.55
8	42.9	0.032	9.0	43.4	0.58
9	0.0	0.020	7.0	0.7	1.00
10	53.8	0.020	7.0	49.0	0.52
11	26.9	0.000	7.0	26.5	0.75
12	26.9	0.040	7.0	26.3	0.75
13	26.9	0.020	3.6	73.9	0.27
14	26.9	0.020	10.4	17.9	0.84
15	26.9	0.020	7.0	33.7	0.68
16	26.9	0.020	7.0	30.3	0.71
17	26.9	0.020	7.0	26.5	0.75
18	26.9	0.020	7.0	30.3	0.71
19	26.9	0.020	7.0	30.1	0.71
20	26.9	0.020	7.0	27.4	0.74

3.1. COD degradation of the synthetic dairy wastewater by the flotation process/ozonation combined with H₂O₂

Figure 1 shows the Pareto chart for the regression performed, which presents the statistical significance of each term of the equation for α levels equal to 5 to 10%.

Figure 1. Pareto chart of the regression performed for COD degradation in the synthetic dairy effluent, using the flotation/ozonation combined with H₂O₂. “L” is the linear coefficient part of the model and “S” is the square coefficient part of the model.

As can be seen in Figure 1, just the linear model coefficients for the interaction of H₂O₂ with ozone and pH was not significant for an α of 5% or 10%, indicating that in the treatment process the three factors had an significant effect and there was a significant interaction between ozone and pH at the range of values tested. The removal of the least-significant term (peroxide-ozone interaction) did not cause changes in the model-fitting. Thus, it was decided to withdraw these two terms from the modeling (peroxide-ozone interaction and interaction peroxide - pH).

Table 5 shows the coefficients values used to evaluate the quality of the model fits to the data, also considering the raw data and transformed data (Box-Cox transformation considering $\lambda = 0.5$). The two regressions were significant at the 5% level.

Table 5. Model-fitting results.

Model/Statistic	Model with natural response	Model with transformed response
R ² (%)	92.14	92.58
R ² adjusted (%)	87.55	88.25
F _{calc} /F _{crit} (regression)	5.15	7.46
F _{calc} /F _{crit} (lack of fit)	2.94	3.41
S (standard error of regression)	0.0836	0.0533

Based on the values obtained (Table 5), it was decided to use the transformed response model. This choice was based on slightly better adjustment values and the fact that the response $(C/C_0)^{0.5}$ does not allow for obtaining negative values of the dependent variable, which is physically more suited to the present study.

Based on data presented in Table 5, the model for the COD removal from the dairy effluent using flotation and combined ozonation O₃/H₂O₂ was significant, with a 95% confidence level, because for the regression the $F_{\text{calculated}}$ is greater than that of F_{critical} . However, the lack of fit was also significant ($F_{\text{calculated}}/F_{\text{critical}} > 1$), although ideally $F_{\text{calculated}}$ should be a smaller value than the F_{critical} , i.e. not significant. However, since the averages of the means were very close and the pure error was very small (0.0003), the model was considered valid for predictive purposes (Barros Neto et al., 2007). The mean square experimental error was very small; thus, the significance tests for the lack of fit may be deemed irrelevant (Waszczyński and Nelsen, 1996).

The regression coefficient (R^2) indicates that 92.58% of the variation observed in the data could be explained by the model (Table 5). According to Barros Neto et al. (2007), R^2 measures the proportion of the total variation of the response that is explained by the model. Thus, the closer to 1 the R^2 value is, the smaller the error and better the model will be. According to these authors, models with $R^2 < 0.60$ should be used only as trend indicators, never for predictive purposes.

With the obtained results, it was possible to determine the regression coefficients and to present the model with variables not coded. The empirical mathematical model, uncoded and in 2nd order, was found to represent the root of the relative concentration of COD in terms of ozone concentrations, H₂O₂, and solution pH with their respective statistical coefficients (Equation 2).

$$(C/C_0)^{0.5} = -1.11900 + 0.01901 [\text{O}_3] + 0.00040 [\text{H}_2\text{O}_2] + 0.45270 [\text{pH}] - 0.00017 [\text{O}_3]^2 - 1.2 \times 10^{-5} [\text{H}_2\text{O}_2]^2 - 0.02535 [\text{pH}]^2 - 0.00188 [\text{O}_3] [\text{pH}] \quad (2)$$

Maintaining the pH in the fixed central point (pH 7) and varying the concentrations of ozone and H₂O₂, the contour plot for the dependent variable (i.e. COD (C/C_0)) is shown in Figure 2 (A). Figure 2 (B) displays the contour plot, keeping the concentration of H₂O₂ fixed at the midpoint (i.e. 673.5 mg L⁻¹) and varying the ozone concentration and the pH of the effluent.

According to Figure 2 (A), in a neutral solution (pH 7) the relative concentration of COD (C/C_0) decreased with increasing concentrations of both ozone and H₂O₂. This is consistent with the positive values of the regression coefficients obtained for the O₃ and H₂O₂ (Equation 2).

Figure 2. Contour plot showing the effect of the concentrations of ozone and H₂O₂ on the relative concentration of COD (C/C_0) with central point fixed at pH 7. (A). Contour plot showing the effect of ozone concentration and pH on the relative concentration of COD (C/C_0), maintaining the fixed H₂O₂ concentration at the midpoint (i.e. 673.5 mg L⁻¹) (B).

A similar result was observed in the work of Cortez et al. (2010), when the increase of H_2O_2 concentration (200 - 400 mg L^{-1}) - led by the use of combined ozonation ($\text{O}_3/\text{H}_2\text{O}_2$) with 112 mg L^{-1} ozone, at pH 7 for 60 min to treat landfill leachate - increased the removal efficiency of COD by 16%.

By further analyzing the contour plot in Figure 2 (A), it can be seen that using an ozone concentration of 26.9 mg L^{-1} (midpoint) to treat the dairy synthetic effluent was more efficient at lower pH values, independent of the added H_2O_2 concentration. A similar result was observed by Torres-Sanchez et al. (2014) using the combination of ozone with Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) in acidic solution (pH 3) applied to synthetic dairy effluent. These authors observed a reduction of up to 30% of COD in the effluent after 25 min of treatment.

On the other hand, the treatment using ozone (26.9 mg L^{-1}) in a basic solution proved to be advantageous only for the removal of COD at high concentrations of H_2O_2 and high pH levels (pH > 9), presenting a quadratic behavior, which indicates a "valley bottom" for H_2O_2 values close to 500 mg L^{-1} .

It can be seen from Figure 2 (B) that flotation/ozonation combined with H_2O_2 was favored under acidic conditions (pH < 5), independent of the concentration of ozone applied. However, the treatment was effective only at high concentrations of ozone and higher pH. In alkaline solutions H_2O_2 becomes more unstable than in acidic solutions (Cavalcante, 2005). Furthermore, H_2O_2 standard electrode potential ranges from 1.78 V to 0.87 V when pH changes from 0 to 14, which makes the treatment of effluents with H_2O_2 most promising at low pH values.

It is noteworthy that the only interaction with significant effect was ozone and pH (Equation 2), presenting a coefficient of -0.002 (negative). Since ozone and pH concentrations are positive, it appears that the ozonation process is acting indirectly at high pH values and high concentrations of ozone (via hydroxyl radicals) (Balcioglu and Ötöker, 2003).

During the ozonation macro- or microbubbles are formed, so the process of flotation can also occur if the coagulation/flocculation characteristics of the wastewater favor the adhesion of the bubbles to the particles/flocs, producing the so-called Ozoflotation process (Edzwald and Harrhoff, 2012). During the ozoflotation process, part of the organic matter (i.e. suspended matter) is removed by flotation by a physical treatment and the other part of the organic matter (i.e. dissolved matter) is removed by the ozone oxidation in a chemical treatment.

For good coagulation, chemistry conditions, and higher flotation efficiencies, it is expected that the flocs formed have little or no electrical charge, so electrostatic forces are low or near zero (Edzwald, 2010). According to Quirk and Matusky (1971), casein is the major protein found in milk (about 80%) and has an average isoelectric point at pH 4.6, so at this pH casein is found at its point of lowest solubility due to the decrease of intermolecular repulsions.

Therefore, a possible explanation for the acidic solution to have produced the best results in the removal of COD from the synthetic dairy effluent is that it is due to the natural coagulation/flocculation of milk proteins in the dairy effluents in an acid medium that favored the flotation process and enhanced the global treatment efficiency (Puget et al., 2004).

3.2. Degradation of COD in the synthetic dairy wastewater by the flotation process/ozonation catalyzed by Mn^{2+}

The attempt to fit a full quadratic regression model was not successful due to the lower R^2 value of the model that was equal to 42.91% and significance was only observed for the linear term of the ozone concentration. Thus, it was decided to withdraw most of the terms, concurrent with the adoption of a changed response by Box-Cox transformation, considering $\lambda = 0.5$. In Figure 3, the Pareto chart corresponding to the regression performed is shown. It is emphasized that the terms related to variable pH were only considered significant at the 10% level.

Figure 3. Pareto chart corresponding to the transformed response (Box-Cox transformation considering $\lambda = 0.5$) for the degradation of COD in synthetic dairy effluent using the flotation/ozonation catalyzed by Mn²⁺.

Table 6 shows the results of the model fitting to the observed data.

Table 6. Model fitting results.

Model/Statistics	Model Transform Response
R ² (%)	61.08
R ² adjusted (%)	53.78
F _{calc} /F _{crit} (regression)	2.88
F _{calc} /F _{crit} (lack of fit)	9.17
S (standard error of regression)	0.0728

For the regression model, the $F_{\text{calculated}}$ divided by the F_{critical} , at 5% of probability, was higher than 1, so the model was significant. Despite the lack of adjustment showing significance ($F_{\text{calc}}/F_{\text{crit}} > 1$), the value obtained for the mean square of the pure error was very low (0.0002), so the model can be considered valid for predictive purposes.

The coefficient of determination obtained (Table 6) showed that only 61.08% of the observed data could be explained and the model could be used for predictive purposes. (Barros Neto et al., 2007).

One clearly sees that this fitting model, even after transformation of the response variable, was inferior to the experiment used for flotation/ozonation combined with H₂O₂. Another indication of the low-response modeling was the $F_{\text{calc}}/F_{\text{crit}}$ of the regression, equal to 2.88 (Table 6). According to Barros Neto et al. (2007), good model fits have $F_{\text{calc}}/F_{\text{crit}}$ greater than or equal to 4.

Even considering the low value of R² obtained, it was possible to determine the regression coefficients and present the model with variables not coded. The empirical mathematical model was found to represent the root of the relative concentration of COD in terms of ozone concentrations, H₂O₂, and solution pH with their respective statistical coefficients, as shown in Equation 3.

$$(C/C_0)^{0.5} = 0.409 - 0.005 [O_3] + 0.152 [pH] - 0.009 [pH]^2 \quad (3)$$

As seen in Figure 3 and Equation 3, even after the Box-Cox transformation, the concentration of Mn^{2+} added to catalyze the treatment of flotation/ozonation was not significant for the removal of COD. This contradicts the work of Assalin et al. (2006), and Mahmoud and Freire (2007) who found that the addition of Mn^{2+} in concentrations greater than 0.5 mg L^{-1} as a catalyst for ozonation effluent was more efficient in removing total organic carbon (TOC) compared to conventional ozonation processes.

Assalin et al. (2006) also compared the TOC degradation efficiency by conventional ozonation process and catalyzed by Mn^{2+} at a concentration of 1.0 mg L^{-1} in an acidic solution (pH 3). The catalytic ozonation enhanced the removal of the organic load increasing from 4% to 63% efficiency in only seven minutes of ozonation. Also the addition of metals to the ozonation process increases the formation of hydroxyl radicals according to the complexation mechanism proposed by Pines and Reckhow (2002), acting as inhibitors of certain anions (carbonates and bicarbonates) that are capable of interfering with the oxidizing ability of the hydroxyl radicals.

One explanation for the insignificant effect of the catalyst during the ozonation process may be the low concentration of Mn^{2+} used in this experiment ($\leq 0.040 \text{ mg L}^{-1}$). According to Xiao et al. (2012), Mn^{2+} concentrations greater than 0.05 mg L^{-1} were effective in aiding ozone degradation of compounds that are difficult to degrade. On the other hand, the same authors found that concentrations greater than 0.1 mg L^{-1} showed no significant increase in efficiency.

Figure 4 shows the variation of the relative concentrations (C/C_0) of COD with pH and concentration of ozone gas.

Figure 4. Contour plot showing the effect of ozone concentration and pH on the relative concentration of COD (C/C_0).

It is observed in Figure 4 that the increased ozone concentration positively influenced the removal of organic matter of the SDW, indicating the action of the ozone as an oxidant (chemical treatment) in the ozoflotation process.

Independent of the concentration of Mn^{2+} used in the experiment, it was observed that the best efficiencies for degradation of COD in the wastewater were achieved under acidic

conditions (pH < 4), indicating a possible better oxidation of the organic matter of the SDW through direct action of the ozone.

Similarly to the combined treatment O₃/H₂O₂ which also showed better results under acidic conditions, part of this result can be explained also by the removal of organic matter due to the casein's clotting ability in acidic media (Puget et al., 2004). Thus, part of the COD of the SDW was removed by flotation in the washer bottle.

3.3. Optimization of the flotation/ozonation process combined with H₂O₂ and catalyzed by Mn²⁺ according to their respective independent variables using the function desirability

The estimate of the optimal conditions for the removal of COD in the SDW was based on the proposed statistical model and with the aid of the simultaneous optimization technique called "desirability function".

The desirability profiles were obtained from the Statistica 10 program through the function called "profiles for predicted values and desirability". This function indicates, based on the statistical analyses, which combination of values from the tested parameters gives the best response for the treatment being studied.

Figures 5 and 6 show the diagrams of the desirability function for describing the optimal conditions for the relative concentration of COD (C/C₀) after flotation/ozonation combined with H₂O₂ and flotation/ozonation catalyzed by Mn²⁺, respectively, within the value ranges stated in the experiments.

Figure 5. Profiles for the predicted values and desirability for relative concentrations of COD (C/C₀) obtained from the flotation process / ozonation combined with H₂O₂.

Figure 6. Profiles for desirability and predicted values for COD relative concentration (C/C_0) obtained from the flotation/ozonation process catalyzed by Mn^{2+} .

Considering the confidence limit for the optimum value, the most desirable values for the three factors of interest are shown in Figure 6. The profile located on the right shows the range of the desirability response ($0 < D < 1$). The larger the “D” value, the more convenient the system response is; i.e., the maximum value of D is the optimal condition of the system.

For the second group, the dashed blue line presents optimum values where trends are revealed only by the factors (Figures 5 and 6). The vertical dotted lines present in the graphic corresponding to the optimum values of the parameters studied.

The concentration of ozone (Figure 5) required to achieve the ideal desirability response ($D = 1.0$) should be greater than 42.9 mg L^{-1} with H_2O_2 concentration exceeding 1071.5 mg L^{-1} for a high pH values of the synthetic dairy effluent ($pH > 9.0$).

For flotation/ozonation catalyzed by Mn^{2+} , the desirability graph (Figure 6) suggests optimum values using $53.8 \text{ mg L}^{-1} O_3$ with any concentration of Mn^{2+} (0 to 0.04 mg L^{-1}) at pH 3.6 to give better removal efficiency of COD ($D = 0.6876$).

Tables 7 and 8 were obtained making use of the desirability function, where possible solutions are presented based on optimal points found for processes of flotation/ozonation combined with H_2O_2 and catalyzed by Mn^{2+} , respectively.

Table 7. Examples of independent variables values that resulted in a great desirability for the process of flotation/ozonation combined with H_2O_2 .

Solution	O_3 - mg L^{-1}	H_2O_2 - mg L^{-1}	pH	Desirability - D
1	6.4	1343.6	3.6	1.00
2	0.5	1326.4	3.8	0.99
3	53.8	1343.6	10.4	0.98

Table 8. Example of independent variable values that resulted in an ideal desirability for the flotation process/ozonation catalyzed by Mn²⁺.

Solution	O ₃ - mg L ⁻¹	pH	Desirability - D
1	53.8	3.6	0.69

It can be seen in Table 7 that there was no need for the addition of ozone in strongly acidic medium (Solutions 1 and 2). However, the treatment should consist of flotation combined with high ozone concentration to achieve COD removal desirable in a basic medium (Solution 3).

In the process of flotation/ozonation catalyzed by Mn²⁺ (Table 8), manganese had no significant effect on the removal of the COD of the effluent, confirming the results above. Therefore, the desirability function presents a solution for obtaining a maximum desirability for the case where the optimum point would be at high ozone concentrations and acidic conditions. Thus, it is suggested that further experiments be conducted to evaluate the optimal conditions of treatment to the operational and economic feasibility of the process.

4. CONCLUSIONS

For the process of flotation/ozonation combined with H₂O₂, the optimal treatment point was found to be for high concentrations of O₃ (more than 42.9 mg L⁻¹) and H₂O₂ (greater than 1071.5 mg L⁻¹) in acidic solutions. However, in basic solutions (pH > 5.0) the addition of ozone gas can be neglected.

In the process of flotation/ozonation catalyzed by Mn²⁺, the addition of metal Mn²⁺ was not efficient, so the maximum removal efficiency of COD was obtained using concentrations of O₃ equal to 53.8 mg L⁻¹ in an acidic solution (pH 3.6), independent of the concentration of Mn²⁺ used.

In general, the best COD removal efficiencies were obtained by the process of flotation/ozonation combined with H₂O₂ compared to the process of flotation/ozonation catalyzed by Mn²⁺ for the synthetic dairy effluent. An acidic environment was more efficient for both processes (O₃/H₂O₂ and O₃/Mn²⁺), due to the organic load removal of the synthetic effluent, by the precipitation of milk casein which was subsequently removed by flotation in the bottle gas scrubber.

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Assessment of a subtropical riparian forest focusing on botanical, meteorological, ecological characterization and chemical analysis of rainwater

ARTICLES doi:10.4136/ambi-agua.2140

Received: 01 Jun. 2017; Accepted: 05 Jan. 2018

**Vanessa Graeff; Ivi Galetto Mottin; Ledyane Rocha-Uriartt;
Daniela Montanari Migliavacca Osório*; Jairo Lizandro Schmitt**

Universidade FEEVALE (FEEVALE), Novo Hamburgo, RS, Brasil

Programa de Pós-Graduação em Qualidade Ambiental (PPGQA)

E-mail: graeffvanessa@hotmail.com, ivi_mottin@yahoo.com.br, ledyane@gmail.com,
danielaosorio@feevale.br, jairols@feevale.br

*Corresponding author

ABSTRACT

Riparian forests are heterogeneous environments, in which epiphytes find ideal conditions to develop. These plants absorb the necessary nutrients for survival from the atmosphere, and their occurrence and distribution can be influenced by the quality and quantity of precipitation. The objective of this research was to perform an integrated analysis of botanical, meteorological and chemical precipitation parameters so as to compare them in fragments of the riparian forest in the lower (São Leopoldo-SL) and upper (Caraá-CA) stretches of the Rio dos Sinos Hydrographic Basin (RSHB), RS, Brazil. Rainwater was chemically analyzed, the community structure of epiphytic ferns was surveyed and the ecological characterization was evaluated through the Rapid Habitat Assessment Protocol (RHAP). The results showed that the chemical composition of rainwater is influenced by the environment of each area. In the upper stretch (CA), for instance, the main contribution is that of marine ions, while in the lower stretch (SL), the most impacting aspects are urbanization and industrialization. Similarly, the results depict a reduction of richness and a simplification of the community structure of epiphytic ferns and their environmental quality according to the RHAP categories, towards the base level of the RSHB. The integrated analysis, in which different methods were applied, proved to be an efficient tool to evaluate environmental quality. This analysis considers that a greater number of biotic and abiotic variables may be applied in different scenarios.

Keywords: ecological characterization, environmental analysis, epiphytic ferns, rainwater.

Análise integrada de mata ciliar subtropical focando parâmetros botânicos, meteorológicos e químicos da precipitação

RESUMO

Matas ciliares são ambientes heterogêneos, no qual, epífitos encontram condições ideais para se desenvolverem. Essas plantas, retiram da atmosfera os nutrientes necessários à sobrevivência, podendo ter sua ocorrência e distribuição influenciada pela qualidade e quantidade das precipitações. O objetivo foi realizar uma análise integrada de parâmetros

botânicos, meteorológicos e químicos da precipitação, a fim de compará-los em fragmentos de mata ciliar, nos trechos inferior (São Leopoldo-SL) e superior (Caraá-CA) da Bacia Hidrográfica do Rio dos Sinos (BHRS), RS Brasil. Para tal, foram realizadas análises químicas da água de chuva, analisada a estrutura comunitária das samambaias epifíticas e, avaliada a caracterização ecológica, através do Protocolo de Avaliação Rápida de Hábitats (PARH). Os resultados demonstraram que a composição química da água de chuva é influenciada pelo entorno de cada local estudado, sendo que do terço superior (CA), a maior contribuição é de íons de origem marinha, enquanto que, no trecho inferior (SL), a mesma é oriunda da urbanização e industrialização. Da mesma forma, ficou evidenciada a redução da riqueza e simplificação da estrutura comunitária de samambaias epifíticas e de sua qualidade ambiental de acordo com as categorias do PARH, em direção à foz da BHRS. A análise integrada aplicando diferentes métodos foi uma ferramenta eficiente para avaliar a sua qualidade ambiental, pois permite integrar um maior número de variáveis bióticas e abióticas, podendo ser aplicada em diferentes cenários.

Palavras-chave: água de chuva, análise ambiental, caracterização ecológica, samambaias epifíticas.

1. INTRODUCTION

Riparian forests are formations found along waterways (Mueller, 1996), characterized by high-environmental heterogeneity due to the physical and biological interactions in these environments (Rodrigues and Nave, 2000). One of its main functions is to protect the lotic environment and local biodiversity (Gregory et al., 1992). Despite being extremely important and being protected by specific legislation (Brasil, 2012), these environments suffer from fragmentation and edge effects, which end up increasing erosion; consequently, losing a biologically active soil layer, suffering silting and flooding, and to an invaluable loss of biodiversity (Joly et al., 2000).

Rainfall is one of the main processes for the removal of pollutants and chemical compounds from the atmosphere. The natural process of wet deposition results from the combination of chemical compounds and particles, which are removed by droplets or cloud droplets incorporated during precipitation (Seinfeld and Pandis, 2006; Souza et al. 2006; Herrera et al., 2009; Migliavacca et al., 2012). Therefore, rainwater reflects characteristics of the content of soluble gases and the particles of the atmosphere itself (Xiao et al., 2013; Wu et al., 2016).

Epiphytism is a harmonic interaction between two species, in which the epiphyte uses the host plant only as a carrier, removing the nutrients that are necessary for survival (Benzing, 1990). Epiphytes are good indicators of the environmental quality and their monitoring allows researchers to evaluate the effects of forest disturbance, since epiphytic richness has an inverse relation to environmental degradation (Engwald et al., 2000; Barthlott et al., 2001; Rocha-Uriarte et al., 2015). Ferns, which add to 29% of the species, constitute the second group of vascular plants in terms of epiphytic diversity (Kress, 1986). Thus, they absorb humidity from the air (Benzing, 1990), and may have their occurrence and distribution influenced by the quality and quantity of precipitations.

The Rio dos Sinos Hydrographic Basin (RSHB) is located in the lower northeast of the state of Rio Grande do Sul, southern Brazil. It covers an area of 3,820 km², in which 32 municipalities are distributed, with a population of approximately 1,343.558 inhabitants. Of this total, 94% are residents of urban areas, while only 6% reside in rural areas (IBGE, 2015). Its main watercourse is Rio dos Sinos, with its source in the municipality of Caraá, which has rural surroundings and it is less impacted. Rio dos Sinos is divided into upper, middle and lower stretches, transcending an urban-industrial matrix at its mouth, near the Jacuí delta

(PROSINOS, 2014). Kieling-Rubio et al. (2015) and Rocha-Uriarte et al. (2016) surveyed the environmental scenario of this basin, integrating botanical, meteorological and air genotoxicity parameters, based on which they demonstrated the existence of a decreasing gradient of environmental quality from the source to the mouth of Rio dos Sinos.

The objectives of the present study were: I) to evaluate the chemical composition of rainwater in a fragment of riparian forest of the lower stretch of Rio dos Sinos – one of the most important and impacted rivers of Rio Grande do Sul, Brazil; II) to determine the richness, composition and community structure of the epiphytic ferns in the same area; III) to perform ecological characterization in the same environment and IV) to compare the data obtained in I, II and III with the results obtained in the upper stretch of the river.

2. MATERIALS AND METHODS

2.1. Study area

The present study was carried out in a riparian forest fragment, in the lower stretch of the Rio dos Sinos, Rio Grande do Sul, Brazil. The Imperatriz Leopoldina Park (29°45'651'' S 051°07'928'' O, alt. 26 m), where the study area is located, is a Permanent Preservation Area (PPA) of 174 hectares inserted in the municipality of São Leopoldo and is one of the last remnant areas of urban vegetation. The vegetation in the area is altered by anthropic action and irregular deposits of residues and, it is frequently inundated during periods of flood of Rio dos Sinos (São Leopoldo, 2016).

The lower stretch of the RSHB is considered a floodplain, with typical vegetation of plains. It presents smooth slopes, typical of lowland rivers, with the formation of meanders and zones of sedimentation. It is also the most anthropogenic stretch of the basin, with a great concentration of population and industries, and with frequent occurrence of erosion processes, deforestation, soil and water pollution (FEPAM, 2016).

The climate of the region is classified as Cfa, humid subtropical (C), with no dry season (f), and with average annual temperature of the hottest month exceeding 22°C (a), according to Köppen (Peel et al., 2007).

2.2. Rainwater

During the year (Sep/2013 to Aug/2014) rainwater was monitored in the study area and in the region of the source of the Rio dos Sinos. A rainwater collector was installed externally to the rainforest fragment of the Imperatriz Leopoldina Park, and the monthly precipitation data were obtained from meteorological bulletins provided by the automatic meteorological station - Cristo Rei Station (29°46'54.72'' S; 51°09'11.93'' O 33 m altitude). For comparison purposes, in the municipality of Carará, near the source of the Rio dos Sinos, a mobile weather station (Davis Vantage PRO 2 VP USB NS) and another rainwater collector (29°44'15.88'' S; 50°21'34.52'' O 375 m altitude) were installed.

Rainwater samples were collected every 15 days, according to the methodology proposed by Migliavacca et al. (2005a). The collectors were always open, both in rainy and dry periods, to sample the atmospheric components of wet (rainfall) and dry deposition (dispersed gases and suspended particles) (Campos et al., 1998). The collectors consisted of a 21.5 cm diameter polyethylene funnel, 2 m away from the ground and covered with nylon mesh to prevent the entry of leaves and insects. The funnel was coupled to a 5 L collection vial and affixed to a metal rod.

After collection, the samples were sent to the laboratory of the Analytical Center of Feevale University for the chemical analyzes. In the unfiltered samples, pH was checked by using a digital pHmeter (Digimed DM-20, precision ± 0.01) and conductivity was surveyed by using a conductivity meter (Quimis Q795M2, precision ± 0.01), both previously calibrated. For

alkalinity, the analysis was performed according to APHA (2012). Subsequently, two aliquots, approximately 100 mL, were filtered through a cellulose ester membrane (0.22 µm pore and 47 mm diameter). In order to determinate major ions, the samples were preserved with chloroform and for the determination of metals, preserved with Supra Pure HNO₃ (MERCK) up to pH <2. Subsequently, these samples were stored at 4°C, up to a maximum of 30 days, for chemical analysis.

The major ions were determined by ion chromatography (Dionex ICS 5000 with electrical conductivity detector). The Dionex IonPac™ AS9-HC and CS12A columns were used for analyzing the anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, Ca²⁺, Mg²⁺, K⁺ and NH₄⁺), respectively. The limits of detection were: 0.01 mg L⁻¹ for Cl⁻; 0.05 mg L⁻¹ for NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺ and Ca²⁺ and Mg²⁺.

The analysis of metals (Al, Pb, Cd, Cu, Cr, Fe, Mn) was performed by using the Atomic Flame Absorption Spectrometry method (SpectrAA 110, VARIAN). All of the calibration solutions were prepared by dilutions in ultrapure water of Titrisol (Merck) standards of each metal. Detection limits were 0.0005 µg L⁻¹ for Al; 0.12 µg L⁻¹ for Cd; 0.80 µg L⁻¹ for Pb; 0.10 µg L⁻¹ for Cu; 0.11 µg L⁻¹ for Cr; 5.7 µg L⁻¹ for Fe; 0.15 µg L⁻¹ for Ni and 5.8 µg L⁻¹ to Zn.

The data of the accumulated precipitation and chemical composition of rainwater were submitted to the Shapiro-Wilk normality test. The pH, Na⁺ and Ca²⁺ and accumulated precipitation met the normality assumption. The t-test was used for comparison purposes. Further data did not meet normality, being compared by the Mann-Whitney test. These analyzes were conducted using PAST software.

The Enrichment Factor (EF) can be used to estimate the main sources of chemical components present in rainwater (Song and Gao, 2009). In the present study, two EF were used to estimate anthropic, marine and terrestrial crust sources. The Enrichment Factor for marine origin (EF_m) (Equation 1) was used as the reference ion Na⁺ and the marine ratio (Xi/Na⁺) according to Akkoyunlu and Tayan (2003). For the Earth's Crust Enrichment Factor (EF_c) (Equation 2) Al and the ratio (Xi/Al) were used as the reference ion, according to Taylor and McLennan (1995). The EF were calculated according to the equations below, where X is the concentration of the reference ion and Xi is the concentration of the ions of interest:

$$EF_m = \frac{(X/Na^+)_{sample}}{(X/Na^+)_{marine}} \quad (1)$$

$$EF_c = \frac{(X/Al)_{sample}}{(X/Al)_{marine}} \quad (2)$$

EF was interpreted using a scale according to Poissant et al. (1994) in which EF from 1 to 10 indicate marine or terrestrial crust contribution, consequently a low EF; EF > 10 to 500 moderate enrichment and over 500, extreme enrichments.

2.3. Floristic inventory and community structure

Throughout the riparian vegetation, a continuous transect of 800 meters, parallel to the course of the river was traced. An arboreal individual was selected at every 20 m, totaling 40 sample units in the fragment. These were divided into five ecological zones based on height (1 base, 2 low shaft, 3 high shaft, 4 inner cup, and 5 external cup).

For the inventory of the epiphytic ferns, monthly visits were carried out for one year. Representative and fertile specimens were collected and herborized according to Windisch (1992). The classification of epiphytic ferns followed the system proposed by Schuettpelz et al. (2016) and the validity of scientific names was verified in the List of Species of the Brazilian

Flora (Prado and Sylvestre, 2016). Sample specimens were deposited in the *Herbarium Anchieta* (PACA), from the Anchietano Institute of Research (UNISINOS).

For the community structure, coverage notes (1, 3, 5, 7 and 10) were given for each species according to size and abundance in the area of occurrence (Kersten and Waechter 2011). The epiphytic importance value (IVs) was obtained from the arithmetic mean of the sum of the relative frequencies in the phorophytes, in the zones and the relative coverage.

The floristic composition and the community structure of the present study were compared to the inventory performed by Becker et al. (2014), in a riparian forest, in the source of the Rio dos Sinos, in the municipality of Caraá, upper stretch of the basin.

2.4. Rapid Habitat Assessment Protocol

The rapid habitat assessment protocol (RHAP) was applied in the study area. The protocol was adapted from the Environmental Protection Agency (USEPA, 1987), Barbour et al. (1999) and Callisto et al. (2002). Sixteen parameters were analyzed based on visual observations: 1. Type of occupation of the margins; 2. Erosion on the banks and silting of the river; 3. Anthropogenic alterations; 4. Vegetation cover on the river channel; 5. Water odor and sediment; 6. Water and sediment oils; 7. Water transparency; 8. Type of background (composition); 9. Type of bed (diversification); 10. Extension and frequency of rapids; 11. Type of substrate; 12. Sedimentary deposits; 13. Changes in the river channel; 14. Water flow characteristics; 15. Stability of the margins; 16. Extension of riparian forest. After applying the protocol, the sum of points of each parameter was performed, which were converted into the scale proposed by Callisto et al. (2002) in which the obtained values represent: from 0 to 40 points - impacted stretch; from 41 to 60 points - altered stretch; from 61 to 100 points - natural stretch.

The rapid habitat assessment protocol (RHAP) of the present study was compared to the study by Rocha-Uriartt et al. (2015), which was undertaken also along the riparian forest of Rio dos Sinos.

3. RESULTS AND DISCUSSION

3.1. Rainwater

The accumulated precipitation was 1842.2 mm e 2548.2 mm in São Leopoldo and in Caraá, respectively, and there was no significant difference during the evaluated period ($t=1.81$, $p>0.05$) (Table 1). However, Rocha-Uriartt et al. (2015) showed that, when the precipitation is monitored over a longer period, precipitation tends to be significantly higher in the Rio dos Sinos source region than in the lower stretch of the basin.

The cumulative monthly precipitation was equivalent in the month of Sep/2014 in the two areas (124.6 mm and 122.7 mm, respectively). The minimum precipitation in São Leopoldo occurred in March 2014 (95.5 mm) and Caraá in October 2013 (94.0 mm). During February 2014, the highest precipitation was recorded in São Leopoldo (253.3 mm), and in Caraá this occurred in June 2014 (420.4 mm) (Figure 1). Rocha-Uriartt et al. (2015) recorded, in Caraá, twice the maximum value of accumulated monthly precipitation in relation to the lower stretch (Caraá: 698.8 mm and Campo Bom: 370.3 mm).

Table 1. Average $\pm$ standard deviation of physical-chemical parameters and precipitation enrichment factor in Caraá and São Leopoldo.

Parameter	Unit	Caraá				São Leopoldo				p value	
		Min	Average ± SD	Max	EF	Min	Average ± SD	Max	EF		
											t-test
Precipitation	(mm)	94.00	2548.2 ± 97.36	420.40	--	95.50	1842.2 ± 56.20	253.5	--	1.81	0.08
pH		5.25	6.14 ± 0.48	6.77	--	5.29	6.24 ± 0.51	7.13	--	-0.50	0.62
Na ⁺	(µeq L ⁻¹)	2.83	43.76 ± 21.14	74.62	--	5.49	22.60 ± 18.46	72.28	--	2.45	0.02
Ca ²⁺	(µg L ⁻¹)	2.99	49.78 ± 26.77	100.55	32*	2.49	38.57 ± 36.50	117.68	47*	0.84	0.40
											Mann-Whitney
Conductivity	(µS cm ⁻¹)	6.41	19.23 ± 17.15	71.35	--	6.16	12.71 ± 7.52	33.15	--	42.0	0.14
N-NH ₄ ⁺	(µeq L ⁻¹)	4.44	30.44 ± 25.63	75.50	--	2.81	53.51 ± 66.90	166.96	--	23.0	0.85
N-NO ₃ ⁻	(µeq L ⁻¹)	0.69	11.80 ± 7.18	28.33	--	0.80	7.10 ± 11.50	33.51	--	34.0	0.06
Cl ⁻	(µeq L ⁻¹)	6.68	74.50 ± 49.34	177.09	2*	9.99	32.70 ± 28.15	91.93	2*	21.0	0.06
SO ₄ ²⁻	(µeq L ⁻¹)	6.26	45.84 ± 29.91	91.25	10*	3.63	20.58 ± 27.20	97.35	7*	24.0	0.03
K ⁺	(µeq L ⁻¹)	2.14	38.16 ± 34.54	135.66	56*	1.26	11.01 ± 11.04	36.55	24*	21.0	<0.01
Mg ²⁺	(µeq L ⁻¹)	44.90	60.18 ± 16.12	87.22	5*	2.05	9.03 ± 5.70	20.8	2*	0.0	<0.01
Pb	(µg L ⁻¹)	0.24	0.64 ± 0.49	2.12	1**	0.27	0.75± 0.70	1.76	1**	21.0	0.71
Al	(µg L ⁻¹)	2.04	12.30 ± 11.40	30.00	15**	1.12	12.76 ± 17.30	50.61	13**	50.0	0.75
Cd	(µg L ⁻¹)	0.002	0.04 ± 0.05	0.11	3229**	0.11	0.28 ± 0.24	0.45	14838**	2.0	0.09
Cu	(µg L ⁻¹)	0.05	1.13 ± 1.31	4.19	552**	0.10	1.64 ± 2.60	8.63	4899**	56.0	0.79
Cr Total	(µg L ⁻¹)	0.02	0.04 ± 0.01	0.06	17**	0.02	0.50 ± 0.50	1.09	82**	1.50	<0.01
Fe	(µg L ⁻¹)	0.02	12.95 ± 10.60	31.10	4**	3.63	24.54 ± 31.54	106.1	13**	57.0	0.60
Mn	(µg L ⁻¹)	0.06	6.16 ± 8.70	32.19	142**	0.007	2.16± 2.55	7.67	144**	38.0	0.09

Legend: EF: Enrichment Factor; * marine EF; ** crust EF; p value: significance level of 5%.

Figure 1. Monthly accumulated precipitation in a 12-month period at São Leopoldo and Caraá.

In the analysis of rainwater, the ions SO_4^{2-} , Na^+ , K^+ and Mg^{2+} showed significantly higher average concentrations in Caraá than the concentrations recorded in São Leopoldo. Only Cr T had a significantly higher concentration in São Leopoldo than in Caraá (Table 1). The values of conductivity, pH and other ions and metals did not present significant differences between the study sites.

Only in 18% of the events (4) the pH was lower than 5.6, which characterizes acid rain. Thus, for the studied sites, a slightly alkaline pH can be considered when compared to the rainfall reference value (Seinfeld and Pandis, 2006). The presence of alkaline compounds in rainwater, such as NH_3 and carbonates, aid in its neutralization process. Alkaline pH values were also recorded in the Guaíba Hydrographic Basin (Migliavacca et al., 2005b) in 16% of samples, and in the Metropolitan Region of Porto Alegre in 22% of samples (Migliavacca et al., 2012), both located near the Rio dos Sinos basin.

The marine enrichment factor (EF_m) for the analyzed elements followed the sequence $\text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^-$ in Caará and $\text{Ca}^{2+} > \text{K}^+ > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^-$ in São Leopoldo (Table 1). The presence of sulfate (SO_4^{2-}) in the atmosphere comes from natural sources such as the oxidation of dimethyl sulphide (CH_3SCH_3) emitted by ocean waters (Oliveira Junior et al., 2015). The EF_m for this chemical compounds was low, reinforcing the indication of the presence of marine ions in rainwater samples (Oliveira Junior et al., 2015), especially in Caraá, where it was significantly larger. This occurs, therefore, in the source of Rio dos Sinos, which is located approximately 32 km in a straight line from the Atlantic Ocean, confirming the influence of rainwater in these ions. In addition, Na^+ e Cl^- (EF_m=4 low), which are ions derived from marine aerosols (Migliavacca et al., 2005a; 2005b) were also detected in high concentrations in Caraá. In fact, Na^+ was significantly higher at the site.

Incorporation of Mg^{2+} e K^+ (low and moderate EF_m, respectively) comes from soil dust, by the dissolution of minerals, silicates or by arable soils that have traces of fertilizers. These can then release particulate material into the atmosphere during precipitation (Sardinha et al., 2013). These ions were significantly higher in Caraá, which is an essentially a rural municipality, and could have been incorporated to the rain of the region (Table 1).

The enrichment factor for Ca^{2+} enrichment may be related to the dissolution of CaCO_3 present in suspended soil dust, due to the intense vehicular traffic (Migliavacca et al., 2012), mainly in São Leopoldo, where a moderate EF_m (47) was verified. This result reinforces the possible anthropic origin for this ion in rainwater samples. The Imperatriz Leopoldina Park is

directly influenced by vehicular sources coming from the highway BR-116, Imperatriz Leopoldina and Mauá avenues, and from the downtown area of the municipality, corroborating with the high concentration of these metals in the rainwater (Blume et al., 2014; Costa et al., 2016).

The concentrations of NO_3^- and NO_2^- are derived from agricultural sources, from phosphate fertilizers, in which the NH_4^+ ion can be converted to NH_3 by chemical reactions in the atmosphere and potentiate the process of rainwater neutralization (Migliavacca et al., 2012). The presence of these ions comes from subsistence agriculture and monocultures of rice in the upper and lower stretches of the RSHB, respectively. (Roy et al., 2016).

The crust Enrichment Factor (EF_c) values (Table 1) ranged from 1 to 9034, with an EF_c of less than 10 for Pb and Fe (only in Caraá), indicating a low enrichment of rainwater samples from the terrestrial crust. The presence of Pb in rainwater does not come from the Earth's crust and its origin may be related to the enrichment of particles originating from anthropic sources, such as coal combustion, founding and vehicular emissions (Migliavacca, et al., 2012, Wu et al., 2016, Herrera et al., 2009). As to the other metals, $\text{Cr} > \text{Cu} > \text{Cd}$, a strong (Cr) to extreme (Cu and Cd) enrichment is observed.

The Cu and Cd elements are derived from vehicular emissions because they are present in practically all types of brake linings and are used for tire manufacturing (Manahan, 2005; Alleman et al., 2010; Moreira, 2010; Loyola et al., 2012; Alves et al., 2015). The extreme EF_c values for both study areas, especially in the lower stretch of the RSHB, show that the contribution of vehicular traffic dust is incorporated into precipitation, especially in São Leopoldo. This is confirmed by the higher vehicular fleet in this municipality (74.412 vehicles) than in Caraá (1.531 vehicles) (IBGE, 2017). Costa et al. (2016), who counted vehicles in an area near Imperatriz Leopoldina Park in São Leopoldo, indicated that the circulation of vehicles over an hour is from 1420 to 2349. In São Leopoldo, the significantly higher concentration of total chromium (Cr T) is related to the great industrialization of the lower stretch of the RSHB, derived from steel and metallurgical processes, and especially from leather tanning (Alves et al., 2015) in the studied region.

3.2. Floristic Inventory and community structure

Seven species were inventoried. They belong to five genera and two families, being Polypodiaceae with six species and Dryopteridaceae with only one species (Table 2). The analysis of distribution of epiphytic ferns along the RSHB shows a simplification in the richness and a change in the floristic composition of the area. Studies that applied the same methodology demonstrate the same results. For instance, Becker et al. (2014) recorded 30 species near the source of the Rio dos Sinos in Caraá, out of which only three were shared with the present study. Barbosa et al. (2015), in a study carried out in an urban park in the lower stretch of the basin, recorded only nine species of epiphytic ferns, four of which were shared with this study. This fact may be associated to vegetation and environment characteristics, since epiphytes, especially ferns, need a healthy environment to develop (Johansson, 1974) and Rocha-Uriarte et al. (2015) showed that there is a decreasing gradient in vegetation degradation from the source towards the mouth of the river in the RSHB.

The community structure of the present study did not present an equitable distribution, since the three most important species of the community (*Microgramma vacciniifolia*, *Pleopeltis pleopeltifolia* and *M. squamulosa*) contribute with more than 95% of IVs. The other species (four) registered less than 5% of IVs, but their contribution in the wealth was more than 57%. The opposite happens if we compare the community structure near the source of Rio dos Sinos, analyzed by Becker et al. (2014). In that case, the epiphytic fern community presented a more equitable distribution with about 76.66% more wealth.

The morphological characteristics, such as succulent rhizome, presence of trichomes and scales, are considered functional attributes (Rocha-Uriarte et al., 2016) and adaptive strategies of the epiphytic ferns against water stress (Benzing, 1989). In this study, these characteristics were also found in the inventoried specimens of Polypodiaceae, relating their occurrence to a drier environment, such as the lower stretch of the RSHB.

Polypodiaceae is also the most diverse within the epiphytic environment (Dubuisson et al., 2009), and is commonly found in urban and impacted environments (Sehnem, 1970; Becker et al., 2015). In these environments, plants have adaptive strategies that favor their development. For example, species of the genus *Microgramma* present a long-crawling rhizome that allows the occupation of extensive areas in the forophytes (Waechter 1998; Kersten and Silva, 2001). Specifically, *M. vacciniifolia* could have taken the highest IVs due to its aleopathic potential (Peres et al. 2009) and this species is cyanogenic, what can be reducing the predation (Santos et al., 2005) and increase its population. *Microgramma squamulosa* has a high sclerophylly index (Rocha et al., 2013), stomatal density and higher thickness of hypoderm in more polluted environments (Rocha et al., 2014), and these adaptations are important under water stress (Fahn and Cutler, 1992). *Pleopeltis pleopeltifolia*, on the other hand, reduces its exposed leaf surface, thus lessening the damage caused by the solar incidence and the lack of humidity in the environment, a strategy known as poikilohydry (Benzing, 1990), in which it can live with only 25% of its water content over long periods (Moran, 2012). These adaptations are fundamental for their survival in anthropic areas with less water availability.

Table 2. Phytosociological structure of species of epiphytic ferns inventoried in present study (São Leopoldo), in descending order of Specific Importance Value (IVs).

Family	Species	nf	nz	FRf %	FRz %	NCr %	IVs %
Polypodiaceae	<i>Microgramma vacciniifolia</i> (Langsd. & Fisch.) Copel.	35	118	53.8	58.1	60.3	57.4
Polypodiaceae	<i>Pleopeltis pleopeltifolia</i> (Raddi) Alston	20	61	30.8	30.0	26.0	29.0
Polypodiaceae	<i>Microgramma squamulosa</i> (Kaulf.) de la Sota	6	19	9.2	9.4	12.6	10.4
Polypodiaceae	<i>Pecluma sicca</i> (Lindm.) M.G.Price	1	2	1.5	1.0	0.2	0.9
Polypodiaceae	<i>Serpocaulon catharinae</i> (Langsd. & Fisch.) A.R.Sm.	1	1	1.5	0.5	0.4	0.8
Polypodiaceae	<i>Pleopeltis hirsutissima</i> (Raddi) de la Sota	1	1	1.5	0.5	0.4	0.8
Dryopteridaee	<i>Rumhora adiantiformis</i> (G.Forst.) Ching	1	1	1.5	0.5	0.1	0.7

Legend: Nf and nz: number of forophytes and species occurrence zones, respectively; FRf: relative frequency in the forophytes; FRz: relative frequency in zones; NCr: relative coverage note; IVs: importance value.

3.3. Rapid Habitat Assessment Protocol (RHAP)

The result of the RHAP in the surveyed area totalled 33 points, thus classifying the stretch as impacted. The parameter “1-Occupancy type” had a maximum score. Being a Permanent Preservation Area (PPA), this riparian forest, although altered due to recreational trails, has original vegetation and few signs of suppression. At the opposite extreme, parameters 4 and 11 (vegetal cover over the river and type of substrate) scored zero. The absence of vegetation cover in the Rio dos Sinos gutter occurs due to the widening of the river, which also causes erosion in its banks. This reflects the deposition of mud on the river bed, demonstrated by the analysis of the RHAP.

The evaluation of the habitat quality is considered fundamental for the ecological integrity analysis, and the final scores reflect the level of conservation of the area (Barbour et al., 1999; Callisto et al., 2002). The result of the RHAP in the present study, obtained the same (impacted) framework from another stretch. Rocha-Uriarte et al. (2015) also analyzed the lower stretch of the RSHB. This location is at a distance of 12 km from the Imperatriz Leopoldina Park, showing that both are under the same environmental pressures and have the same characteristics of vegetation. A significant contribution to this result is caused by the population density and the consequent urban impact, mainly regarding the type of occupation of the margins and the

devastation of the riparian forests (Barrella et al., 2000; Rodrigues and Gandolfi, 2000), which leads to the loss of environmental quality along the area.

Towards the mouth the river basin, the characteristics of the vegetation follows the change of landscape. This is valid from the headwaters of formative streams to the main river, with heterogeneous environmental conditions towards the floodplain with more homogeneous characteristics (Barrella et al., 2000). Throughout the RSHB, this change in landscape is observed, evidenced by the RHAP score (Table 3), a significant reduction of epiphytic fern richness, and the concentration of IVs in a few species. In addition, the influence of lower altitude and significantly lower precipitation in the lower stretch of the RSHB (Rocha-Uriartt et al., 2015), prove to be natural causes and characteristics that become more homogeneous toward the mouth of the Rio dos Sinos.

Table 3. Score applied to RHAP parameters at Imperatriz Leopoldina Park compared to another study.

Assessed Parameter	Comparative Studies			
	Rocha-Uriartt et al. (2015)			Present Study
	Upper Stretch (Caraá)	Middle Stretch (Taquara)	Lower Stretch (Campo Bom)	Lower stretch (São Leopoldo)
1	4	2	0	4
2	4	2	2	2
3	4	2	2	2
4	4	0	0	0
5	4	2	2	2
6	4	2	2	2
7	4	2	2	2
8	4	2	2	2
9	5	3	3	2
10	5	2	2	2
11	5	2	2	0
12	5	3	2	3
13	5	2	2	3
14	5	2	2	2
15	5	2	0	3
16	5	2	2	2
Score	72	32	27	33
Assessment	Natural Stretch	Impacted Stretch	Impacted Stretch	Impacted Stretch

Legend: Parameters 1 - 8: maximum score (4: natural situation), intermediate (2: slight alteration) and minimum score: (0: severe alteration); Parameters 9 - 16: maximum score (4: natural situation), intermediate (3: slight alteration, 2: median alteration) and minimum score (0: severe change).

4. FINAL CONSIDERATIONS

This study showed that the chemical composition of rainwater is influenced by the environment of each area studied. In the upper stretch (Caraá), the greatest contribution is of marine origin, while in the lower stretch (São Leopoldo) it is basically derived from urbanization and industrialization.

In the riparian forest of Imperatriz Leopoldina Park, a reduction of the wealth and a simplification of the community structure of epiphytic ferns is evidenced, compared to the region of the source of the Rio dos Sinos. Likewise, the riparian forest of the area has lost its

natural characteristics, and its environmental quality diminished according to the categories of RHAP and receives rainwater with a predominantly non-natural chemical composition.

The analysis of the riparian forest of the park applying different methods was an efficient tool to evaluate its environmental quality as it allowed the integration of a greater number of biotic and abiotic variables. The proposed integrated analysis can be applied to other scenarios as well.

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Urban solid waste challenges in the BRICS countries: a systematic literature review

ARTICLES doi:10.4136/ambi-agua.2157

Received: 06 Jul. 2017; Accepted: 23 Jan. 2018

**Andriani Tavares Tenório Gonçalves* ; Flávia Tuane Ferreira Moraes;
Guilherme Lima Marques; Josiane Palma Lima; Renato da Silva Lima**

Universidade Federal de Itajubá (UNIFEI), Itajubá, MG, Brasil

Instituto de Engenharia de Produção e Gestão (IEPG). E-mail: andriani_dri@yahoo.com.br,
flaviatuane@yahoo.com.br, limarques8@gmail.com, jpalmalima@gmail.com, rslima74@gmail.com

*Corresponding author

ABSTRACT

Urban Solid Waste Management (USWM) is a worldwide challenge. The problems faced are even greater due to the disproportional increase of Urban Solid Waste (USW) generation in volume, especially in a context of increased urbanization, population growth and economic globalization in the BRICS countries (Brazil, Russia, India, China and South Africa). In this context, the objective of this work is to analyze the status of MSW management in the BRICS countries, as well as to promote an exchange of experience and management strategies, pointing out possible ways to improve USWM systems that have to be adapted to each local reality. Focusing on this, a systematic literature revision was carried out through a bibliometric analysis. Results showed that the management system of these BRICS countries does not possess well-developed structures. The collection stage is quite often inefficient, the solid waste being stored in inappropriate ways and also disposed of in irregular locations. The participation of the informal sector is a trademark characteristic in USWM for BRICS countries, highlighting the need to integrate and formalize these activities for USW collection. Due to the high organic fraction, it is known that composting offers advantages as a way to promote a better use of organic waste and also as a means of reducing the amount of waste sent to sanitary landfills. Finally, with a better knowledge about solid waste generation and decentralization of the offered services, the decision makers will be able to successfully provide this essential public service.

Keywords: BRICS, systematic literature review, urban solid waste management (USWM).

Os desafios da gestão de resíduos sólidos urbanos nos países do BRICS: uma revisão sistemática de literatura

RESUMO

A Gestão de Resíduos Sólidos Urbanos (GRSU) é um desafio mundial. Com o rápido processo de urbanização, crescimento populacional e econômico nos países pertencentes ao BRICS (Brasil, Rússia, Índia, China e África do Sul) o desafio é ainda maior, decorrente do aumento do volume de Resíduos Sólidos Urbanos (RSU) gerados por esses processos. Neste contexto, o presente trabalho tem por objetivo analisar o status da gestão dos RSU nos países do BRICS, bem como promover um intercâmbio de experiência e estratégias de gestão,

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apontando possíveis caminhos para melhorar os sistemas de GRSU, cuja a implementação deve ser adaptada à realidade de cada país. Para isso, foi realizada uma revisão sistemática de literatura a partir de uma análise bibliométrica. Os resultados mostraram que os sistemas de gestão de RSU nos países membros do BRICS não apresentam uma estrutura bem desenvolvida, muitas vezes a coleta não é eficiente, os resíduos são armazenados de maneira imprópria e destinados em áreas irregulares. A participação do setor informal é característica marcante na GRSU dos países do BRICS, notando-se, portanto, a necessidade de integração do setor informal ao sistema formal de coleta destes resíduos. Devido à alta fração orgânica, é notória as vantagens da compostagem como forma de aproveitamento dos resíduos orgânicos e como meio de reduzir a quantidade de resíduos enviados a aterros. O conhecimento da geração de RSU e a descentralização dos serviços oferecidos de GRSU possibilitaria um maior êxito no atendimento à população.

Palavras-chave: BRICS, gestão de resíduos sólidos urbanos (GRSU), revisão sistemática de literatura.

1. INTRODUCTION

Urban Solid Waste (USW) is made up of residuals and byproducts from domestic activities, street sweeping, and household and public cleaning (Loureiro et al., 2013; Santiago e Dias, 2012; Singh et al., 2014). The increased generation of USW is a growing concern in cities worldwide (Patel et al., 2010), mainly due to the fact that specific municipal management strategies have become more necessary.

Urban Solid Waste Management (USWM) is a multi-disciplinary activity which includes the generation, separation, storage, collection, transportation, processing, recovery and disposal of these materials (Rada et al., 2013). It involves the cooperation of many stakeholders who make up the municipality, as well as the population and local authorities for the pertinent activities (Chen, 2010). The main objective in USWM is to protect public health and the environment through conservation of natural resources (Allesch and Brunner, 2014).

Thus, USWM has become an international challenge, especially in urban areas of developing countries (Jin et al., 2006; Sharholly et al., 2008; Damghani et al., 2008). Rapid urbanization has been seen in these nations, especially in the BRICS (Brazil, Russia, India, China and South Africa), over the last three decades (Wang et al., 2016). This urbanization has sparked a significant growth in waste material. The main reason for this magnitude of growth in USW is related to the Gross Domestic Product (GDP), industrialization, population growth (Linzner and Salhofer, 2014), along with urbanization and an overall increase in living standards (Batoool et al., 2008).

Generation rates for USW are influenced by economic development, industrialization levels, public habits and local climate (Hoornweg and Bhada-Tata, 2012). From this perspective, according to the Human Development Report (UNDP, 2015), Russia, Brazil, and China have a very similar Human Development Index (HDI) (0.804, 0.754, and 0.738, respectively), classifying these countries with an elevated score for human development. Furthermore, the report classified South Africa and India as countries of medium human development (0.666 and 0.624, respectively). Further, according to the Ministry of Foreign Affairs (Brazil, 2014), these countries, taken together, account for 19.8% of world GDP and 41.6% of the total global population.

In analyzing BRICS legislation about USWM, it is possible to see that they are seeking solutions to the problem of solid waste. In Brazil, the National Solid Waste Policy (Brazil, 2010) and, in India, the Municipal Solid Waste (Management and Handling - 2000) are examples of laws that seek to create guidelines regarding the collection, separation, storage, transport process and final disposal of MSW. Although the BRICS countries are regulating

USWM, the standards often do not fit the local reality. According to Tai et al. (2011), in China, specific laws (Prevention of Environmental Pollution Caused by Solid Waste and Administrative Measures for Urban Living Garbage) have not achieved expected effects, since the goals were ambitious, making these laws impossible to be applied by the responsible departments. Massod et al. (2014) argue that misapplication of laws is the main reason for the poor USWM efficiency.

Based on the data above, studies directed to USWM in BRICS are important to aid countries in the process of adapting to the rapid changes, which are ongoing in the national territories. For this reason, it is necessary to guide decision-making about the best strategies to adopt in each country, promoting an exchange of experiences and management policies. Thus, the purpose of this article is to understand the management of USW in the BRICS countries, through a systematic review of literature based on a bibliometric analysis.

This article is structured in the following manner: after this introduction, Section 2 presents the methodology. Section 3 presents results and discussion. Recommendations are given in Section 4, and conclusions are provided in Section 5, followed by the bibliographic references.

2. RESEARCH METHODOLOGY

The bibliometric methodology is used as a means of comparing and quantifying scientific productions based on the process of data aggregation analysis such as year of publication, countries, publication names, authors and citations, among other things (Sun and Grimes, 2016). Citation studies for scientific articles have important implications for greater understanding of the knowledge accumulation process as well as for the research applications in many different fields of knowledge (Walters, 2011). For these reasons, this methodology presents itself as a significant method for mapping scientific processes and as a tool for selecting the best articles to carry out SLR.

The Systematic Literature Review (SLR) is an instrument to map published studies on specific topics so that the researcher can elaborate and synthesize knowledge about the subject of study (Biolchini et al., 2007). The study is carried out according to a previously established protocol which can be replicated by other professionals, who will be able to evaluate the chosen patterns for the case; it differs from traditional reviews because it adopts a replicable process which is scientific, transparent and aids in developing guidelines for searching, selecting, critical analysis and synthesis of results (Cook et al., 1997).

For the means of this study, the SLR procedure from Brereton et al. (2007) and Biolchini et al. (2007) was adopted. According to these authors, the development of an SLR is made up of three phases: Planning, Execution and Results Analysis. In the first phase, the study protocol must be developed, including the main objective, the methods to be used and the criteria to be adopted in selecting the articles (Biolchini et al., 2007). The second phase of the process, the execution, involves the search for information, material selection and evaluation. The research method and criteria for inclusion and exclusion of publications should be rigidly adhered to, as each one is defined in the research protocol (Biolchini et al., 2007). The third and final phase consists of the analysis of all the information considered relevant for the study's objective, which should be collected and stored in a synthetic form. Although the SLR process seems sequential, it involves iterations. Some activities may start during the protocol development and only later will be defined, just when they are ready to be put into practice (Biolchini et al., 2007).

2.1. Execution of Bibliometric Analysis and Systematic Literature Review

2.1.1. Planning

The database used in this research was the ISI Web of Knowledge (Web of Science), which is an indexed database that allows users to export the metadata necessary for the bibliometric

analysis. The keywords used in the search were "Municipal Solid Waste Management" and "Urban Solid Waste Management" from 2006 to 2016. In the Web of Science (WoS) platform, the search resulted in a total sample, for both keywords, of 3214 publications of thematic and environmental areas, mainly related to Environmental Science and Environmental Engineering.

For this first phase of the planning, a bibliometric analysis was performed using the HistCite software with data from 3214 articles. From the publications imported into the software, the results were evaluated under the following aspects: number of publications per year (Figure 1), number of articles per journal (Table 1) and citation analysis.

Figure 1. Number of publications per year.

Table 1. Number of Publications, TGCS and JCR for each journal.

Journals	Number of Publications	TGCS	JCR
Waste Management	509	8954	3,829
Waste Management & Research	235	1862	1,338
Resources Conservation and Recycling	153	1880	3,280
Journal of Cleaner Production	91	1118	4,959
Journal of Environmental Management	67	1397	3,131
Environmental Engineering and Management Journal	46	255	1,008
Renewable & Sustainable Energy Reviews	46	547	6,798
Journal of Hazardous Materials	42	1124	4,836

The number of publications in USWM has grown over the years (Figure 1) due to an increase of waste generation and management expenses. According to projections from the World Bank, the generation and expenses related to these materials have advanced significantly

since 2010. In a timeframe of 15 years, it is forecast that USW will jump by 42% in 161 countries (3,532,255 tons/day in 2010 to 6,069,705 tons/day in 2025), while costs related to USWM will expand by 45% (\$205.4 billion in 2010 to \$375 billion in 2025) (Hoornweg and Bhada-Tata, 2012). Thus, with the increase of the generation and public expenses with USWM, research is necessary to develop new strategies and policies.

The 3214 articles were published in 820 journals, the 10 most published journals are presented in Table 1. The Total Global Citation Score (TGCS) of each journal, which represents the total number of citations per journal on the WoS platform among the analyzed publications, is presented and indicates their reachability. The Journal Citation Reports (JCR), also presented in this research, indicates the average number of citations received by the periodical publications of the journal of the previous two years.

The goal of this research is to evaluate how the USW management occurs in the BRICS countries, following an SLR from the collection of 3214 articles searched on the WoS platform. In this way, it is possible to verify the current status of USW generation and also to propose better practices in order to leverage management efficiency. From this objective, some research questions (RQ) were formulated so as to guide the analysis and identify the USW generation gaps:

RQ1: What is the generation and composition of USW?

RQ2: How is the storage of waste carried out?

RQ3: How are the waste collection, transfer, and transportation performed?

RQ4: What are the main types of treatment and final disposal of USW?

RQ5: Is the USW management in the BRICS countries carried out in a decentralized or centralized manner?

RQ6: What are the improvements actions related to USWM adopted by the BRICS countries?

After developing the research questions (RQ) and the objective of the SLR, the research protocol was established based on two pillars: (1) criteria, related to the composition and construction of articles such as year of publication, country, language, title, abstract and keywords; and (2) perspectives, which refers to the basis of a good USW generation, in other words, generation, composition, storage, collection, transfer, transportation, treatment, and final disposal.

2.1.2. Execution

Through the collection of 3214 articles searched on the WoS platform, the following search filters were applied to perform the SLR: type of document, in which only articles were selected, mainly because of the peer review processes that they go through in their full version; consequently, the database returned a total of 2493 articles. Only English-language articles were selected, decreasing the selection to a total of 2396 articles. The later selection criteria were related to countries, where the BRICS countries were selected: China, India, Brazil, South Africa and Russia. With these filters applied, the sample for the WoS platform was reduced to 558 publications. These articles were also submitted to the selection filter, which included the application of the inclusion criteria by the process of reading the title, abstract and keywords. Only articles in the context of urban solid waste management were selected, thus reducing the sample to 46 articles submitted for review.

2.1.3. Result Analysis

Finally, the 46 articles selected, with USW generation in the BRICS countries presented, were subjected to exhaustive reading and analysis aimed to answer the six research questions

generated in the planning stage of the SLR. Tables with summary information of the articles were developed aiming to present data of how USW management, by country, is made. Also, the general management view allows the exchange of experience and management strategies among countries, seeking to identify the points to be improved. Along these lines, the review sought to present the status of MSW management in the five BRICS countries by analysing the pillar of the perspectives outlined in the planning stage.

3. RESULTS AND ANALYSIS OF THE SYSTEMATIC LITERATURE REVIEW

Urban Solid Waste Management is made up of six basic services: Storage, Collection, Transfer and Transportation; Processing/Treatment and, finally, Disposal of materials which cannot be recovered economically for recycling or reuse. Furthermore, according to Patel et al. (2010), to implement a correct USWM policy, the quantity and composition of the USW must be known.

Thus, the results of the SLR are presented and analyzed first in terms of generation and composition (Table 2), then, according to each one of the USWM activities (storage, collection, transfer, transportation, treatment, and final disposal) for the BRICS countries (Table 3 and Table 7).

3.1. Generation and Composition of USW

According to Abduli et al. (2013), it is essential to comprehend the quantity and type of USW generated in order to plan and develop a suitable management policy for these materials in a specific location. Moreover, the lack of knowledge, mainly about MSW quantity and its characteristics, can make some stages not viable, such as treatment and the final disposal (Costa et al., 2012). The concern with the MSW classification has been growing in the BRICS, encouraged through regulations, such as The People's Republic of China's regulation on Prevention of Environmental Pollution Caused by Solid Waste and The Administrative Measures for Urban Living Garbage, as well as The Brazilian National Policy on Solid Waste (Brazil, 2011). It may be noticed that all these regulations establish administrative measures and specific methods for MSW classification.

Regarding the generation of MSW, Campos (2012) states that this is driven by economic and behavioral factors, besides the influence of population factors, which are related to population growth and its concentration in urban areas. Table 2 presents a synthesis of the generation and composition of USW in BRICS countries. It can be observed that there has been an increase in waste production, specifically in China and India, in parallel with rapid urbanization over the last three decades, according to Wang et al. (2016).

According to Sharholy et al. (2008), the per capita generation of MSW ranges from 0.2 to 0.5 kg/inhabitant/day, in India, and it has annual growth of 1 to 1.33%. Further, in some cities, the generation may be even higher because of the high levels of urbanization standards. Patel et al. (2010) also emphasize that both population and economic growth have influenced significant changes in the quantity and characteristics of waste generated in the last 20 years in the country, making the management waste a problem to be solved through formulation and adoption of appropriate techniques for each type of waste generated.

Zhang et al. (2010) also point out that China has been facing challenges to manage its waste due to the increase in per capita generation, which is around 1.134 kg/inhabitant/day. In Brazil, as can be seen in Table 2, the generation is 1.062 kg/inhabitant/day and in Russia 0.63 kg/inhabitant/day. In the studied articles, there is no information for the per capita generation in South Africa.

Table 2. Generation and composition of USW in BRICS.

Authors	Countries (Cities under study)	Generation and Composition
Couth and Trois (2010); Snyman and Vorster (2011)	South Africa (Cape Town and Tshwane)	Generation: 870,000 tons of recyclable material. Generation <i>per capita</i> : NI* Composition: South Africa – 50% of USW is organic (Liebenberg, 2007) Projection: Estimation of diminishing fraction of organic waste to 42.5% by 2022 in the city of Tshwane
Lino and Ismail (2013); Toso and Alem (2014); Leme et al. (2014); Rutkowski and Rutkowski (2015)	Brazil (Campinas, Sorocaba and Betim)	Generation: 200 tons of USW per day in Betim Generation <i>per capita</i> : 1,062 kg/inhabitant/day for Brazil (ABRELPE, 2015) Composition: Campinas – 46% organic material, 20% paper, 15% plastic, 4% metal, 2% glass and 13% other materials Sorocaba – of recyclable material, 30.2% are cardboard, 25.5% paper, 4.3 tetra pack, 9% metal, 17.4% plastic and 12.3% glass Projection: NI*
Hui et al. (2006); Song et al. (2013); Jiang et al. (2009); Zhen-Shan et al. (2009); Minghua et al. (2009); Liu and Wu (2010); Liu et al. (2015); Fei et al. (2016); Zhao et al. (2008); Dorn et al. (2012); Wang and Wang (2013); Chen et al. (2010); Dai et al. (2011); Fu et al. (2015)	China (Chongqing, Macao, Lhasa, Shigatse, Nedong District, Bayi District in Nyingchi, Beijing, Shanghai (Pudong), Suzhou, Zhejiang, Guangdong, Hebei, Henan and Sichuan)	Generation: 1,805 million tons of solid waste for domestic urban areas in 2013 Generation <i>per capita</i> : 1.134 kg/inhabitant/day for China Composition: Macao – 45.65% organic material, 16.3 paper, 14.13% plastic, 5.43% glass, 3.25% metal, 2.17% cloth, 8.7% wood, and 4.35% other materials. Projection: estimated generation of 4,942 tons/day in 2020 in Tibet region
Pattnaik and Reddy (2010); Sharma et al. (2010); Patel et al. (2010); Chattopadhyay et al. (2009); Kumar et al. (2009); Sharholi et al. (2008); Ravindra et al. (2015); Chakrabarti et al. (2009); Kumar et al. (2009); Goel (2009)	India (Pune, Puducherry, Hardwar, Madhya Pradesh, Kolkata, Rajasthan, Uttar Pradesh, Uttarakhand, Delhi, Haryana, Punjab, Himachal Pradesh, Jammu, Kashmir, Cashmere and Kharagpur)	Generation: 48 million tons, annual, of USW. Generation <i>per capita</i> : 0.561 kg/inhabitant/day for India Composition: 81.41% of USW are biodegradable and 18.59% are not Projection: Increase to 250 million tons by 2047 (Sharholi et al., 2007)
Starostina et al. (2014)	Russia (Irkutsk)	Generation: 500 million tons in 2011 of USW, for Irkutsk (MNREIR, 2012) Generation <i>per capita</i> : 230 kg/inhabitant for solid waste in Irkutsk (MOI, 2008) Composition: 30% organic material, 23.5% paper, 11.3% glass, 15.8% plastic, 7% textile, 2.6% metal, 1.2% rubber, 1% leather, 1% wood and 6.6% others Projeção: NI*

*Not included.

Thus, in the BRICS countries, despite the fact that they present an increase in waste generation, are still less than the average of 2.2 kg/inhabitant/day for the OECD (Organisation for Economic Co-operation and Development) (Hoornweg and Bhada-Tata, 2012), which is made up of mainly developed countries. The quantity and composition of the waste reveals consumption and disposal habits of the inhabitants which do not reflect measures implemented to reduce waste generation.

Regarding composition, the largest part of USW generated in South Africa, Brazil, China, India, and Russia is made up of organic material, reflecting consumption patterns of these populations. This scenario can be expected, given that in studies by Singh et al. (2014) and

Sharholly et al. (2008), in countries considered underdeveloped or developing, there is a growing rate of USW generation and the main contributor is organic material.

Table 3. Storage of USW in BRICS countries.

Authors	Countries (Cities Under Study)	Storage
Jiang et al. (2009); Minghua et al. (2009); Tai et al. (2011); Dai et al. (2011)	China (Lhasa, Shigatse, Nedong District, Bayi District in Nyingchi, Beijing, Guangzhou, Shenzhen, Hangzhou, Nanjing, Xiamen and Guilin)	Types of Recipients: Containers, dumpsters and closed locations Location: Residential and commercial streets, scheduled collection points, transfer stations or stored by USW collection companies
Kumar and Goel (2009); Pattnaik and Reddy (2010); Kumar et al. (2009); Zia and Devadas (2008); Talyan et al. (2008); Ravindra et al. (2015)	India (Kharagpur, Puducherry, Metropolitan Cities, States Capitals, Deli, States of Rajasthan, Uttar Pradesh, Uttarakhand, Delhi, Hariyana, Punjab, Himachal Pradesh, Jammu, Cashmere and Chandigarh)	Types of recipients: Small trash recipients at the source, community containers and concrete deposits (open and closed) Location: Open areas and in streets, without source separation
Starostina et al. (2014)	Russia (Irkutsk)	Type of Recipient: Common trash cans (containers around 0.75m ²) Location: Residencies

3.2. Storage

Storage represents an essential procedure for suitable USWM. As one step before collection, the way that solid waste is stored influences how it will be transported. It is recommended that at the points of generation the waste be placed in waste containers selected according to its characteristics; for example, the container must be mechanically and chemically compatible with each waste (Barros, 2012).

Table 3 presents the storage characteristics in China, India and Russia. In the studied articles, no information was found on the remaining BRICS countries.

In China, the use of waste containers, collection points and transfer stations all stand out for temporary storage, in order to aid in transferring USW from small collection vehicles to larger ones. Storage in domestic dumpsters or trash deposits is the method utilized in Russia. In India, the storage is inadequate, generally in open areas and streets, without separation at the source; in certain part of the country, community waste containers are used.

Jiang et al. (2009) and Zia and Devadas (2008) state in their studies on China and India, respectively, that they observed problems in conserving the quality of the public waste containers and the existence of clandestine disposal spots in the storage areas.

3.3. Collection, Transfer and Transportation

Collection and transfer of USW must be carried out with suitable frequency in order to avoid excessive accumulation of materials, minimizing risks to the environment and public health. Transportation must be done in adequate vehicles, chosen according to the quantity and type of solid waste being transported, the topographical characteristics and the region's transportation network, as suggested by Rutkowski and Rutkowski (2015).

Analyzing the data presented in Table 4 regarding the way the collection, transfer and transport of USW is carried out in BRICS countries, it can be seen that the collection system adopted is door-to-door in South Africa, Brazil and India, and specific delivery points in Brazil, China, India and Russia. Collection at specific delivery points depends on the population's participation and awareness, given that residents have to go to the locations where the

dumpsters or containers are placed for waste disposal. In many cases, this does not happen, which creates clandestine deposits.

The collection services in these countries are carried out by public and private companies, which contributes to differences in performance. According to Sharholy et al. (2008), the collection service is more efficient when a third-party is hired for the activity. However, Rajamanikam et al. (2014) detected problems in the city of Puducherry (India) in the execution of services by Non-Governmental Organizations (NGOs) and third-party contractors, who carried out the collection two times per week in order to economize transportation costs. Thus, some regions have low collection frequencies, which lead to overflowing storage locations, which cause uncontrolled burning of urban solid waste around the city.

Table 4. Collection, transfer and transportation of USW in the BRICS countries.

Authors	Countries (Cities Under Study)	Collection, Transportation and Transfer
Snyman and Vorster (2011); Couth and Trois (2010).	South Africa (Cape Town, Tshwane and Johannesburg)	Collection method: Door-to-door Utilization of transfer stations: Yes (10 stations in Tshwane). Form of Transportation: NI* Responsible: NI* Frequency: NI* Efficiency: NI*
Rutkowski and Rutkowski (2015).	Brazil (25 Brazilian Cities)	Collection method: Door-to-door and/or delivery point. Utilization of transfer stations: Form of Transportation: Choice made in relation to topography. Responsible: NI* Frequency: NI* Efficiency: Collection efficiency is 90% (ABRELPE, 2015).
Hui et al. (2006); Song et al. (2013); Jiang et al. (2009); Zhen-Shan et al. (2009); Dai et al. (2011); Wang and Wang (2013); Minghua et al. (2009); Liu et al. (2015); Wang et al. (2008); Yang et al. (2015).	China (Chongqing, Macao, Lhasa, Shigatse, Nedong District, Bayi District in Nyingchi, Beijing and Shanghai)	Collection method: Delivery points Utilization of transfer stations: Yes Form of Transportation: Trucks (with and without compaction) Responsible: State owned and private companies. Frequency: NI* Efficiency: NI*
Narayana (2009); Pattnaik and Reddy (2010); Sharma et al. (2010); Chattopadhyay et al. (2009); Kumar et al. (2009); Sharholy et al. (2008); Zia and Devadas (2008); Talyan et al. (2008); Pandey et al. (2012); Rajamanikam et al. (2014); Ravindra et al. (2015); Chakrabarti et al. (2009); Kumar and Goel (2009).	India (Puducherry, Hardwar, Kolkata, Metropolitan Cities, States Capitals, Kanpur, Delhi, Bhagalpur and Kharagpur)	Form of Collection: Door-to-door and/or delivery points. Utilization of Transfer Stations: Yes Form of Transportation: Trucks (with and without compaction) Responsible: State owned and private companies. Street sweepers and recyclable materials collectors. Frequency: From Monday to Friday Efficiency: The efficiency measurement in India is around 60 to 70%.
Starostina et al. (2014).	Russia (Irkutsk)	Form of Collection: Delivery points. Utilization of Transfer Stations: NI* Form of Transportation: NI* Responsible: NI* Frequency: Every day, every-other day or two times per week, depending on necessity. Efficiency: NI*

*Not included.

The participation of the informal sector, by means of street sweepers and recyclable material gatherers is a trademark characteristic of the collection system used in Brazil, China and India. In terms of optimizing USW transportation, most studied cities have transfer stations, which help to reduce transportation costs. However, the number of stations is not sufficient, in many cases, mainly in large-scale cities, where studies must be done to optimize routes and locations for containers and dumpsters in order to improve the selective collection.

3.3.1. Selective Collection

The activity of selective collection feeds the cycle of reuse, recycling and composting. It is through this process that recyclable materials are sorted from non-recyclable and organic material. Organic material will be destined for composting. Table 5 presents the synthesis of selective collection in BRICS.

Toso and Alem (2014) highlight the difference between Brazil and the other countries, mainly in the way that USW is separated for recycling. Other countries sort them by type (paper, cardboard, etc.), while in Brazil they are broken into sub-groups of recyclable materials (and, obviously, non-recyclables).

In Brazil, the selective collection activity is done mainly through door-to-door and Voluntary Delivery Points (VDP), carried out by public authorities and, in some cases, partnership with the informal sector. The inclusion of the informal sector through associations and cooperatives has been increasingly incentivized throughout the country, since the approval of the National Solid Waste Policy (Brazil, 2010). However, according to Ferri et al. (2015), a great challenge resides in the task of integration of the recyclable material gatherers and the overall USWM system, often due to their lack of capacity to carry out this activity, which is essential mainly to deal with the health and safety aspects of these workers in the operation of associations and cooperatives.

In China and India, according to Sharholy et al. (2008), the task is predominantly done by the informal sector; the role of the government in recovering these materials is small. The presence of the informal sector in these countries does not occur in a planned fashion, but rather as a result of economic conditions seen by the population. In China, for example, the informal workers organization was always a challenge for the Chinese government, bringing social problems (Wang et al., 2008 e Liu et al., 2015). Liu et al. (2015) also emphasize that one way to solve this social issue would be to employ informal waste pickers in recycling companies.

Table 5. USW Treatment in BRICS countries.

Authors	Countries (Cities under study)	Treatment
Snyman and Vorster (2011); Couth and Trois (2010).	South Africa (Cape Town, Tshwane and Johannesburg)	Type of treatment: Composting for urban solid waste. (Coetzee et al., 2007)
Rutkowski and Rutkowski (2015).	Brazil (25 Brazilian Cities)	Type of treatment: recycling and of reuse of urban solid waste.
Song et al. (2013); Jiang et al. (2009); Zhen-Shan et al. (2009); Minghua et al. (2009); Liu et al. (2015); Tai et al. (2011); Dorn et al. (2012); Chen et al. (2010); Dai et al. (2011); Wang and Wang (2013); Zhao et al. (2008).	China (Macao, Lhasa, Shigatse, Nedong Lhoka District, Bayi District in Nyingchi, Beijing, Shanghai, Guangzhou, Shenzhen, Hangzhou, Nanjing, Xiamen and Guilin)	Type of treatment: incineration, compost and recycling.
Narayana (2009); Jha et al. (2008); Chattopadhyay et al. (2009); Kumar et al. (2009); Zia and Devadas (2008); Sharholy et al. (2008); Rajamanikam et al. (2014); Chakrabarti et al. (2009); Kumar and Goel (2009).	India (Delhi, Mumbai, Calcutta, Chennai, Metropolitan Cities, State Capitals, Kanpur, Puducherry and Kharagpur)	Type of treatment: 47% of USW generated were recovered through active recycling and composting practices in the area of Raj Bhavan and Puducherry.
Starostina et al. (2014).	Russia (Irkutsk)	Type of Treatment: Only 3% of USW are recycled in the city.

3.4. Treatment

Inadequate management of USW in terms of treatment results in economic losses and poses a threat to public health and natural resources (Abduli et al., 2013). Zhang et al. (2010) affirm that any activity for USW treatment not only diminishes the total amount of waste generated but also the costs of disposal. Even with these clear gains through treatment, all the studied articles highlight treatment activities as hurdles to be overcome in BRICS countries. Table 6 presents the types of treatments which already exist.

The articles about South Africa, China and India affirm the existence of composting. However, some problems are identified, such as low quality and lack of market for the composted product. Based on the fact that USW in BRICS countries have a large portion of organic material, composting should be considered in these locations. Some authors, such as Abduli et al. (2013), Zhang et al. (2010) and Sharholy et al. (2008), suggest that composting needs to be improved, which is essential to the implementation of the separation of waste material from the generating source so that recyclable materials can be routed to recycling processes and organic material to composting.

Incineration, on the other hand, is a common practice in large cities in China. In small cities, USW presents a low heat-generating power, as pointed out by Chen et al. (2010). However, incineration has been increasing due to subsidies from the Chinese government and private investments aimed at reducing the volume of USW and the generation of energy. In India, Narayana (2009) affirms that this activity has not been so common due to high humidity levels, low heat-generating content and reduced volumes, which will not meet the needs of central incineration installations. In Brazil, treatment by incineration is in a secondary context (Brazil, 2010). Incinerators within the country are used mainly to process waste considered as needing special treatment, such as health-service waste.

Related to recycling, the informal sector has a strong participation in the BRICS countries. Wang et al. (2008) point out that recyclable material gatherers sustain the entire recycling system in developing countries. Therefore, there is a need to formally integrate these important members of the system, considering that many times these workers suffer from government negligence and need professional training and legalized work. Among these countries, Brazil stands out as a reference in social inclusion for recyclable material gatherers through cooperatives and associations (Ezeah et al., 2013).

Table 6. Selective Collection in BRICS countries.

Authors	Countries (Cities under study)	Selective Collection
Couth and Trois (2010)	South Africa (Cape Town and Johannesburg)	Type of collection: NI* Separation: Dry and wet waste materials Responsible: NI*
Lino and Ismail (2013); Toso and Alem (2014); Ferri et al. (2015); Rutkowski and Rutkowski (2015)	Brazil (Campinas, Sorocaba and others 25 Brazilian Cities)	Type of collection: Door-to-door and VDP Separation: Recyclable Wastes are collected and then sorted. Responsible: Public authorities, private companies, associations and cooperatives.
Hui et al. (2006); Liu et al. (2015); Fei et al. (2016); Xu et al. (2015); Wang et al. (2008)	China (Chongqing, Beijing, Suzhou and Haidian (Beijing District))	Type of collection: NI* Separation: Separated in trash cans, streets and/or locations for final disposal. Responsible: Informal sector – by gatherers and informal buyers of recyclable materials.
Zia and Devadas (2008); Rajamanikam et al. (2014)	India (Kanpur, State of Rajasthan, Uttar Pradesh, Uttarakhand, Delhi, Haryana, Punjab, Himachal Pradesh, Jammu, Cashmere and Puducherry)	Type of collection: Inhabitants sell them in recycling areas. Separation: Dry and wet waste materials. Responsible: Informal sector.
Starostina et al. (2014)	Russia (Irkutsk)	Type of collection: Paper and glass are commercialized on the market. Separation: NI* Responsible: NI*

*Not included.

3.5. Final Disposal

Final disposal of USW consists of the adoption of procedures which aim to release the waste into the ground, minimizing environmental impacts by following operational norms to avoid public health problems and promote population safety. In Brazil, final disposal is restricted to USW which cannot be treated or recovered, classified as rejected (Brazil, 2010).

In this sense, the study showed the strong presence of landfills in the investigated countries (Table 7), which many times are irregular, or do not present a collection system, nor leachate or gas/drainage treatment system (with or without energy generation). Urban Solid Waste is also disposed of in open-air environments without any concern for the environment, which can cause public health problems.

Table 7. Final disposal in BRICS countries.

Authors	Countries (Cities under study)	Final Disposition
Snyman and Vorster (2011).	South Africa (Tshwane)	Type of final disposal: Landfills
Lino and Ismail (2013); Toso and Alem (2014); Leme et al. (2014); Rutkowski and Rutkowski (2015).	Brazil (Campinas, Sorocaba, Betim and others 25 Brazilian Cities)	Type of final disposal: open dump (open-air, without treatment), controlled landfills
Song et al. (2013); Jiang et al. (2009); Zhen-Shan et al. (2009); Minghua et al. (2009); Liu et al. (2015); Tai et al. (2011); Chen et al. (2010); Dai et al. (2011); Wang and Wang (2013).	China (Macao, Lhasa, Shigatse, Nedong Lhoka District, Bayi Nyingtri District, Beijing, Shanghai, Guangzhou, Shenzhen, Hangzhou, Nanjing, Xiamen and Guilin)	Type of final disposal: Landfills and dumps
Narayana (2009); Jha et al. (2008); Pattnaik and Reddy (2010); Chattopadhyay et al. (2009); Kumar et al. (2009); Zia and Devadas (2008); Talyan et al. (2008); Hazra and Goel (2009); Pandey et al. (2012); Ravindra et al. (2015); Chakrabarti et al. (2009); Kumar and Goel (2009); Sharma et al. (2010).	India (Delhi, Mumbai, Calcutta, Chennai, Puducherry, Kolkata, Metropolitan Cities, States Capitals, Kanpur, Bhagalpur, State of Rajasthan, Uttar Pradesh, Uttarakhand, Haryana, Punjab, Himachal Pradesh, Jammu, Cashmere, Chandigarh, Kharagpur and Haridwar)	Type of final disposal: uncontrolled landfills, dumps and clandestine dumping sites (highways and empty lots)
Starostina et al. (2014).	Russia (Irkutsk)	Type of disposal: 500,000 tons of USW deposited, per year, in the landfills.

In Brazil in 2014, dumps represented 28% of the final destination per municipality; controlled landfills were 32% and sanitary landfills, 40% (ABRELPE, 2015). In India, according to Narayana (2009), 90% of generated waste is deposited in open places. The limitation of space for landfills, due to dramatic urban growth and scarcity of resources, has hindered the construction of safe, controlled landfills in Indian cities (Chakrabarti et al., 2009).

It was observed that most of the BRICS countries do not have adequate waste management systems. Wastes with high pollution potential, which should have special disposal treatment, are erroneously sent to domestic waste landfills. According to studies by Snyman and Vorster (2011), in South Africa, for example, 50% of domestic waste, 28% of green waste, 14% of civil construction waste, and 8% of industrial waste are deposited in the Tshwane landfill.

4. FINDINGS

The BRICS countries face constraints in the USWM that can be solved, but this requires the more active participation of the population, the government and the private sector, as Narayana (2009) argues. In this way, it was possible to observe these points of improvement and good practices in the five countries studied from the USWM status study. The positive initiatives can be reproduced with modifications that respect characteristics, dimensions, generation of waste, population and individualities of each country.

The centralization of the USWM services in public agencies, in the BRICS countries, was observed in the articles studied. Thus, in order to ensure the participation of all sectors, incentives are recommended for the decentralization of the management stages from the definition of responsibilities between private initiative, public authority and population. Chen et al. (2010) emphasize that an integrated approach to the services offered by the system is necessary, considering the roles of these three stakeholders.

Focusing on the MSW generation stage, China shows that an absence of a volume limit of MSW generated is a real gap during all the generation process (Zhang et al, 2010); consequently, more investments are required for the final disposal of the waste. The authors themselves suggest the implementation of a charge for waste generation. In this way it would be possible to recover USWM costs and increase financial support for waste disposal facilities.

The analyzed articles pointed to some faults in the storage and collection of MSW in India, where some municipalities have community containers with excessive waste, clandestine disposal sites and poor conservation of the waste containers. The article by Rajamanikam et al. (2014) concludes that the cause of high MSW stocking in community waste containers in India is due to the low frequency of waste collection in the municipality of Puducherry. As a good practice of collection and storage, the article by Starostina et al. (2014) states that in the city of Irkutsk (Russia) the waste is stored in individual waste containers for each household; these containers are emptied frequently (every day, every two days or twice a week). Consequently, there is a decrease in USW accumulation and also in waste-burning, as reported by Rajamanikam et al. (2014). In this way, it is suggested that collection frequency should be designed to take into account the amount of waste generated and the waste containers' storage capacity, as in the Irkutsk city.

Regarding waste treatment, composting is the most viable treatment form, due to the great proportion of organic material present in the overall breakdown of USW in BRICS countries, as indicated by Zia and Devadas (2008), Kumar et al. (2009) and Narayana (2009). However, to initiate this activity, the material must be separated at the generating source in order that the recyclable material can be directed to recycling, and organic material to composting. An example of good management practice is the Sao Paulo Project (Sao Paulo, 2014), which is connected to the Sao Paulo city government and aims to orient and reduce the waste of tons of organic waste. This organic waste is not reused but is sent without treatment to the city sanitary landfills. Therefore, it is important to emphasize that the treatment choice will also be influenced by political, social, economic and environmental factors, such as political interests, financial resources availability and environmental awareness.

The main form of final disposal in BRICS countries is sanitary landfills, which are frequently found to be in irregular and/or clandestine operation. Practices of reduction of generation, separation at the source, recycling and composting are all important tools to diminish the volume of USW destined for landfills, and, in turn, encourage only rejected material to be sent to these deposits. This reduction in the waste volume sent to final disposal is extremely important to increase the landfills lifespan and to reduce both new disposal areas and investments.

Thus, in the case of future directions for USWM, benchmarking the use of the best management practices in countries and municipalities is fundamental. Moreover, engagement and discipline of the three sectors (population, public and private authorities) in the USWM are meaningful characteristics to increase performance and efficiency in the stages of management.

5. CONCLUSIONS

The objective of this article was to analyze the status of urban solid waste management in BRICS countries through a Systematic Literature Review. Essential points were taken into account in the USWM, such as the generation rate, composition, storage form, collection, besides the main ways of treatments and final disposal of MSW. This initial stage of research and data collection sought to information and knowledge about the techniques, strategies and methods used in these countries. From the results and discussions about the analysis of the 46 articles selected for this work, it was possible to make some recommendations, contributing in this way to better waste management in these countries.

The BRICS countries present a lot of common characteristics, such as problems in their management systems, the participation of the informal sector, considerable quantities of organic material, the use of landfills and irregular areas for final disposal.

The main barriers to USWM faced by these countries are directly related to a lack of financial resources, adequate local infrastructure, planning, quantity data, types of waste generated and definition of responsibilities of the agents involved in the process. The implementation of long-term planning measures that encourage the reduction of generation, separation at source, recycling, composting and landfill volume reduction are some actions that can be taken by these countries to improve the USWM system.

It is important to highlight the meaningful role of the informal sector in the collection and separation stages of MSW in BRICS countries. However, it is evident that the informal sector is not integrated into the formal management system and this integration is necessary to increase the efficiency of USWM. Regarding the integration process, this can occur through professional training, as well as through the legalization of the work of these waste pickers, which lead to an increase in the amount of recyclable waste collected and, consequently, facilitate treatment and final disposal stages. In this sense, economic, environmental and social gains are generated.

The decentralization of USWM services, along with definitions of clear roles and responsibilities for the public and private sectors, in cooperation with the population, is noted as a necessary measure for the creation of efficient USWM in BRICS countries. This decentralization can favor the management system as it begins to consider the typical features of each locality throughout management system planning. Inadequate MSW management, in terms of treatment technologies, recycling, final disposal and management strategy, leads to economic loss while posing a threat to public health and natural resources.

It is worth mentioning that there is no single model for USWM which would meet the needs of all countries. Each solution must be based on location, taking into account not only the physical characteristics of the system, but also the governmental and cultural factors. Although, regardless of the location, for the management to guarantee a minimum level of satisfaction there must be both administrative (public policies, legislation, financial and human resources) and technical-operational (storage, collection, transportation, treatment and final disposal) structures in place.

Furthermore, before any USWM implementation, municipalities must put themselves through multiple assessments in terms of technology and possible methods to be used. Thus, studies which identify local characteristics and necessities must be elaborated. The system must be structured to attend the local reality through suitable regulations, contributing to sustainable

management of urban solid waste and seeking to work in conjunction with the public sector, the private sector and society, all with well-defined roles and responsibilities.

6. ACKNOWLEDGEMENTS

The authors would like to thank CAPES, CNPq, and FAPEMIG for their financial support given to many projects that helped develop this study.

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Qualidade da água utilizada em quiosques de praia

ARTICLES doi:10.4136/ambi-agua.2003

Received: 13 Sep. 2016; Accepted: 06 Feb. 2018

**Diésse Nascimento Norete; Quezia Botelho Correia;
Jackline Freitas Brilhante São José***

Universidade Federal do Espírito Santo (UFES), Vitória, ES, Brasil
Departamento de Educação Integrada em Saúde. E-mail: diesse.nascimento@hotmail.com,
queziabotelho@hotmail.com, jackline.jose@ufes.br

*Autor correspondente

RESUMO

Objetivou avaliar as condições higiênicossanitárias relacionadas ao abastecimento e a qualidade microbiológica da água utilizada por quiosques de praia. A coleta dos dados ocorreu por meio de observação direta com aplicação de lista de verificação que continha itens como procedência da água, realização de tratamento de desinfecção antes do uso em alimentos, frequência de higienização da caixa da água, qualidade microbiológica da água, existência de licença sanitária e registro da última visita da vigilância sanitária. Foram coletadas amostras de água em dez quiosques de praia e para a coleta foram utilizados recipientes esterilizados e identificados. Para contagem de bactérias heterotróficas foi utilizada a técnica de plaqueamento em profundidade em ágar padrão para contagem, sendo os resultados expressos em UFC/mL. Para coliformes foi utilizado o teste do número mais provável (coliformes a 35°C e a 45°C) e o resultado obtido foi expresso em NMP/100 mL. Foi observado por meio da aplicação da lista de verificação que 70% dos quiosques utilizavam apenas água da rede de abastecimento público e um dos estabelecimentos funcionava sem licença sanitária. Das amostras coletadas, 30% apresentaram contagem total de bactérias acima de 500 UFC/mL. Não foi detectada a presença de coliformes e *E. coli* em nenhuma das amostras analisadas. Apesar dos resultados observados terem sido satisfatórios, deve-se reforçar a necessidade do acompanhamento da qualidade da água como estratégia de prevenção de riscos aos consumidores.

Palavras-chave: água para consumo, análise de água, coliformes.

Quality of water used by beach kiosks

ABSTRACT

This study evaluated the sanitary conditions and the microbiological quality of the water used by beach kiosks. Data was collected through direct observation, using a checklist with such items as water source, disinfection treatment before use, frequency of water container sanitation, microbiological quality of water, existence of sanitary license and records of the last inspection by health authorities. Water samples were collected in labeled, sterilized containers from 10 beach kiosks. The plate technique in depth in standard agar was used for counting heterotrophic bacteria and the results were expressed in CFU/mL. The most-probable number test was used to evaluate coliforms (coliforms at 35°C and 45°C) and the

results were expressed in NMP/100 mL. It was observed that 70% of the kiosks used only water from the public supply and one of the establishments operated without a sanitary license. Of the samples collected, 30% had a total bacterial count above 500 CFU/mL. No presence of coliforms and *E. coli*. was detected in the samples analyzed. While the results were satisfactory, the study reinforced the need to monitor water quality as a strategy to prevent risks to consumers.

Keywords: analysis of water, coliforms, drinking water.

1. INTRODUÇÃO

A água é fundamental para os seres humanos e sua importância para a saúde pública é largamente reconhecida, com a garantia da potabilidade que é essencial para a população (Scorsafava et al., 2013; Volkweis et al., 2015). Destaca-se que a água que será consumida pelo homem não deve conter substâncias dissolvidas em quantidades que causam toxicidade e nem veicular micro-organismos patogênicos causadores de doenças (Santos et al., 2013). Deste modo, a água é própria para o consumo humano quando atende aos parâmetros microbiológicos e físico-químicos das especificações de potabilidade estabelecidas pela Portaria nº 2.914/2011 do Ministério da Saúde (MS) (Brasil, 2011). Caso não atenda a estes requisitos, a água pode afetar ou depreciar equipamentos, instalações e, principalmente, favorecer a possibilidade de contaminação e ocorrência de enfermidades aos consumidores (Mouchrek e Carvalho, 2016).

O uso de água sem controle de qualidade pode comprometer a saúde pública de forma a proporcionar riscos individuais ou coletivos, imediatos ou de longo prazo. O consumo de água contaminada, não só para beber, mas também para uso diário, pode acarretar a ocorrência de doenças de transmissão hídrica. Este contexto de negligência colabora para o alto custo e a necessidade de serviços especializados para o tratamento destas doenças (Araújo et al., 2013).

A contaminação da água por micro-organismos patogênicos pode ocorrer principalmente por fezes de origem humana e animal. As enfermidades mais comuns causadas por estes agentes etiológicos são a febre tifóide, febre paratífóide, cólera, disenteria bacilar, diarreias e hepatites (Nkere et al., 2011). A pesquisa de micro-organismos patogênicos na água requer procedimentos complexos e longos, sendo indispensável a utilização de indicadores de contaminação de origem fecal para avaliar a qualidade microbiológica da água. Dentre os principais destacam-se os coliformes totais (coliformes a 35°C), coliformes termotolerantes (coliformes a 45°C) e *Escherichia coli* (WHO, 2011). Os coliformes a 35°C são bacilos gram negativos, aeróbios ou anaeróbios facultativos, não formadores de esporos, oxidase-negativos, e fermentam lactose com produção de ácido e gás. Neste grupo, a maioria pertence aos gêneros *Escherichia*, *Citrobacter*, *Klebsiella* e *Enterobacter*. Já os coliformes a 45°C tem como principal representante a *Escherichia coli*, de origem exclusivamente fecal (Souza, 2012).

No preparo de alimentos existem muitos procedimentos nos quais o uso da água está envolvido como por exemplo, limpeza e sanitização de alimentos, higienização de mãos de manipuladores, higienização de utensílios e superfícies que entram em contato com alimentos, bem como na cocção dos alimentos (Silveira et al., 2011). Assim, torna-se crucial a potabilidade da água para contribuir para melhor qualidade higiênicossanitária das preparações elaboradas em estabelecimentos comerciais, como os quiosques de praia.

Deste modo, este trabalho teve como objetivo avaliar as condições higiênicossanitárias relacionadas ao abastecimento de água e avaliar a qualidade microbiológica da água utilizada por quiosques de praia.

2. MATERIAL E MÉTODOS

Foi realizado no período de novembro a dezembro de 2014 um estudo transversal, observacional e analítico em quiosques de praia localizados em Vila Velha-ES. Inicialmente, os responsáveis pelos estabelecimentos foram contatados por meio de carta convite para apresentação dos objetivos da pesquisa e, em seguida foi solicitada a permissão para visita, aplicação da lista de verificação e coleta das amostras de água.

Dos 30 quiosques existentes no local estudado, dez concordaram em participar da pesquisa, representando 33,33% do número total de estabelecimentos.

2.1. Aplicação da Lista de Verificação

A coleta dos dados ocorreu por meio de observação direta durante as visitas realizadas por pesquisadores treinados. Foi aplicada uma lista de verificação, baseada nos itens relacionados ao abastecimento de água contidos na Resolução 216/2004 do Ministério da Saúde (Anvisa, 2004). A lista de verificação foi composta por 10 itens que estavam relacionados à procedência da água; à realização de tratamento de desinfecção antes do uso em alimentos (para preparo ou higienização, por exemplo), e no caso de realização de tratamento prévio quem era o responsável pelo procedimento; à frequência de higienização da caixa da água: se realizava e com que frequência era efetuado o acompanhamento da qualidade microbiológica da água; existência de licença sanitária; e registro da última visita da vigilância sanitária. Em cada visita realizada os pesquisadores permaneceram aproximadamente por uma hora, durante o funcionamento do estabelecimento, para observação dos itens presentes na lista de verificação bem como checagem de registros disponíveis.

2.2. Análise Microbiológica das Amostras de Água

Foram realizadas coletas de amostras de águas em 10 quiosques de praia, sendo incluídos estabelecimentos que utilizavam ou não águas subterrâneas. Para coleta utilizou-se recipiente esterilizado e devidamente identificado. Nos recipientes esterilizados para coleta de amostras provenientes do abastecimento público foram adicionados substância neutralizante do cloro residual da água. Após a coleta, os frascos foram transportados ao laboratório, em caixas isotérmicas, para execução das análises microbiológicas. O processo de coleta foi precedido por limpeza e descontaminação da superfície das torneiras, com a finalidade de evitar a coleta de água com componentes que não pertencem à amostra. Foram coletadas amostras da água das torneiras da cozinha do estabelecimento.

Realizou-se higienização da torneira com aplicação de álcool a 70%. Foram realizadas coletas de amostras de água em 10 quiosques (n=10) de praia, sendo incluídos estabelecimentos que utilizavam ou não águas subterrâneas, totalizando 12 amostras de água (m=12), pois dois quiosques eram abastecidos por duas fontes. Os quiosques foram identificados com números de 1 a 10.

Para as análises, utilizaram-se procedimentos de acordo com *American Public Health Association* (APHA), descrita no *Compendium of Methods for the Microbiological Examination of Foods* (Downes e Ito, 2001).

Foram realizados os seguintes testes: presuntivo para coliformes, confirmativo para coliformes a 35°C, e confirmativo para coliformes a 45°C. Alíquotas foram colocadas em séries de três tubos contendo caldo lauril sulfato triptose (LST), com tubo de Durham invertidos (teste presuntivo) e estes foram incubados a 35°C por 24 – 48 h. Deste modo, a partir dos tubos com leitura positiva (turbidez e formação de gás), foram realizados os testes confirmativos para coliformes 35°C em caldo Lactose Bile Verdes Brilhante (VB) a 2% a 35°C por 24 – 48 h, e, coliformes 45°C em caldo *Escherichia coli* (EC) a 45°C por 24 – 48 h. Ao avaliar a combinação de números correspondentes aos tubos que apresentaram resultado

positivo, foi verificado o Número Mais Provável de acordo com a tabela de NMP, conforme os procedimentos básicos de contagem. O valor obtido foi expresso em NMP/100 mL. Para a contagem total de heterotróficos foi feita semeadura em profundidade em Agar Padrão para Contagem (PCA), sendo os resultados expressos em UFC/mL.

Os resultados obtidos foram analisados e comparados com os padrões previstos na Portaria nº 2914 de 2011 (Brasil, 2011). Para análise dos dados coletados a partir da lista de verificação foi realizada estatística descritiva com uso de frequência e valores percentuais com auxílio do software *Microsoft Office Excel*®, 2010.

3. RESULTADOS E DISCUSSÃO

Foi observada por meio da aplicação da lista de verificação que 70% dos quiosques utilizavam apenas água da rede de abastecimento público (Tabela 1). Os demais utilizavam água proveniente da rede de abastecimento público e/ou de poços subterrâneos. Mouchrek e Carvalho (2016), em estudo com serviços de alimentação, também observaram predomínio do abastecimento de água pelo serviço público.

A água de abastecimento público é um recurso hídrico que deve ser retirado da natureza e oferecido à população em quantidade e qualidade adequadas. Esta água pode ser proveniente de diferentes fontes como água de superfície (lagos, rios e açudes) e águas do lençol freático que são subterrâneas (Liguori et al., 2010). A água subterrânea é um sistema alternativo de abastecimento e representa 97% dos recursos hídricos disponíveis ao homem e atende mais da metade da população mundial, principalmente em regiões de clima semiárido (Colvara et al., 2009).

Tabela 1. Frequência do abastecimento de água por serviço público e/ ou poço artesiano em dez quiosques de praia, Vila Velha-ES.

Fonte de Abastecimento	Frequência	%
Público	7	70
Público + Poços artesianos	2	20
Poços artesianos	1	10

Quanto ao tratamento prévio à utilização da água, verificou-se que apenas 10% dos quiosques realizavam tal procedimento. Ressalta-se que este estabelecimento era o mesmo que utilizava água proveniente de poços artesianos. Assim, entende-se que a maioria dos donos dos estabelecimentos confiavam na qualidade da água que recebiam por meio do abastecimento público. Aqueles que tomavam precauções com relação a tratamentos de água realizavam procedimentos como a fervura ou a adição de hipoclorito de sódio antes do uso em alimentos.

Quanto à frequência da limpeza da caixa d'água, foram consultados registros, sendo observado que 70% dos quiosques realizavam a cada 6 meses e este procedimento era realizado pelo próprio responsável pelo estabelecimento. Estes quiosques eram os mesmos que utilizavam apenas água proveniente do abastecimento público. Os demais estabelecimentos realizavam a cada dois meses, o que indica maior preocupação destes com o controle de qualidade da água. Os resultados do presente estudo foram superiores ao observado por Silveira et al. (2011) que verificaram que somente 18,8% das escolas avaliadas tinham reservatório de água em condições adequadas com limpeza semestral. Segundo a legislação vigente sobre boas práticas para serviços de alimentação (Anvisa, 2004), o reservatório de água deve ser edificado e mantido em perfeito estado de higiene e conservação de modo que a qualidade da água não seja afetada. O procedimento de higienização do

reservatório deve ser realizado em um intervalo máximo de seis meses e devem ser feitos registros da operação. Quando este procedimento for realizado por empresa terceirizada é necessária a apresentação de certificado de execução do serviço (Anvisa, 2004).

O controle de qualidade da água para uso na produção de alimentos é imprescindível para reduzir riscos à saúde dos consumidores. Portanto, a água deve ser potável, e para manter a qualidade é necessário que o reservatório esteja íntegro, limpo e tapado, bem como, deve ser realizado periodicamente o acompanhamento da qualidade microbiológico da água (Portugal et al., 2015).

Com relação às análises microbiológicas da água utilizada nos quiosques, 50% destes realizavam coleta e encaminhavam amostras para análise pelo menos uma vez ao ano. Vale destacar que este controle da qualidade microbiológica era realizado por quiosques que recebiam água do abastecimento público. Entretanto, os laudos de potabilidade não estavam disponíveis no local. No estudo de Silveira et al. (2011), somente 20,5% das escolas apresentavam o laudo de potabilidade da água. Verificou-se que 10% (n=1) dos quiosques não apresentavam alvará emitido pela Vigilância Sanitária. Quanto ao registro da última visita realizada pela Vigilância Sanitária no estabelecimento, 80% dos quiosques haviam recebido a fiscalização há mais de seis meses.

Os resultados das análises microbiológicas estão apresentados na Tabela 2. Verifica-se que todas as amostras de todos os quiosques (100%) atenderam ao padrão para coliformes 35°C e 45°C, estabelecido pela legislação vigente. O consumo de água precisa atender a padrões de potabilidade recomendados pelos órgãos regulamentadores e trata-se de uma ação de política pública para a prevenção de doenças e redução da mortalidade, por ser um solvente universal e utilizado na produção de alimentos (Mouchrek e Carvalho, 2016), como em quiosques de praia.

Castro (2013) observou que para as amostras analisadas em restaurantes, dois estabelecimentos apresentaram água fora do padrão microbiológico exigido pela legislação vigente. Mouchrek e Carvalho (2016), ao avaliar amostras de água de oito serviços de alimentação (sendo quatro lanchonetes e quatro restaurantes), observaram que em 75% (n=6) dos estabelecimentos visitados apresentavam água com qualidade microbiológica adequada.

A análise de bactérias heterotróficas não é um parâmetro exigido pela legislação brasileira relacionada à potabilidade de água para consumo humano, mas permite avaliar a qualidade da água utilizada tanto para cocção dos alimentos quanto para higienização de mãos, de superfícies e dos alimentos. Em estudo realizado por Vasconcelos et al. (2015), com água de bebedouros de três Campi da Universidade Federal do Ceará, foram analisadas amostras de água de cinco bebedouros, e obteve-se 6 amostras de águas contaminadas que correspondiam a 2 bebedouros, cujos números de bactérias heterotróficas encontradas estavam acima do limite permitido, sendo este achado diferente do registrado no presente estudo.

Segundo a Portaria 2914/2011 (Brasil, 2011), alterações bruscas ou acima do normal na contagem de bactérias heterotróficas necessitam ser averiguadas para identificação de irregularidade e providências devem ser tomadas para restaurar a integridade do sistema de distribuição, sendo indicado que não se ultrapasse 500 UFC/mL. Das amostras analisadas, 50% (m=6) apresentaram contagem superior ao recomendado para bactérias heterotróficas, sendo que metade (m=3) destas eram amostras provenientes de poços subterrâneos. Resultado semelhante foi observado por Silveira et al. (2011) que verificaram que em três escolas a água utilizada apresentou contagem superior a 500 UFC/mL.

Apesar do resultado observado no presente estudo, vale ressaltar que no Brasil entre 1999 e 2008 foram notificados 343 surtos relacionados ao consumo de água, sendo a origem deste desconhecida (Brasil, 2008). O controle da qualidade da água para consumo humano é um conjunto de ações exercidas de forma continuada, destinadas a averiguar se a água fornecida à

população é potável, de forma a assegurar a manutenção desta condição (Castro, 2013). A água que é utilizada para o consumo direto ou no preparo dos alimentos deve ser controlada independente das rotinas de manipulação dos alimentos (Anvisa, 2004). A água é rotineiramente utilizada para a lavagem de frutas e hortaliças com objetivo de obter alimento microbiologicamente seguro (Abreu et al., 2010). Sendo assim, é imprescindível que a água utilizada seja de qualidade.

Destaca-se ainda que 30% (n= 3) dos quiosques utilizavam águas provenientes de poços subterrâneos. Segundo Queiroz et al. (2002) populações que dependem de fontes alternativas, como poços, estão expostas a maiores contaminações. Apesar disso, no presente estudo nenhuma das amostras de poços foi considerada imprópria. Este resultado difere-se do observado por Araújo et al. (2013) que constataram que 75% dos poços avaliados apresentaram água imprópria para consumo devido à presença de coliformes a 35°C e coliformes 45°C acima do preconizado.

Tabela 2. Determinação de coliformes a 35°C, a 45°C e contagem de bactérias heterotróficas de amostras de águas coletadas em quiosques de praia, Vila Velha-ES.

Amostras de água	Quiosque	Origem	Coliformes a 35°C (NMP/100 mL)	Coliformes a 45°C (NMP/100 mL)	Contagem de Bactérias Heterotróficas (UFC/mL)
1	1	Rede de Abastecimento	< 1,0	< 1,0	1,0 x10 ²
2	1	Poço subterrâneo	< 1,0	< 1,0	1,3 x10 ³
3	2	Rede de Abastecimento	< 1,0	< 1,0	2,0 x10 ²
4	3	Rede de Abastecimento	< 1,0	< 1,0	6,0 x10 ²
5	4	Rede de Abastecimento	< 1,0	< 1,0	2,0 x10 ²
6	4	Poço subterrâneo	< 1,0	< 1,0	2,9 x10 ³
7	5	Rede de Abastecimento	< 1,0	< 1,0	5,0 x10 ²
8	6	Rede de Abastecimento	< 1,0	< 1,0	1,1 x10 ²
9	7	Rede de Abastecimento	< 1,0	< 1,0	2,1 x10 ²
10	8	Rede de Abastecimento	< 1,0	< 1,0	5,7 x10 ²
11	9	Poço subterrâneo	< 1,0	< 1,0	2,3 x10 ³
12	10	Rede de Abastecimento	< 1,0	< 1,0	1,2 x10 ³

* Padrão microbiológico para água para consumo humano no sistema de distribuição (reservatórios e rede) estabelecido pela Portaria 2914/2011: *Escherichia coli*- Ausência em 100 mL; Coliformes totais: Ausência em 100 mL em 95% das amostras examinadas (Sistemas ou soluções alternativas coletivas que abastecem a partir de 20.000 habitantes).

As águas extraídas por poços têm sido cada vez mais utilizadas para o consumo humano, pois são de fácil obtenção e custo, principalmente para pessoas que não tem acesso à rede pública de abastecimento. Porém, este tipo de abastecimento pode se tornar uma preocupação devido ao fato de muitas vezes estarem próximas às residências, onde podem ser contaminados por dejetos humanos e de animais (Volkweis et al., 2015). As principais causas de contaminação da água de poços estão relacionadas à entrada de impurezas por meio do procedimento de abertura superior do poço, contaminação na ocasião da retirada de água, infiltração de águas de enxurradas de locais próximos ao poço, fossa negra ou poço absorvente (Souza, 2012). Quiosques que utilizam água de poço sem o tratamento para garantir a potabilidade põem em risco à qualidade dos alimentos servidos (Portugal et al., 2015).

Destaca-se que a recusa dos demais quiosques quanto à participação da pesquisa e

autorização para as coletas possa estar relacionada à falhas no controle de qualidade de água reconhecidas pelos próprios responsáveis pelo estabelecimento.

Ao final do desenvolvimento da pesquisa foram apresentados os resultados das análises aos responsáveis pelos estabelecimentos e houve esclarecimento quanto à necessidade da manutenção da qualidade da água utilizada para promoção da saúde pública.

4. CONCLUSÃO

Os resultados obtidos a partir da lista de verificação indicam que a maioria dos estabelecimentos tem preocupação com a qualidade da água utilizada. A análise microbiológica das amostras de água não revelou resultados preocupantes, mas não se deve desconsiderar a necessidade do acompanhamento pelos órgãos competentes para verificação ao atendimento a legislação vigente.

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Avaliação sazonal e espacial da qualidade das águas superficiais da bacia hidrográfica do rio Longá, Piauí, Brasil

ARTICLES doi:10.4136/ambi-agua.2054

Received: 01 Dec. 2016; Accepted: 05 Jan. 2018

**Waneska Maria Vasconcelos Medeiros^{1*}; Carlos Ernando da Silva²;
Ruceline Paiva Melo Lins³**

¹Universidade Federal do Piauí (UFPI), Teresina, PI, Brasil
Programa de Pós-Graduação em Desenvolvimento e Meio Ambiente (PRODEMA)
E-mail: wkvasconcelos@gmail.com

²Universidade Federal do Piauí (UFPI), Teresina, PI, Brasil
Departamento Recursos Hídricos, Geotecnia e Saneamento Ambiental (DRHGSA)
E-mail: carlosernando@gmail.com

³Universidade Federal do Piauí (UFPI), Parnaíba, PI, Brasil
Departamento de Ciências Biológicas. E-mail: rmlins@ufpi.edu.br

*Autor correspondente

RESUMO

Este artigo teve como objetivo avaliar a qualidade das águas superficiais da bacia hidrográfica do rio Longá no Estado do Piauí, Brasil. Sete pontos foram monitorados, com base na proximidade de estações meteorológicas e acessibilidade, para obter melhores caracterizações espaciais e de ocupação da bacia hidrográfica. As amostras de água foram coletadas mensalmente (01/2015-12/2015). Foram medidas as variáveis: temperatura, pH, turbidez, condutividade elétrica, sólidos totais, fósforo total, nitrato, oxigênio dissolvido, demanda bioquímica de oxigênio (DBO) e *Escherichia coli* (*E. coli*). Os resultados foram avaliados individualmente e comparados aos padrões brasileiros para águas doces de classe 2, conforme Resolução nº 357/2005 do Conselho Nacional do Meio Ambiente (CONAMA). Os dados foram avaliados utilizando-se análises multivariadas (agrupamento e análise de componentes principais - ACP). As variáveis *E. coli*, pH, turbidez, nitrato, DBO e condutividade elétrica variaram entre os dois períodos analisados (seco e chuvoso). As variáveis DBO, *E. coli* estiveram em desacordo com os padrões do CONAMA nos pontos urbanos P2, P3 e P5, devido à poluição difusa observada no período chuvoso. O agrupamento mostrou uma tendência espacial, apresentando dois grupos distintos (rural e urbano). A ACP identificou quatro componentes principais que explicaram uma variação de 58,64% nos dados. O Componente 1 (CP1) refletiu uma contribuição de poluentes relacionados à poluição difusa de áreas agrícolas e urbanas. O Componente 2 (CP2) foi fortemente associado à poluição, especialmente por esgoto doméstico não tratado. As outras ACPs também refletiram pressões de atividades antropogênicas nos corpos d'água.

Palavras-chave: bacias hidrográficas, monitoramento ambiental, qualidade da água.

Seasonal and spatial evaluation of the surface water quality in the Longá river watershed, Piauí, Brazil

ABSTRACT

This article evaluates the quality of the surface waters in the Longá River watershed in the State of Piauí, Brazil. Seven points were monitored, based on their proximity to meteorological stations and accessibility, to obtain better spatial and land-use characterizations of the watershed. Water samples were collected monthly (01/2015–12/2015). The variables temperature, pH, turbidity, electrical conductivity, total solids, total phosphorus, nitrate, dissolved oxygen, biochemical oxygen demand (BOD) and *Escherichia coli* (*E. coli*) were measured. The results were evaluated individually and compared to Brazilian standards for Class 2 fresh waters, according to the National Environment Council's (CONAMA) Resolution 357/2005. The data were evaluated using multivariate analyses (clustering and principal component analysis - PCA). *E. coli*, pH, turbidity, nitrate, BOD, and electrical conductivity varied between the two periods analyzed (dry and rainy). The BOD and *E. coli* variants were noncompliant with the CONAMA standards at urban points P2, P3, and P5, because of nonpoint source pollution (NPS) during the rainy season. Clustering showed a spatial trend, presenting two distinct groups (rural and urban). PCA identified four main components that explained a 58.64% change in the data. Component 1 (CP1) reflected a contribution of pollutants related to NPS from agricultural and urban areas, in addition to environmental factors. CP2 was strongly associated with pollution, especially by untreated sewage releases. The other CPs also reflect pressures from anthropogenic activities on the water bodies.

Keywords: environmental monitoring, water quality, watershed.

1. INTRODUÇÃO

Nas últimas décadas, a qualidade da água dos rios, lagos e reservatórios têm passado por alterações que comprometem diretamente a manutenção dos usos múltiplos dos recursos hídricos, assegurados por força da lei (Arruda et al., 2015). Nos ecossistemas aquáticos, a heterogeneidade da qualidade da água pode ser influenciada principalmente pela contribuição natural da bacia hidrográfica (conhecidas como *background*, concentrações naturais afetadas pelas características geológicas e pedológicas do local) e pela magnitude dos impactos antrópicos como o consumo de água, lançamento de efluentes domésticos e industriais, escoamento superficial de áreas urbanas e rurais. Do ponto de vista temporal, as oscilações de qualidade da água podem refletir as formas de uso e ocupação do solo (Kalscheur et al., 2012; Cunha et al., 2013).

Diversos estudos apontam a agricultura e outras atividades agropecuárias, como uma atividade de alto potencial degradador, sendo responsáveis pela elevação da concentração de nutrientes nas águas superficiais, como por exemplo, fósforo e nitrogênio, bem como o uso e o manejo do solo em áreas agrícolas acarretam alterações na qualidade da água (Menezes et al., 2016). Em áreas urbanas e industrializadas é comum a poluição orgânica associada ao uso e ocupação do solo (Damasceno et al., 2015). Segundo Pompêo et al. (2011), a maioria dos rios nas cidades brasileiras está substancialmente degradada. Sendo assim, as características físicas, químicas e biológicas de um curso d'água refletem tanto a configuração geológica quanto os insumos da bacia hidrográfica circundante (Voza et al., 2015). Dessa forma, o monitoramento das variáveis de qualidade da água pode ser considerado como um dos pré-requisitos para o sucesso de qualquer sistema de gestão das águas, já que o monitoramento possibilita a obtenção de informações necessárias, a atualização dos bancos de dados, e o acompanhamento do

processo de uso dos corpos hídricos, que apresenta os efeitos sobre as características qualitativas das águas, visando subsidiar as ações de controle ambiental (Carvalho et al., 2015).

No entanto, na região Nordeste do Brasil, são poucas as séries históricas de informações quanto às vazões nos cursos de água e praticamente inexistentes aquelas relativas à qualidade da água. No Estado do Piauí, particularmente, o maior problema enfrentado consiste exatamente na insuficiência de dados de qualidade de água superficiais das bacias hidrográficas (Piauí, 2010). Entre as bacias hidrográficas do Estado do Piauí, a do rio Longá chama a atenção por estar em uma região de grande importância social, econômica e ambiental. Localizada na região norte do Estado, em uma área de transição dos biomas Caatinga e Cerrado, tem como principais usos do solo o extrativismo vegetal (carnaúba e babaçu), a pecuária de subsistência e a agricultura (Brasil, 2002; Sousa e Araújo, 2009; Piauí, 2010).

As questões que nortearam este estudo foram: como se encontra a qualidade da água da bacia hidrográfica do rio Longá, considerando a sua variação sazonal e espacial? Esse corpo hídrico está de acordo com os limites estabelecidos pela Resolução CONAMA 357/2005 (CONAMA, 2005)? Tendo em vista que os usos múltiplos da água e as atividades antrópicas realizadas em uma bacia hidrográfica causam significativas alterações na qualidade dos recursos hídricos e, a pouca informação sobre a qualidade das águas da bacia hidrográfica do rio Longá, o presente estudo teve como objetivo avaliar a variação sazonal e espacial da qualidade da água da bacia hidrográfica do rio Longá, Piauí.

2. MATERIAL E MÉTODOS

2.1. Caracterização da área de estudo

A bacia hidrográfica do rio Longá está situada na porção norte do Estado do Piauí. Ela estende-se entre as coordenadas 3°03' e 5°16' de latitude sul e 41°04' e 42°43' de longitude, a oeste de Greenwich, correspondendo 8,99% da área total do Estado piauiense. Esta bacia tem como rio principal o rio Longá que nasce na localidade Lagoa do Mato, no município de Alto Longá, a uma altitude de 150 m. Trata-se de um rio perene no médio e baixo curso e alimenta inúmeras lagoas de pequeno porte. Possui uma área de drenagem de 22.623 km² abrangendo um total de 26 sedes municipais piauienses, nas quais vive uma população de aproximadamente 480 mil habitantes (IBGE, 2010).

Segundo a classificação de Köppen, o clima predominante da região é do tipo tropical quente úmido (Aw'), com chuvas de verão/outono como resultado dos deslocamentos sazonais da Convergência Intertropical (CIT), sob a forma de massa de ar convectiva. A estação chuvosa dessa região estende-se de janeiro a maio, sendo o trimestre fevereiro/março/abril o mais chuvoso e, agosto/setembro/outubro, o mais seco (Piauí, 2010).

A cobertura vegetal da bacia do rio Longá apresenta na porção leste da bacia uma área de tensão ecológica, com espécies da caatinga arbustiva, correspondendo a 25% da cobertura vegetal da região. Na região central encontra-se a vegetação do tipo cerrado que corresponde a 50% da vegetação do território da bacia do rio Longá. Na região sudoeste encontra-se uma vegetação do tipo floresta decidual, onde se observa espécies vegetais como o babaçu e a carnaúba, que são de grande importância econômica para a região e ainda, o buriti e o tucum (Piauí, 2010).

As atividades econômicas mais desenvolvidas na bacia hidrográfica do rio Longá, estão relacionadas às atividades de extrativismo vegetal, com a extração do pó da carnaúba e a amêndoa do babaçu (para produção de óleo); a extração de madeiras com preponderância da lenha para utilização em fornos industriais (padarias, cerâmicas, extração de óleos, sabão, entre outras); a extração de madeira para obtenção de matéria-prima para construção de casas, cercas, currais e outros usos. Também existe a criação de bovinos, suínos, caprinos e ovinos, que na sua grande maioria são criados por pequenos e médios proprietários que utilizam esses animais

como forma de subsistência e de comercialização da carne e do couro. Entre os municípios produtores estão Batalha e Campo Maior. Aliada à pecuária encontram-se os projetos de irrigação que configuram um importante instrumento econômico em alguns municípios ao longo do curso do rio Longá, como é o caso do município Barras no cultivo de melancia e os municípios Alto Longá e Buriti dos Lopes no cultivo do arroz (Sousa e Araújo, 2009).

2.2. Estratégias de amostragem e metodologias analíticas

Para as amostragens foram selecionados sete locais de coleta, sendo quatro ao longo do rio principal Longá e os demais localizados em três afluentes: rio Maratoã, rio dos Matos e rio Piracuruca. Os pontos foram escolhidos levando em consideração a presença de estações meteorológicas e a acessibilidade e; também visando obter uma melhor representatividade espacial e de ocupação da bacia. Os locais foram denominados P1, P2, P3, P4, P5, P6 e P7, sendo P1 mais próximo à nascente e P7 próximo ao exutório da bacia (Tabela 1). Os locais escolhidos para o monitoramento P2, P3 e P5, estão localizados em centros urbanos dos municípios de Barras, Esperantina e Piracuruca, respectivamente. Já P1, P4, P6 e P7 estão localizados na zona rural dos municípios de Barras, Batalha, São José do Divino e Buriti dos Lopes, respectivamente. A localização da bacia do rio Longá, os pontos de coleta de água e as estações meteorológicas consultadas são ilustradas na Figura 1.

As campanhas de amostragem foram realizadas com a periodicidade mensal de janeiro a dezembro de 2015. Alíquotas de água foram coletadas na subsuperfície no ponto central da seção transversal do rio, à profundidade de 20 cm, aproximadamente. As variáveis de qualidade de água investigadas foram: temperatura, oxigênio dissolvido (OD), turbidez, potencial hidrogeniônico (pH), condutividade elétrica, sólidos totais, demanda bioquímica de oxigênio (DBO), nitrato, fósforo total e *Escherichia coli* (*E. coli*).

Tabela 1. Posição geográfica dos pontos de coleta.

Pontos	Rio	Município	Latitude	Longitude	Localização
P1	Longá	Barras	04°24'34.92" S	42°10'53.04" W	rural
P2	Maratoã	Barras	04°14'16.08" S	42°18'19.08" W	urbana
P3	Longá	Esperantina	03°54'10.30" S	42°13'44.60" W	urbana
P4	Matos	Batalha	04°02'42.52" S	41°53'45.13" W	rural
P5	Piracuruca	Piracuruca	03°56'13.38" S	41°43'01.63" W	urbana
P6	Longá	São José do Divino	03°43'26.04" S	41°58'27.12" W	rural
P7	Longá	Buriti dos Lopes	03°19'09.85" S	41°53'45.40" W	rural

A temperatura e a concentração do oxigênio dissolvido foram medidas *in situ* utilizando-se um medidor portátil Oxímetro AT 160 Microprocessado da Al Fakite. Para a determinação das demais variáveis foram coletadas amostras de água e armazenadas em frascos de vidro e polietileno. Para a análise bacteriológica utilizou-se sacos esterilizados. As amostras foram conservadas por meio de refrigeração (em caixas de isopor com gelo) e transportadas para o Laboratório de Saneamento Ambiental da Universidade Federal do Piauí. As análises dos parâmetros de qualidade da água foram realizadas segundo metodologias descritas no APHA et al. (2005) (Tabela 2).

Para avaliar a variação da qualidade da água nos períodos seco e chuvoso buscou-se analisar o regime de sazonalidade da região. A série pluviométrica com os dados de precipitação diária da bacia hidrográfica do rio Longá, no período de janeiro a dezembro de 2015, foi obtida na Agência Nacional de Águas (ANA) através do sistema Hidroweb (ANA, 2015) e no Instituto Nacional de Meteorologia (INMET, 2015). Os dados foram coletados das estações Fazenda Alegria (34930000) e Pedrinhas (34936000) localizadas no município de Barras, Piracuruca (34976000) localizada no município de Piracuruca, Tinguis (34980000) localizada no

município de São José do Divino, Piripiri (OMM: 82480) localizada no município de Piripiri e Esperantina (OMM: 82298) localizada no município de Esperantina.

Figura 1. Mapa de localização da bacia hidrográfica do rio Longá, locais de amostragem da água e estações meteorológicas.

Tabela 2. Metodologia da determinação das variáveis de qualidade da água.

Parâmetros	Método
Temperatura da água	Filamento de mercúrio
Condutividade elétrica	Condutimétrico
Turbidez	Turbidimétrico
Sólidos totais	Gravimétrico
pH	Eletrométrico
Fosfato	Espectrofotométrico
Nitrato	Espectrofotométrico
Demanda Bioquímica de Oxigênio	Winkler/incubação
Oxigênio dissolvido	Eletrométrico
<i>Escherichia coli</i>	Enzimático substrato definido

Para averiguar a conformidade do enquadramento dos rios da bacia hidrográfica do rio Longá, os resultados das análises foram confrontados com os parâmetros estabelecidos pela Resolução CONAMA n° 357/2005 (CONAMA, 2005). Após a comparação dos dados foram analisadas as diferenças espaciais e temporais das variáveis.

2.3. Análise estatística

Para obter o perfil das variáveis de qualidade da água foi utilizada a estatística descritiva (média, mediana, mínimo e máximo) e para testar as diferenças entre pontos e períodos sazonais foi utilizado o teste não-paramétrico Kruskal-Wallis, com nível de significância de 5%. Para

quantificar o grau de associação entre variáveis da qualidade da água os dados foram submetidos a uma análise de correlação de Spearman.

O conjunto de dados de qualidade da água da bacia hidrográfica do rio Longá foi submetido à avaliação por meio de análises multivariadas, empregando as técnicas de análises de agrupamento e para a realização da análise fatorial (AF), adotou-se o método da análise de componentes principais (ACP). A adequabilidade dos dados quanto à estrutura da AF foi avaliada por meio do teste de esfericidade de Bartlett e da medida de adequabilidade da amostra de Kaiser-Meyer-Olkin (KMO) (Hair Junior et al., 2009). A estimação do número de CP a serem retidos foi determinada pelo critério de Kaiser (Kaiser, 1958), no qual consiste em incluir somente componentes cujos autovalores sejam superiores a 1. Adotou-se o procedimento de rotação ortogonal da matriz das cargas fatoriais, o que possibilita melhor interpretação dos fatores ao redistribuir a variância explicada pelas componentes, não alterando a variância acumulada do conjunto de componentes. A utilização da rotação ortogonal pelo método Varimax permite um melhor ajuste ao modelo fatorial possível de explicação, sendo frequentemente utilizada em estudos de qualidade de água e processos hidrológicos (Rocha e Pereira, 2016). O programa utilizado nas análises estatísticas multivariadas foi o SPSS versão 20.

3. RESULTADOS E DISCUSSÃO

3.1. Análise da qualidade da água da bacia

Com relação à precipitação e à temperatura do ar mensal na bacia hidrográfica do rio Longá no ano de 2015 (Figura 2), os meses fevereiro, março e abril foram classificados como período chuvoso, onde a precipitação média foi de 185 mm mês⁻¹ e os meses de maio a janeiro foram classificados como período seco com precipitação média de 32 mm mês⁻¹.

Figura 2. Valores médios mensais da precipitação pluviométrica e temperatura do ar obtidos das estações meteorológicas inseridas na bacia hidrográfica do rio Longá, no período entre janeiro e dezembro de 2015.

As Figuras 3 e 4 ilustram os *boxplots* da distribuição sazonal e espacial, respectivamente, construídos a partir dos dados obtidos nas análises das variáveis de qualidade da água. Durante o período de coleta houve variações nos valores obtidos por meio das análises laboratoriais para algumas variáveis em função da sazonalidade e também em função da localização dos pontos de coleta.

Figura 3. Variação sazonal das variáveis DBO (A), *E. coli* (B), turbidez (C), pH (D), condutividade (E), nitrato (F), temperatura (G), sólidos totais (H), OD (I) e fósforo total (J), durante o período seco e chuvoso (2015). Limites estabelecidos pela Res. CONAMA 357/2005.

Figura 4. Variação espacial das variáveis DBO (A), *E. coli* (B), turbidez (C), pH (D), condutividade (E), nitrato (F), temperatura (G), sólidos totais (H), OD (I) e fósforo total (J), no período de janeiro a dezembro de 2015. Limites estabelecidos pela Res. CONAMA 357/2005.

A Figura 3A apresenta a variação da concentração da matéria orgânica em termos de DBO nos períodos seco e chuvoso. Para o período seco, a mediana foi de 1,66 mg L⁻¹ com concentrações variando de 0,85 mg L⁻¹ a 2,21 mg L⁻¹ e o período chuvoso apresentou mediana de 2,88 mg L⁻¹, com valores mínimo de 1,8 mg L⁻¹ e máximo de 7,72 mg L⁻¹. Observa-se que no período chuvoso apresentou valores mais elevados na concentração da matéria orgânica e também maior dispersão dos dados quando comparados com o período seco. O teste Kruskal-Wallis inferiu que houve diferença estatística significativa entre os dois períodos ($H=2,941$ e $p=0,086$). Em 10% das amostras analisadas para essa variável houve valores acima do recomendado pela Resolução CONAMA nº 357/05 de 5 mg L⁻¹. Melhores resultados em função da concentração da matéria orgânica foram encontrados em P6 e P7, onde apresentaram medianas de 1,00 e 0,78 mg L⁻¹, respectivamente, com 75% das amostras abaixo de 1,41 mg L⁻¹. Os pontos P3 e P5 foram os que apresentaram os piores resultados com valores máximos de 7,6 mg L⁻¹ e 5,67 mg L⁻¹ de concentração da matéria orgânica, expressa em DBO (Figura 4A). O aumento da DBO ocorreu logo após os primeiros registros de precipitação, incidindo na diminuição dos seus valores após as primeiras chuvas, fato observado em P2, P3 e P5, que estão localizados nos centros urbanos das cidades de Barras, Esperantina e Piracuruca, respectivamente. Esse comportamento é atribuído à poluição difusa, característica de cidades onde não há sistema de saneamento, fato ocorrido na maioria das cidades do Estado do Piauí. Nos pontos P4, P6 e P7, localizados na zona rural dos municípios de Batalha, São José do Divino e Buriti dos Lopes, respectivamente, apresentaram valores elevados para DBO, acima do limite permissível, apenas no mês de fevereiro. Observou-se que neste mês houve registro de precipitação pluvial nas 72 horas que antecederam a coleta em todos os pontos monitorados. Os dados apresentados para a DBO indicam que a qualidade da água da bacia do rio Longá deteriorou no período chuvoso. A DBO apresentou uma correlação significativa positiva com a variável temperatura ($p=0,23$) (Tabela 3).

Tabela 3. Matriz de correlação das variáveis de qualidade da água da bacia hidrográfica do rio Longá.

	Temperatura	pH	Condutividade	Turbidez	Sólidos totais	OD	DBO	Nitrato	Fósforo total	<i>E. coli</i>
Temperatura	1,00									
pH	0,23	1,00								
Condutividade	-0,34	-0,04	1,00							
Turbidez	-0,03	-0,05	-0,45	1,00						
Sólidos totais	0,09	0,31	0,03	0,16	1,00					
OD	0,13	-0,02	0,07	0,06	0,00	1,00				
DBO	0,23	-0,14	0,00	0,10	-0,21	0,12	1,00			
Nitrato	-0,10	0,12	0,05	0,26	0,07	-0,03	0,04	1,00		
Fósforo total	-0,10	-0,10	-0,08	0,29	-0,07	-0,08	0,14	0,20	1,00	
<i>E. coli</i>	0,22	-0,02	-0,15	-0,14	-0,28	0,10	0,10	0,08	0,09	1,00

Nota: Os valores em negrito são estatisticamente significativos para $p < 0,05$.

Para a contagem de células de *Escherichia coli* (Figura 3B), entre as campanhas realizadas os valores mais altos foram observados no período chuvoso, com máxima de 1.380 NMP 100 mL⁻¹. Células de *E. coli* foram registradas em 98,8% das amostras analisadas, mas somente

em P2, P3 e P5 apresentaram amostras com valores maiores do que o limite de 1000 NMP 100 mL⁻¹, recomendado pela legislação para rios Classe 2, que estão representados pelos *outliers* na Figura 4B. Os resultados da determinação de *E. coli* exibiu um comportamento semelhante às concentrações de DBO, apresentando valores elevados de contagem de *E. coli* nos pontos localizados em área urbana e coincidindo com período chuvoso. Em P2, o valor de *E. coli* ultrapassou o limite permissível no mês de março, enquanto que em P3 ultrapassou nos meses de março e julho e em P5 nos meses de março e setembro. Esses resultados sugerem contribuições distintas de *E. coli*. Os valores elevados nos meses de março (em P5) e julho (em P3) não estão relacionados com a precipitação pluviométrica. Acredita-se que tal fato se deve às fontes pontuais de lançamento de esgotos sanitários. Conforme a análise de variância, a variável *E. coli* apresentou diferenças estatísticas significativas entre os dois períodos estudados ($H=10,442$ e $p=0,001$) e também apresentou diferenças estatísticas significativas entre os pontos monitorados ($H=21,064$ e $p=0,002$). Resultado semelhante foi encontrado por Souza e Gastaldini (2014) ao estudar a qualidade da água da bacia hidrográfica do rio Vacaraí-Mirim no Rio Grande do Sul e por Menezes et al. (2016) estudando a relação entre o uso e ocupação do solo com a qualidade da água na bacia hidrográfica do Ribeirão Vermelho em Minas Gerais, onde obtiveram maiores valores da variável *E. coli* nas estações de coleta com influência da urbanização. Na análise de correlação de Spearman (Tabela 3) a variável *E. coli*, apresentou correlação significativa positiva com a temperatura ($p=0,22$) e correlação negativa com a variável sólidos totais ($p=-0,28$).

A turbidez (Figura 3C) apresentou mediana de 7,9 e 75 UNT no período seco e chuvoso, respectivamente. Em relação ao intervalo interquartil o período chuvoso apresentou maior variação (103,5 UNT) em relação ao período seco (57,7 UNT). Os pontos P1 e P7 foram os que apresentaram os maiores valores para turbidez, com 83% e 42% das amostras com valores acima do limite permitido de 100 UNT, conforme Resolução CONAMA nº 357/2005 (Figura 4C). Houve diferença estatística significativa entre os períodos seco e chuvoso ($H=4,887$ e $p=0,027$) e diferença extremamente significativa entre os pontos analisados ($H=61,559$ e $p<0,0001$). Foi possível observar em campo que P1 e P7 possuem características semelhantes quanto à geologia, como também apresentaram áreas desprovidas de vegetação nativa, explicando a semelhança no comportamento da turbidez durante o período monitorado. Os valores elevados de turbidez nesses pontos indicam processo de erosão, cuja origem está relacionada ao manejo inadequado do solo pela atividade agropecuária, aliada à ausência de vegetação nas margens dos cursos d'água. Haddad e Magalhães (2010) apontaram diferenças espaciais em relação à concentração da turbidez, mostrando como áreas críticas aquelas desprovidas de vegetação ripária, e que contribuem para valores elevados de turbidez. A variável turbidez correlacionou-se negativamente com a variável condutividade elétrica ($p=-0,45$) e positivamente com fósforo total ($p=0,29$) e nitrato ($p=0,26$).

O pH (Figura 3D) apresentou mediana de 7,0 e 6,9 no período seco e chuvoso, respectivamente, com máxima de 7,2 no período seco e mínimo de 6,8 no período chuvoso. Damasceno et al. (2015) no estudo sobre a avaliação sazonal da qualidade da água no rio Amazonas, no Amapá, também observou que no período chuvoso apresentou águas mais ácidas quando comparado ao período seco, podendo estar associada ao aumento do teor de ácidos orgânicos. O pH em todos os pontos monitorados apresentou valores dentro do intervalo de 6 a 9, conforme descrito na legislação ambiental para rios de Classe 2 (Figura 4D). Valores semelhantes foram observados por Passig et al. (2015) ao estudar a qualidade da água da bacia hidrográfica do rio Mourão no Paraná. A análise estatística apresentou diferença significativa entre os períodos avaliados ($H=5,184$ e $p=0,023$), mas não apresentou diferença entre os pontos monitorados. A análise de correlação (Tabela 3) apontou uma correlação significativa positiva do pH com sólidos totais ($p=0,31$) e temperatura ($p=0,23$).

A condutividade elétrica (Figura 3E) apresentou mediana $132,2 \mu\text{S cm}^{-1}$ e $80,4 \mu\text{S cm}^{-1}$ no período seco e chuvoso, respectivamente. Em relação ao intervalo interquartil, o período seco apresentou variação um pouco maior ($73 \mu\text{S cm}^{-1}$) que o período chuvoso ($40,6 \mu\text{S cm}^{-1}$), mas o teste de Kruskal-Wallis afirma que não houve diferença estatística significativa para essa variável em relação aos dois períodos avaliados ($H=3,249$ e $p=0,071$). Já entre os pontos a análise de variância apresentou uma diferença estatística significativa ($H=51,096$ e $p<0,0001$). Observou-se valores elevados da condutividade elétrica em P4, P5, P6 e P7 (Figura 4E), apresentando as seguintes medianas, respectivamente: $194,8 \mu\text{S cm}^{-1}$, $147,6 \mu\text{S cm}^{-1}$, $111,5 \mu\text{S cm}^{-1}$ e $99,7 \mu\text{S cm}^{-1}$. Os valores elevados para a condutividade elétrica são provavelmente devido às contribuições distintas. As áreas urbanas onde há lançamento de efluentes domésticos sem tratamento, contribuem para o aumento da condutividade elétrica, tal qual a situação observada em P5, que está localizado na cidade de Piracuruca. Resultado semelhante foi observado por Girardi et al. (2016) ao estudar a qualidade da água da bacia hidrográfica do rio Cubatão do Sul em Santa Catarina e por Mateus et al. (2015) estudando a qualidade da água do rio Uberaba em Minas Gerais. Os valores elevados para condutividade elétrica em P7 situado em área rural com grande atividade de rizicultura, pode ser atribuído devido ao transporte de compostos iônicos utilizados na agricultura, tais como potássio, fósforo e nitrogênio. Viswanathan et al. (2015) estudando a sazonalidade da qualidade da água do rio Thur na Suíça, encontraram os maiores valores de condutividade elétrica no período seco, dando o motivo o solo rico em solutos acumulado e capturado durante as precipitações recorrentes do período chuvoso. Os valores elevados de condutividade elétrica em P4 e P6, localizados em áreas rurais, também podem estar relacionados com as características naturais da bacia hidrográfica do rio Longá. O intemperismo das rochas pode contribuir para tal fenômeno. Esteves (2011) descreve que em regiões tropicais, os valores de condutividade nos ambientes aquáticos estão mais relacionados com as características geoquímicas e com as condições climáticas da região onde se localizam. A condutividade elétrica (Tabela 3) correlacionou-se negativamente com as variáveis turbidez ($\rho=-0,45$) e temperatura ($\rho=-0,34$).

A concentração do íon nitrato apresentou um aumento em seu limite superior, de $0,191 \text{ mg L}^{-1}$ para $0,273 \text{ mg L}^{-1}$ e medianas de $0,72 \text{ mg L}^{-1}$ para $0,93 \text{ mg L}^{-1}$, o primeiro e terceiro quartil, no período chuvoso (Figura 3F). Apesar do período chuvoso apresentar valores mais elevados, não houve diferença estatística significativa entre os dois períodos analisados ($H=3,571$ e $p=0,059$) e nem entre os pontos monitorados ($H=8,170$ e $p=0,226$). Em todas as amostras recolhidas os resultados foram inferiores a 10 mg L^{-1} , valor definido na Resolução CONAMA 357/2005 para rios de classe 2, estando a bacia hidrográfica do rio Longá em conformidade com a dita legislação (Figura 4F).

A Figura 3G ilustra a variação da temperatura da água nos pontos de amostragem durante os períodos seco e chuvoso, os valores mínimo e máximo, mediana e quartis inferior e superior das amostras. A análise de variância indicou que não houve diferença estatística significativa ($H=0,378$ e $p=0,539$) entre os períodos, oscilando no período seco com máxima de $32,4^{\circ}\text{C}$ e no período chuvoso na faixa de $32,2^{\circ}\text{C}$ (Figura 4G).

Os sólidos totais (Figura 3H) apresentaram medianas de $275,6 \text{ mg L}^{-1}$ e $228,0 \text{ mg L}^{-1}$ nos períodos seco e chuvoso, respectivamente. Portanto, não houve diferença estatística significativa entre os períodos ($H=0,659$ e $p=0,417$) e nem entre os pontos monitorados ($H=11,653$ e $p=0,070$). As maiores produções de sedimentos foram observadas nas estações de coleta com características rurais que são P1, P4 e P7, apresentando os maiores valores de medianas, 310 mg L^{-1} , 340 mg L^{-1} e 240 mg L^{-1} , respectivamente (Figura 4H). Acredita-se que seja devido às práticas agrícolas caracterizadas pelo plantio próximo ao leito do rio, bem como, criação de animais com desmatamento da vegetação nativa, práticas que aumentam o risco de erosão e a perda de solo. Já o ponto P3 foi o que apresentou o maior valor observado para essa variável, apresentando concentração máxima de 860 mg L^{-1} no mês de janeiro. Essa estação de

coleta está localizada na zona urbana no município de Esperantina. Característica semelhante foi observado por Menezes et al. (2016) estudando a relação entre os padrões de uso e ocupação do solo e a qualidade da água na bacia hidrográfica do Ribeirão Vermelho em Minas Gerais, onde observaram que os maiores valores de sólidos na água (sólidos totais e turbidez) são em seções com forte ocupação agrícola e urbana. Observou-se que 14,3% das amostras coletadas apresentaram valores acima do limite permitido estabelecida pela Resolução CONAMA nº 357/2005 de 500 mg L⁻¹, sendo P1 e P3 os que apresentaram maior frequência em desacordo, 25% cada e apenas P2 não apresentou amostras fora dos padrões estabelecidos.

Para o oxigênio dissolvido (Figura 3I) foi observado que os períodos seco e chuvoso apresentaram medianas de 7,9 mg L⁻¹ e 8,0 mg L⁻¹, respectivamente. Não houve diferenças estatísticas significativas entre os períodos ($H=0,059$ e $p=0,808$) e entre os pontos ($H=8,435$ e $p=0,208$) para essa variável. A mediana, em todos os pontos monitorados, esteve acima do limite exigido pela legislação ambiental (CONAMA, 2005) para rios classe 2 (5 mg L⁻¹), embora 7,1% das amostras apresentaram valores inferiores. Os menores valores de OD foram observados em áreas urbanas (P2, P3 e P5), que apresentaram 4,7 mg L⁻¹, 4,3 mg L⁻¹ e 3,8 mg L⁻¹, respectivamente (Figura 4I).

Com relação aos resultados observados em períodos distintos, o fósforo total (Figura 3J), expressou medianas 0,027 mg L⁻¹ e 0,022 mg L⁻¹ nos períodos seco e chuvoso, respectivamente. Apesar do intervalo interquartil no período chuvoso apresentar maior variação (0,48 mg L⁻¹) em relação ao período seco (0,39 mg L⁻¹), essa variável não apresentou diferença estatística significativa entre os dois períodos ($H=0,904$ e $p=0,342$), mas apresentou diferença significativa entre os pontos monitorados ($H=13,111$ e $p=0,041$). Considerando que a maior concentração de fósforo coincidiu com o período chuvoso (fonte difusa), possivelmente sua origem pode ser da lixiviação do solo pelas águas das chuvas. Apenas P1 apresentou mediana acima do limite exigido pela Resolução CONAMA nº 357/2005 de 0,030 mg L⁻¹. Os maiores valores não *outliers* foram observados em P1 e P7, que apresentaram 0,077 mg L⁻¹ e 0,070 mg L⁻¹, respectivamente (Figura 4J).

3.2. Análises estatísticas multivariadas

Com o intuito de avaliar a tendência espacial, foi realizada a análise multivariada de agrupamento com os dados de qualidade de água. O procedimento de agrupamento gerou dois grupos distintos, com características semelhantes quanto ao uso e ocupação do solo (Figura 5A). O Grupo 1 correspondente à área rural e caracterizado pelas seções contendo os pontos P1, P4, P6 e P7 e o Grupo 2 correspondente às áreas urbanas e caracterizado pelas seções contendo os pontos P2, P3 e P5. Em relação às variáveis, o procedimento de agrupamento gerou quatro grupos distintos com características semelhantes em relação aos tipos de contaminação (Figura 5B). O Grupo 1 correspondente à *E. coli*, indicativo de contaminação por meio de despejos de efluentes domésticos *in natura*; o Grupo 2 correspondente aos sólidos totais; o Grupo 3 correspondente à condutividade elétrica e turbidez, indicativo de poluição difusa por material oriundo de áreas agrícolas e urbanas e o Grupo 4 correspondente às variáveis nitrato, fósforo total, DBO, pH, OD e temperatura.

No teste de esfericidade de Bartlett ($p < 0,005$) foi possível descartar a hipótese nula, verificando a existência de correlações significativas entre as variáveis. Para o índice de adequação da amostra (KMO) o resultado encontrado foi de 0,507, o que permite a aplicação da análise fatorial.

Figura 5. Dendrograma do agrupamento das seções monitoradas (A) e das variáveis analisadas (B).

A ACP realizada para as dez variáveis revelou a existência de quatro componentes principais (CP), sendo que a variância acumulada foi de 58,64% para os dados de qualidade da água. A Tabela 4 apresenta a matriz rotacionada de pesos fatoriais que indica a contribuição que cada variável possui na componente principal.

Tabela 4. Cargas fatoriais com rotação das variáveis para os CP encontrados.

Parâmetros	Componente Principal			
	1	2	3	4
Condutividade	-0,80	0,01	0,02	0,21
Turbidez	0,60	0,00	-0,21	0,47
DBO	0,00	0,81	0,06	0,05
<i>E. coli</i>	0,02	0,50	-0,04	-0,16
Temperatura	0,36	0,15	0,55	-0,18
pH	-0,08	-0,27	0,49	0,10
Fósforo total	0,08	0,05	-0,38	0,08
OD	-0,02	0,10	0,20	0,05
Sólidos totais	0,06	-0,25	0,28	0,38
Nitrato	-0,07	-0,02	-0,03	0,30
Autovalor	1,74	1,53	1,48	1,12
% Variância explicada	17,37	15,28	14,83	11,16
% Variância acumulada	17,37	32,65	47,48	58,64

Nota: Método de rotação de variáveis VARIMAX com normalização de Kaiser.

A CP1 explicou 17,37% da variância total dos dados e teve como variável mais expressiva a condutividade elétrica cujo autovalor foi de -0,800 (Tabela 4). A variável turbidez também desta componente apresentou resultado expressivo de 0,600 e foi a que apresentou maior número de correlações (Tabela 4). A CP1 demonstra uma relação inversa entre as variáveis condutividade e turbidez. Situações como essas já foram registradas em outros estudos, como o de Arruda et al. (2015) pesquisando sobre a qualidade da água do reservatório Foz do Areia – Paraná e, Maimuna e Victor (2012), em rios da Nigéria. Segundos os autores, essa relação inversa ocorreu tanto no período seco como no período chuvoso. Sendo a condutividade a medida indireta de íons dissolvidos na água e a turbidez podendo estar associada à ocorrência de poluentes não iônicos, como matéria orgânica. Além do indicativo de poluição difusa por material oriundo de áreas agrícolas e urbanas da bacia hidrográfica do rio Longá, acredita-se que houve contribuição de fatores ambientais, pois como já mencionado, a composição geológica da região de estudo pode ter influenciado nos valores elevados para a variável turbidez.

A CP2 correspondeu a 15,28% da variação total dos dados para a qualidade da água, formada pelas variáveis DBO e *E. coli*. Dentre todas as componentes, a DBO foi a que apresentou resultado mais expressivo, com valor de 0,810. Esse resultado reforça a importância dessa variável, que é uma das mais utilizadas para indicação de qualidade da água (Rocha e Pereira, 2016). A associação dessas variáveis indica que as águas da bacia hidrográfica do rio Longá sofrem contaminação por meio de despejos de efluentes domésticos in natura. Considera-se justificada tal condição, pois não existe tratamento de esgoto nos municípios inseridos na bacia hidrográfica do rio Longá.

As demais CPs são formadas por variáveis menos expressivas, abaixo de 0,500 (exceto temperatura) e de modo geral, são resultados da pressão que as atividades antropogênicas exercem sobre os corpos hídricos. A CP3 explicou uma variação de 14,83% e as variáveis que a compõem são temperatura, pH e fósforo total, sendo o último apresentando uma correlação negativa. Acredita-se que a relação inversa entre os valores de pH e fósforo total seja devido à precipitação dos íons fosfatos presentes na água provocada pela elevação do pH. Esta

componente está relacionada com fontes de poluição antrópicas causadas pelo uso de fertilizantes nas atividades agrícolas. A CP4 apresentou uma correlação positiva com sólidos totais e nitrato, correspondendo a uma variação de 11,16% nos dados (Tabela 4). As variáveis significativas na quarta componente podem ser indicativas de fonte de poluição agrícola oriunda do escoamento superficial de insumos como fertilizantes utilizados nos projetos de irrigação. A correlação entre sólidos totais e nitrato também foi observada por Voza et al. (2015) estudando a qualidade da água do rio Danúbio, Sérvia.

4. CONCLUSÕES

Os corpos hídricos da bacia hidrográfica do rio Longá apresentaram qualidade satisfatória segundo os padrões estabelecidos pela legislação ambiental para rios de classe 2, sendo observadas uma variabilidade sazonal e espacial. A não conformidade das variáveis DBO e *E. coli* referentes aos limites estabelecidos pela Resolução CONAMA nº 357/2005 foi devido principalmente à poluição difusa observada no período chuvoso. A análise estatística multivariada indicou o agrupamento das variáveis conforme o uso e ocupação do solo. A análise de componentes principais identificou as variáveis condutividade elétrica, *E. coli*, DBO e turbidez como sendo as mais significativas na variabilidade da qualidade da água do rio Longá.

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Avaliação sazonal da qualidade das águas superficiais e subterrâneas na área de influência do Lixão de Salinópolis, PA

ARTICLES doi:10.4136/ambi-agua.2072

Received: 23 Dec. 2016; Accepted: 06 Feb. 2018

**Régia Simony Braz Da Silva^{1*}; Adriano Marlisom Leão de Sousa²;
Silvana do Socorro Veloso Sodré²; Maria Isabel Vitorino³**

¹Instituto Federal de Educação, Ciência e Tecnologia do Maranhão (IFMA), Porto Franco, MA, Brasil
Departamento de Ensino e Extensão (DEE). E-mail: regia.silva@ifma.edu.br

²Universidade Federal Rural da Amazônia (UFRA), Belém, PA, Brasil
Instituto Socioambiental e dos Recursos Hídricos (ISARH). E-mail: adriano.souza@ufra.edu.br,
silvana.veloso@ufra.edu.br

³Universidade Federal do Pará (UFPA), Belém, PA, Brasil
Instituto de Geociências (IG). E-mail: vitorino@ufpa.br

*Autor correspondente

RESUMO

O objetivo deste trabalho foi avaliar a sazonalidade da qualidade da água superficial e subterrânea nas proximidades do lixão de Salinópolis, situado na Vila de Cuilarana, por meio da caracterização da precipitação da região e da sua influência na composição físico-química e microbiológica das águas locais. Para isso, foram observados os dados dos acumulados mensais da precipitação local, medição da velocidade de infiltração no solo e medição da vazão dos rios Cachoeira e Teixeira. Foram selecionados os parâmetros físico-químicos e bacteriológicos: pH, oxigênio dissolvido (OD), temperatura da água, sólidos totais dissolvidos (TDS), turbidez, condutividade elétrica (CE), salinidade, amônia, nitrato, coliformes totais e *Escherichia coli*; e os metais: alumínio, cádmio, chumbo, cobre, cromo, ferro, manganês, mercúrio, níquel e zinco. Tanto as águas superficiais quanto as subterrâneas se apresentaram inadequadas para uso e consumo humano. Parâmetros como OD, ferro, alumínio, chumbo, mercúrio, coliformes totais e *E. coli* estão em desconformidade com as legislações vigentes. O período chuvoso influenciou negativamente a qualidade em águas superficiais. Em águas subterrâneas, parâmetros como amônia, nitrato, ferro, mercúrio e chumbo estiveram em maiores concentrações no período menos chuvoso; enquanto, CE, *E. coli*, coliformes totais e alumínio aumentaram suas concentrações no período chuvoso.

Palavras-chave: Cuilarana, precipitação, qualidade da água.

Seasonal evaluation of surface and groundwater quality in the area of influence of the Lixão de Salinópolis, PA

ABSTRACT

This work evaluated the seasonality of surface and groundwater quality in the vicinity of the Salinópolis dump, located in the Cuilarana village, by characterizing precipitation in the region and its influence on the physicochemical and microbiological composition of local waters. To accomplish this, data regarding monthly local precipitation were reviewed, and

measurements were taken of the rate of soil infiltration and the rate of flow of the Cachoeira and Teixeira Rivers. The physico-chemical and bacteriological parameters selected were pH, dissolved oxygen (OD), water temperature, total dissolved solids (TDS), turbidity, electrical conductivity (EC), salinity, ammonia, nitrate, total coliforms and *Escherichia coli*; and the metals aluminum, cadmium, lead, copper, chromium, iron, manganese, mercury, nickel and zinc. Both surface and groundwater were inadequate for human consumption and use. Parameters such as OD, iron, aluminum, lead, mercury, total coliforms and *E. coli* are not in compliance with current legislation in both surface and underground waters. The rainy season had a negative impact on surface water quality. In groundwater, parameters such as ammonia, nitrate, iron, mercury and lead were higher in the less rainy period, whereas EC, *E. coli*, total coliforms and aluminum increased their concentrations in the rainy period.

Keywords: Cuiarana, rainfall, water quality.

1. INTRODUÇÃO

A precipitação é um elemento climático importante na indução do comportamento e das características de outras variáveis meteorológicas, como temperatura do ar, umidade relativa e ventos (Nobre et al., 2009). Além disso, é fundamental na manutenção do equilíbrio hídrico em uma região e influi na composição físico-química e microbiológica dos corpos hídricos, por meio de processos complexos de interação superfície-atmosfera (Machado e Pacheco, 2010).

Entretanto, a qualidade da água não depende apenas de condições naturais. A ação antrópica interfere qualitativa e quantitativamente à medida que afeta as características químicas, físicas e biológicas dos sistemas hídricos (Pinto et al., 2009). A urbanização engendrada de forma acelerada e sem o devido planejamento aumentou a pressão antrópica sobre os recursos hídricos, sobretudo no que se refere àqueles usados para o abastecimento urbano. Isso gerou numerosos impactos sobre esse recurso natural, principalmente por meio do lançamento de esgotos e de resíduos urbanos e industriais nas águas (Tucci, 2008).

A constante e crescente produção de resíduos sólidos e sua posterior destinação inadequada, sobretudo nos centros urbanos, como ocorre nos lixões, geram inúmeros impactos ambientais e sociais, dentre os quais, destacam-se: a contaminação do solo, das águas superficiais e do lençol freático, a transmissão de doenças às pessoas pelo contato direto com os resíduos ou animais vetores, ou pelo uso de recursos contaminados indiretamente pelos poluentes provenientes dos lixões (Oliveira e Pasqual, 2004; Pereira et al., 2013).

A contaminação de águas superficiais e subterrâneas por compostos orgânicos e inorgânicos provenientes do chorume de lixões e aterros mal planejados é verificada comumente por meio de elevadas concentrações de metais pesados, compostos nitrogenados e/ou coliformes (Medeiros et al., 2008; Galarpe e Parilla, 2012; Pereira et al., 2013).

Desse modo, o presente trabalho tem por objetivo avaliar a qualidade das águas superficiais e subterrâneas nas proximidades do lixão de Salinópolis, situado na Vila de Cuiarana, e investigar a influência da precipitação sazonal na composição físico-química e microbiológica das águas locais.

2. MATERIAL E MÉTODOS

2.1. Área de estudo

O município de Salinópolis (Figura 1) pertence à mesorregião nordeste paraense e à microrregião Salgado. Possui as seguintes coordenadas geográficas: 0°63'13.4" S e 47°34'61.3" W, distante 227 km de Belém, com elevação de 19 metros acima do nível do mar. Segundo dados do IBGE (2010), tem uma população estimada em 37.421 habitantes, com área

territorial de 237,738 km². O lixão de Salinópolis está localizado na Vila de Cuiarana, situada a cerca de 7 km do centro urbano do município, no ramal conhecido como São Sebastião.

O município apresenta precipitação anual que varia entre 1.800 e 2.300 mm, sendo que cerca de 90% da precipitação se distribui nos seis primeiros meses do ano (Figuerola e Nobre, 1990; Moraes et al., 2005). Segundo a classificação de Köppen, o clima predominante na região é Aw, com temperatura média anual de 27,7°C, com oscilações que variam entre 25° e 31°C. (Mengawaco, 1995; Rodrigues et al., 2013).

Figura 1. Mapa de localização da área de estudo na Vila de Cuiarana. Nascentes: N1, N2 e N3; Rios Perenes: RP1 e RP2; Rios intermitentes: RI1 e RI2; Poços: P1, P2, P3 e P4.

2.2. Variáveis hidrológicas

Os dados de precipitação (mm) mensal foram estimados por sensoriamento CPC MORPHing technique (CMORPH) no ponto de grade referente à coordenada do lixão de Salinópolis. Os dados disponíveis no banco de dados do CMORPH correspondem ao período de 1998 a 2015. Para caracterização climática da precipitação foram somados os acumulados mensais do CMORPH desde 1998. Estudos como o de Sodré e Rodrigues (2013) comprovam a acurácia dos dados do CMORPH quando comparados a dados coletados por estações meteorológicas do Instituto Nacional de Meteorologia (INMET) em diversas regiões brasileiras.

A análise da precipitação local para o período de estudo foi realizada por meio do cálculo da anomalia mensal, o que possibilita caracterizar a precipitação local durante o período de estudo.

Os dados da velocidade de infiltração (cm h⁻¹) foram obtidos nos meses de março (período chuvoso) e outubro (período menos chuvoso) de 2015, em duas áreas residenciais. A área residencial a montante do lixão fica localizada no sítio Teixeira. Já a área habitada a jusante fica às margens do ramal de São Sebastião, na estrada que dá acesso ao lixão. Os pontos de coleta de dados foram escolhidos próximos aos poços P1 e P2 (sítio Teixeira) e P3 e P4 (ramal de São Sebastião), o que fornece informações adicionais para a avaliação da qualidade da água nos poços. O método utilizado para obter a velocidade de infiltração no solo foi o infiltrômetro de anéis concêntricos, descrito detalhadamente por Brandão et al. (2006).

A vazão (m³ s⁻¹) dos rios foi determinada no mês de março de 2015, época que corresponde ao período chuvoso na região. A vazão (m³ s⁻¹) foi calculada em dois locais, à jusante do lixão o local escolhido foi o riacho Cachoeira, em um trecho próximo ao ramal São Sebastião. Já na

área a montante foi selecionada um trecho do rio Teixeira, nas proximidades da área residencial do sítio Teixeira.

Os dados de vazão foram calculados por meio do método convencional com medição direta e uso de molinete hidrométrico, conforme Carvalho (2008) e Santos (2014). Em virtude da pequena largura e profundidade dos riachos estudados, a medição foi feita com o uso do método de medição a vau, com a escolha de seis seções de diferentes profundidades para cada rio. A vazão total foi obtida pela soma das vazões parciais.

Para compreender a dinâmica da água precipitada no solo e, consequentemente, a influência dessa dinâmica na dispersão dos compostos químicos autóctones e alóctones, foi calculado o armazenamento de água no solo por meio do método do balanço hídrico de Thornthwaite e Mather (1955), descrito por Costa (1994). Para efeito de cálculo, foi considerada a capacidade de armazenamento de água no solo (CAD) de 100 mm, conforme orientado por Pereira et al. (2007), quando não é realizado cálculo da CAD com dados de campo.

2.3. Variáveis de qualidade das águas

Foram selecionados 11 pontos amostrais (Figura 1), sendo seis localizados a montante do lixão (N1, N2, RP1, RI1, P1 e P2) e cinco a jusante (N3, RP2, RI2, P3 e P4). Ao todo, foram selecionadas 3 nascentes (N1, N2 e N3), 2 rios perenes (RP1 e RP2), 2 rios intermitentes (RI1 e RI2) e 4 poços (P1, P2, P3 e P4).

A nascente 1 (N1) é o ponto mais a montante do lixão e o ponto com menor influência antrópica direta. Enquanto a nascente 3 (N3) é a mais próxima da área do lixão, e está localizada em área residencial. Os pontos amostrais se localizam próximos a áreas habitadas por pequenos agrupamentos familiares e foram selecionados com base na acessibilidade para obtenção das amostras e uso pela população local.

As nascentes foram selecionadas em virtude da importância dessas para a avaliação da qualidade de água, uma vez que alterações, mesmo que pequenas, em seus fluxos e composições podem comprometer a qualidade do ambiente e da água (Oliveira et al., 2013). Os poços P1 e P2 se localizam no Sítio Teixeira e P3 e P4 no ramal de São Sebastião. Os poços são rasos com profundidades entre 3,6 m e 8,15 m, sem revestimento, com exceção de P3 que possui revestimento de tijolos.

Foram realizadas seis campanhas de amostragem de água superficial e subterrânea (poço), entre os meses de novembro de 2014 e outubro de 2015. Ou seja; foram feitas três coletas durante o período menos chuvoso (novembro/2014, julho/2015 e outubro/2015) e três coletas durante o período chuvoso (fevereiro/2015, março/2015 e maio/2015).

Para avaliação da qualidade da água foram selecionados nove parâmetros físico-químicos: pH, oxigênio dissolvido (OD), temperatura da água, turbidez, sólidos totais dissolvidos (TDS), condutividade elétrica (CE), amônia (NH_3) e nitrato (NO_3^-); dois parâmetros bacteriológicos: coliformes totais e *Escherichia coli*; e alguns metais: alumínio (Al), cádmio (Cd), chumbo (Pb), cobre (Cu), cromo (Cr), ferro (Fe), manganês (Mn), mercúrio (Hg), níquel (Ni) e zinco (Zn).

Os parâmetros temperatura da água, pH, condutividade elétrica, salinidade e sólidos totais dissolvidos foram aferidos em campo, conforme as orientações de uso determinado pelo fabricante de cada aparelho, e seguindo rigorosamente a metodologia proposta pelo Guia Nacional de Coleta e Preservação de Amostras (Brandão et al., 2011). O oxigênio dissolvido também foi medido em campo, pelo Método de Winkler (Golterman et al., 1978). Já as medições da turbidez, amônia, nitrato e a bacteriologia foram realizados no Laboratório de Hidroquímica da Universidade Federal do Pará.

A análise das concentrações dos metais (Hg, Al, Cd, Pb, Cr, Cu, Zn, Fe, Ni e Mn) foram realizadas pelo Instituto Evandro Chagas, obedecendo ao método Standard (American Public Health Association - APHA, 2012), por meio de Espectrometria de Emissão Ótica com Plasma

Induzido (ICP OES). O controle das condições operacionais do ICP OES foi realizado com o software ICPEXpert Vista.

As amostras para bacteriologia foram coletadas em frascos de vidro estéreis, devidamente preparados em laboratório e acondicionadas em caixas térmicas. Posteriormente, foram levadas ao Laboratório de Hidroquímica da UFPA, em um prazo inferior a 24 horas. Em virtude da alta densidade de colônias bacterianas desenvolvidas nos meios de cultura, foram necessárias diluições em algumas amostras. Para obtenção da diluição ideal para contagem de todas as amostras foram testadas placas preparadas sem diluição (T1), com diluição 50/100 ml (T2) e 10/100 ml (T3). A diluição T3 apresentou maior viabilidade para contagem das colônias em todas as amostras e, portanto, foi a diluição utilizada para todas as campanhas seguintes. A filtragem, a inoculação das placas, o cultivo das culturas de colônias bacterianas e a posterior contagem foram realizados segundo a metodologia proposta pela CETESB (2007), para a técnica da membrana filtrante.

Os valores de concentração dos parâmetros físico-químicos, bacteriológicos e da análise de metais foram comparados com os valores máximos permitidos pela legislação do CONAMA, Resolução n.º 357/2005 para águas classe 2. Enquanto as concentrações encontradas nos poços foram comparadas aos valores expressos pela Portaria n.º 2.914/2011, do Ministério da Saúde, que estabelece parâmetros de potabilidade da água para consumo humano. A variabilidade sazonal nos resultados dos parâmetros ambientais analisados (águas superficiais e subterrâneas) foi levada em consideração na discussão dos resultados e comparada graficamente.

3. RESULTADOS E DISCUSSÃO

O período chuvoso em Cuiarana abrange os meses de janeiro a maio. O período chuvoso concentrou em 2014 o acumulado correspondente a 2.213,5 mm, enquanto o período menos chuvoso obteve o total de 200,8 mm. Em 2015, os acumulados foram de 1.613,6 mm e 432,9 mm, correspondentes ao período chuvoso e ao menos chuvoso, respectivamente. O maior acumulado mensal de precipitação foi de 631 mm, em fevereiro de 2014 (Figura 2).

A redução do volume total precipitado em 2015 se deve, sobretudo, à ocorrência do fenômeno El Niño, iniciado efetivamente no segundo trimestre de 2015 (National Oceanic and Atmospheric Administration - NOAA, 2016). O ano de 2014 em Cuiarana foi caracterizado por anomalias positivas no primeiro semestre, ou seja, volumes de chuva acima da normal climatológica, e um segundo semestre com anomalias negativas, isto é, volume de chuva abaixo da média climatológica. O ano de 2015 apesar de um volume mais modesto de chuvas no primeiro semestre quando comparado com 2014 obteve, predominantemente, anomalias positivas quando comparada à normal climatológica (Figura 2).

O balanço hídrico do solo de Cuiarana dos anos de 2014 e 2015 demonstrou que o período de reposição hídrica na região ocorre em janeiro, devido ao aumento da ocorrência das chuvas nesse período. A redução de chuvas e o aumento nas temperaturas do ar no segundo semestre provocam a perda de água do solo por evapotranspiração, o que acarreta deficiência hídrica no solo entre os meses de junho e dezembro. Com relação aos anos estudados, o ano de 2014 demonstrou maior déficit hídrico no solo. Pois, conforme demonstra a Figura 2, o segundo semestre de 2014 apresentou um volume de chuvas bem abaixo da média climatológica da região.

A velocidade de infiltração no ramal de São Sebastião, área próxima ao lixão, foi de 18 cm h⁻¹ em março; e de 60 cm h⁻¹, em outubro. Já no sítio Teixeira foi de 57 cm h⁻¹ em outubro; e 160 cm h⁻¹, em março. Segundo Bernardo et al. (2006) solos com velocidade de infiltração acima de 3 cm h⁻¹ são classificados como solos com velocidade de infiltração muito alta. Desse modo, os solos das áreas estudadas se enquadram nessa categoria. A alta taxa de infiltração no mês de outubro se deve ao déficit hídrico do solo nesse período.

Figura 2. Dados de acumulados mensais de precipitação em Cuiarana do período 2014 -2015 e Anomalia de precipitação mensal no período de 2014 a 2015, obtidos pelo CMORPH.

No mês de março, no sítio Teixeira, a infiltração foi muito maior que nos demais ensaios, em decorrência, possivelmente, de algum evento local, pois se trata de uma área próxima a pequenas lavouras e influenciada diretamente por atividades antrópicas (agricultura de subsistência, principalmente). Ademais, a área do sítio Teixeira tem uma cota mais elevada que a área do ramal de São Sebastião (Figura 1), o que favorece, nesta última localidade, o acúmulo de água da chuva em seus declives, o que mantém por mais tempo a saturação do solo local. Segundo Franco et al. (2015), quanto maior a declividade de um terreno, menor a taxa de infiltração.

Enquanto os valores de infiltração foram muito elevados, as vazões nos dois rios estudados foram baixas, como a própria observação *in loco* previa, uma vez que muitos rios da bacia têm comportamento intermitente. No rio Teixeira, a vazão no trecho medido foi de $0,17 \text{ m}^3 \text{ s}^{-1}$; e de $0,16 \text{ m}^3 \text{ s}^{-1}$ no rio Cachoeira. A alta taxa de infiltração contribui para que os contaminantes advindos do lixo cheguem à água subterrânea, ao passo que a baixa vazão dos rios dificulta a dispersão desses contaminantes para áreas mais distantes da fonte poluente.

3.1. Águas Superficiais

Os parâmetros OD, pH e *E. coli* apresentaram valores em desacordo com o estabelecido pela Resolução 357/2005 do CONAMA para águas superficiais (Tabela 1). O OD obteve valores abaixo de 5 mg/L em quase todas as amostras e campanhas, com exceção de RI2 em março, RI1, RP2 e RI2 em maio e RI2 em agosto.

O pH em todas as campanhas esteve abaixo de 6 (3,95 a 5,87). Entretanto, segundo alguns estudos, como o de Gunkel et al. (2000) por exemplo, os rios amazônicos tendem a ter águas levemente ácidas, sem que isso indique, contudo, desequilíbrio no ecossistema local. A *E. coli* esteve acima de 1000 UFC 100 mL⁻¹ somente na amostra RP2 em maio.

Tabela 1. Resultados em rios e nascentes dos parâmetros pH, Oxigênio dissolvido (OD) e *Escherichia coli* e VMP (Valor Máximo Permitido) pela Resolução CONAMA 357/05 para águas superficiais classe 2.

Parâmetro	Mês	N1	RP1	N2	RI1*	N3	RP2	RI2*	VMP
pH	nov	5,04	4,94	5,02		4,85	4,74		
	fev	5,13	4,12	5,52		4,63	3,95		
	mar	4,93	4,85	4,03	4,8	4,37	4,79	5,3	6 a 9
	mai	5,65	4,39	4,4	5,29	5,34	5,12	5,14	
	ago	5,55	5,7	5,2	5,87	5,35	5,35	5,6	
	out	4,78	4,87	4,54	4,76	4,97	4,78		
OD (mg/L)	nov	2,21	2,6	1,25		4,42	3,08		
	fev	1,44	1,63	1,54		0,96	3,65		
	mar	2,16	2,45	1,23	3,04	1,67	2,16	5,39	> 5
	mai	3,14	4,61	3,63	5,39	2,16	5,88	5,49	
	ago	0	1,47	2,94	3,53	0,49	3,14	5,39	
	out	1,76	1,37	0,78	1,47	2,16	1,18		
<i>E. coli</i> (UFC 100 mL ⁻¹)	nov	11	11	20		0	0		
	fev	54	6	2		6	0		
	mar	340	170	0	80	250	140	110	1.000
	mai	200	350	30	330	210	1520	510	
	ago	0	0	0	30	10	10	70	
	out	10	260	0	0	10	0		

*Os rios intermitentes (RI1 e RI2) apresentaram água somente a partir de março de 2015.

Quanto à sazonalidade o OD obteve as maiores concentrações no período chuvoso, em virtude do aumento na cota dos rios e nascentes, o que eleva a turbulência e favorece a aeração da água. Tanto os coliformes fecais quanto a *E. coli* alcançaram maiores concentrações em águas superficiais no período de chuvas, resultado da lixiviação de matéria orgânica e sedimentos para os corpos hídricos nesse período. Já o pH não demonstrou comportamento sazonal, embora o período menos chuvoso tenha obtido valores levemente superiores.

A Figura 3 ilustra a variabilidade sazonal de alguns parâmetros que, embora não tenham apresentado concentrações acima do Valor Máximo Permitido (VMP) pela Resolução 357/2005 do CONAMA, demonstraram variabilidade sazonal importante para a avaliação da qualidade de água.

A turbidez, TDS e condutividade elétrica obtiveram maiores valores no período chuvoso, tanto em rios quanto nas nascentes. A mata ciliar desmatada, o uso e ocupação do solo nas proximidades dos rios e nascentes favorecem o carreamento de sedimentos e sais por meio das chuvas para os corpos hídricos (Silva et al., 2008), fatores que contribuem para justificar esses resultados. Os pontos a jusante do lixão N3, RP2 e RI2 apresentaram valores superiores quando comparados com os demais pontos, o que pressupõe influência do lixão nesses pontos.

Nos pontos amostrados nos rios, a amônia (NH₃) obteve valores superiores no período chuvoso, com destaque para RI2, com exceção de RP1 que obteve a maior concentração em novembro, período menos chuvoso. As nascentes estudadas, entretanto, apresentaram maiores concentrações no período menos chuvoso, exceto N3 que anormalmente obteve pico em março. O fato de que os pontos com maiores concentrações de amônia no período chuvoso estarem na área do lixão (RI2 e N3) corrobora com a hipótese de carreamento de compostos orgânicos do lixão para as águas superficiais. Já o nitrato (NO₃⁻) apresentou maiores concentrações no período menos chuvoso em rios e nascentes, tanto pontos a montante quanto a jusante tiveram resultados similares. Concentrações mais elevadas de compostos nitrogenados em águas superficiais próximas a áreas de depósito de lixo também foram encontrados em trabalhos como o de Ashraf et al. (2013).

Figura 3. Variação sazonal dos parâmetros: Turbidez, Sólidos Totais Dissolvidos (TDS), Condutividade Elétrica (CE), Amônia (NH_3) e Nitrato (NO_3) nas nascentes e rios estudados.

As amostras de água superficial não apresentaram salinidade, com exceção do ponto RI2, que apresentou salinidade 0,1%. O ponto RI2 corresponde a um rio intermitente e só apresentou cota a partir de março, assim o início das chuvas favoreceu o escoamento superficial do solo do lixão em direção ao ramal de São Sebastião. Além da salinidade, os sólidos totais dissolvidos (95 mg L^{-1}) e a condutividade elétrica ($202 \mu\text{S cm}^{-1}$) alcançaram os maiores valores no mês de março. Com o aumento da cota e vazão de RI2 durante o período chuvoso a salinidade, TDS e CE apresentaram valores menores, o que demonstra o efeito de diluição das chuvas.

De modo geral, o período chuvoso influenciou na deterioração da qualidade das águas superficiais, sobretudo nos pontos à jusante do lixão. Fatores como, cobertura vegetal incipiente às margens dos corpos hídricos, localização do lixão em cota mais elevada que os pontos de coleta e alta taxa pluviométrica favorecem para a contaminação das águas por escoamento superficial e lixiviação de poluentes do lixão para os rios e nascentes.

3.2. Águas subterrâneas

De modo semelhante às águas superficiais, os poços apresentaram pH abaixo do estabelecido pela legislação vigente (Tabela 2). Conforme a Portaria nº2.914/2011 do Ministério da Saúde (MS) os parâmetros de turbidez, coliformes totais e *Escherichia coli* estiveram acima do VMP em muitos pontos e campanhas, o que caracteriza a água como imprópria para consumo humano.

Tabela 2. Resultados em poços dos parâmetros pH, Oxigênio dissolvido (OD) e *Escherichia coli* e VMP (Valor Máximo Permitido) pela Portaria nº2.914/2011 do Ministério da Saúde (MS).

Parâmetro	Mês	P1	P2	P3	P4	VMP
pH	nov	5,24	4,51	5,3	4,97	6 a 9,5
	fev	5,25	4,79	4,53	5	
	mar	4,34	4,56	5,51	5,24	
	mai	4,35	5,1	5,6	5	
	ago	5,05	4,96	5,27	5,2	
	out	4,36	4,13	5,77	5,43	
OD (mg/L)	nov	4,71	1,06	3,94	3,46	
	fev	5,48	1,73	1,44	2,98	
	mar	2,94	1,37	4,41	2,25	
	mai	3,43	1,47	1,08	2,84	
	ago	0,98	0,39	1,57	2,45	
	out	1,96	1,27	0,59	2,75	
<i>E. coli</i> (UFC 100 mL ⁻¹)	nov	0	0	0	0	Ausente
	fev	20	14	0	18	
	mar	930	20	300	1610	
	mai	30	0	40	270	
	ago	0	0	40	30	
	out	520	0	0	5000	

De todas as amostras o OD só esteve acima de 5 mg L^{-1} em P1 em fevereiro. Os menores valores de OD foram referentes ao período menos chuvoso, o que pode ser explicado pela diminuição do volume de água nos poços. Segundo a portaria do MS a água para consumo não pode apresentar coliformes totais e *E. coli*, desse modo, somente amostra de P2 em outubro esteve em conformidade com relação a esses parâmetros. O período chuvoso apresentou maior

densidade de colônias, resultado possivelmente do maior carregamento de poluentes no período de chuvas para os poços por infiltração, ou mesmo escoamento superficial.

A Figura 4 ilustra a concentração e variabilidade sazonal de alguns parâmetros. O TDS e a CE apresentaram maiores valores durante o período de chuvas, o que revela a influência direta das chuvas na composição físico-química da água dos poços. Os poços P3 e P4, ambos na área do lixão, obtiveram valores superiores de turbidez, TDS, CE, NH_3 e NO_3^- quando comparados aos poços P1 e P2, o que revela a influência negativa do lixão na qualidade da água subterrânea da região.

Figura 4. Variação sazonal dos parâmetros: Turbidez, Sólidos Totais Dissolvidos (TDS), Condutividade Elétrica (CE), Amônia (NH_3) e Nitrato (NO_3^-) nos poços estudados.

Embora a Portaria 2.914/11 do MS não determine um valor máximo para a condutividade, a CETESB (2009) classifica como ambientes impactados àqueles com valores superiores a $100 \mu\text{S cm}^{-1}$. Desse modo, os poços P3 e P4 podem ser classificados como impactados. Além da alta condutividade os poços P3 e P4 foram os únicos que apresentaram salinidade.

A turbidez, a amônia e o nitrato obtiveram maiores concentrações no período menos chuvoso, sobretudo nos poços P3 e P4, o que demonstra o efeito da diminuição da água nos

poços nesse período e consequente diminuição da diluição dos compostos químicos presentes na água. Esses resultados demonstram lixiviação de matéria orgânica para os poços, sobretudo nos localizados na área à jusante do lixão.

O fato de as fossas serem escavadas bem próximas aos poços e não terem qualquer revestimento, com certeza, contribui para a degradação da qualidade de água nos poços; parâmetros como coliformes totais, *E. coli*, amônia e nitrato sofrem influência direta nesse caso. A matéria orgânica e microrganismos presentes em fossas, quando não construídas adequadamente, podem contaminar a água dos poços próximos. Desse modo, embora os resultados demonstrem influência do lixão, por serem mais significativos nos poços P3 e P4, não deve ser desconsiderada a contribuição das fossas locais.

3.3. Metais pesados

Em águas superficiais os metais Al, Cd, Cu, Fe, Hg e Pb apresentaram valores acima do VMP pela Resolução 357/05 do CONAMA (Tabela 3), tanto em rios e nascentes a montante quanto a jusante do lixão. Os metais Mn, Ni e Zn além de não apresentaram concentrações acima do VMP também não apresentaram sazonalidade evidente em suas concentrações. A variabilidade na concentração destes parece estar mais relacionada a eventos pontuais e a ação antrópica local, o que não exclui a influência do lixão.

O cromo esteve em maiores concentrações no período chuvoso, embora não tenha excedido o VMP em nenhuma amostra e não demonstre diferença significativa em amostras a montante e a jusante do lixão. O cádmio, entretanto, apresentou uma única amostra (N1 em agosto) acima do VMP (0,001 mg L⁻¹). As maiores concentrações de Cd foram registradas no início e no fim do período chuvoso. O cobre também só apresentou uma amostra (N3 em agosto) acima do VMP (0,009 mg L⁻¹). Com exceção de N3 os demais pontos apresentaram pico da concentração de Cu no início do período chuvoso. De maneira geral, o Cd e o Cu obtiveram concentração semelhante tanto em pontos a montante quanto a jusante do lixão.

O alumínio e o ferro foram os metais que apresentaram maiores concentrações em todos os pontos amostrados. As nascentes obtiveram maiores concentrações de Al que nos rios, e o período chuvoso foi o que apresentou as maiores concentrações. Já o Fe obteve maiores concentrações no período menos chuvoso, o que denota o efeito de diluição das chuvas com relação a esse metal.

Segundo Marmontel e Rodrigues (2015), a preservação das matas ciliares em torno de rios e, sobretudo, em nascentes, favorece a boa qualidade da água nesses ambientes. Por exemplo: as altas concentrações de ferro e alumínio em nascentes e rios podem estar associadas ao fato de esses corpos hídricos não possuírem mata ciliar preservada, o que facilita o carreamento dos metais do solo para a água. Segundo Emmett et al. (1994), a vegetação de mata ciliar em uma bacia hidrográfica reduz a concentração de alumínio total em 21% e de ferro em 54%.

Quanto à concentração de Hg todas as amostras superficiais estavam acima do VMP pela Resolução do CONAMA, com as maiores concentrações encontradas no período chuvoso e sem grande variabilidade entre os pontos a montante e a jusante do lixão. A alta concentração de Hg nas águas superficiais representa um risco à saúde humana, uma vez que este é um metal bioacumulativo, podendo contaminar peixes e/ou animais aquáticos, os quais podem ser consumidos pelos moradores da região (Anjos et al., 2016).

O chumbo, entretanto, obteve maiores concentrações tanto em rios como em nascentes a montante do lixão, com picos no período de chuvas. A maior concentração de chumbo a montante do lixão pode ter ocorrido devido à dispersão das partículas de Pb através do ar, como resultado da incineração de materiais compostos de chumbo no lixão. Segundo a World Health Organization (1989), essa é principal forma de dispersão do metal, o qual pode permanecer em suspensão durante dias no ar, podendo ser carregado pela chuva e contaminar água e solo.

Tabela 3. Concentração de metais (mg L⁻¹) em rios e nascentes durante as seis campanhas amostrais e VMP (Valor Máximo Permitido) pela Resolução CONAMA 357/05 para águas superficiais classe 2.

	Pontos	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Nov	N1	0,051	< LD	< LD	0,002	1,192		0,016	< LD	< LD	0,012
	RP1	0,072	< LD	0,000	0,002	3,466		0,020	< LD	< LD	0,002
	N2	0,101	< LD	< LD	0,001	2,877		0,009	< LD	< LD	0,031
	N3	0,115	< LD	< LD	< LD	0,826		0,019	< LD	< LD	0,002
	RP2	< LD	< LD	< LD	0,001	< LD		< LD	< LD	< LD	< LD
Fev	N1	0,470	0,001	0,003	0,005	0,870	0,002	0,022	0,007	0,018	0,013
	RP1	0,102	0,000	0,004	0,007	2,954	0,002	0,045	0,006	0,001	0,013
	N2	0,088	0,000	0,003	0,003	1,160	0,001	0,010	0,003	0,013	0,014
	N3	0,101	0,000	0,003	0,005	0,816	0,001	0,062	0,006	0,004	0,015
	RP2	0,074	0,001	0,002	0,001	0,596	0,001	0,012	0,003	< LD	0,071
Mar	N1	0,087	< LD	0,002	< LD	0,111	0,001	0,013	< LD	< LD	0,001
	RP1	0,072	< LD	0,001	< LD	0,274	0,001	0,014	0,002	< LD	0,003
	N2	0,267	< LD	0,002	< LD	0,229	0,002	0,007	< LD	< LD	0,001
	RI1	0,094	< LD	0,000	< LD	0,163	0,001	0,008	< LD	< LD	0,006
	N3	0,109	< LD	0,002	< LD	0,096	0,001	0,027	0,001	< LD	0,005
	RP2	0,129	< LD	0,001	< LD	0,434	0,001	0,012	0,001	< LD	0,001
	RI2	0,051	< LD	0,000	< LD	0,313	0,001	0,008	< LD	< LD	< LD
Mai	N1	0,243	0,001	< LD	0,002	0,842	0,001	0,006	0,001	0,021	0,006
	RP1	0,099	0,000	< LD	0,001	0,645	0,000	0,012	0,001	0,038	0,012
	N2	0,175	0,000	< LD	0,002	0,185	0,000	0,034	< LD	0,041	0,002
	RI1	0,088	0,000	< LD	< LD	0,272	0,000	0,008	0,003	0,030	0,015
	N3	0,161	0,001	< LD	0,001	0,919	0,001	0,029	0,004	0,009	0,005
	RP2	0,131	0,001	< LD	0,000	0,665	0,000	0,017	< LD	0,016	0,013
	RI2	0,129	0,000	< LD	0,003	0,635	0,001	0,014	0,005	0,015	0,008
Ago	N1	0,084	0,003	< LD	0,003	3,403	0,001	0,008	0,009	< LD	0,002
	RP1	0,106	0,001	< LD	0,002	4,347	0,000	0,022	0,001	< LD	0,006
	N2	0,110	0,001	< LD	< LD	2,152	0,000	0,004	< LD	0,015	< LD
	RI1	0,052	0,000	< LD	0,000	1,206	0,000	0,017	0,000	0,003	< LD
	N3	0,066	0,001	< LD	0,010	1,700	0,000	0,027	< LD	< LD	0,014
	RP2	0,115	0,001	< LD	0,001	1,888	0,000	0,013	< LD	< LD	< LD
	RI2	0,045	0,001	< LD	0,002	1,882	0,000	0,013	< LD	< LD	< LD
Out	N1	0,069	0,000	0,001	< LD	0,435	0,001	0,015	< LD	0,008	0,002
	RP1	0,060	< LD	< LD	< LD	2,854	0,001	0,017	< LD	< LD	< LD
	N2	0,092	< LD	< LD	< LD	1,273	0,001	0,012	< LD	< LD	0,001
	RI1	0,072	< LD	< LD	< LD	2,777	0,001	0,051	0,003	< LD	< LD
	N3	0,045	< LD	< LD	< LD	0,277	0,001	0,033	0,001	< LD	< LD
	RP2	0,077	< LD	< LD	< LD	0,813	0,001	0,015	< LD	< LD	0,001
	VMP	0,1 mg L ⁻¹	0,001 mg L ⁻¹	0,05 mg L ⁻¹	0,009 mg L ⁻¹	0,3 mg L ⁻¹	0,0002 mg L ⁻¹	0,1 mg L ⁻¹	0,025 mg L ⁻¹	0,01 mg L ⁻¹	0,18 mg L ⁻¹

*<LD: Abaixo do Limite de Detecção. As concentrações acima do VMP estão em negrito.

Nos poços estudados, os metais Al, Fe, Hg e Pb estiveram acima do VMP estabelecido pela Portaria 2.914/11 do Ministério da Saúde (Tabela 4). Os metais Cd e Cu não demonstraram diferenças significativas entre os poços a montante do lixão (P1 e P2) e os poços a jusante do lixão (P3 e P4), e obtiveram as maiores concentrações no início do período de chuvas e no início do período menos chuvoso.

Tabela 4. Concentração de metais (mg L^{-1}) em poços durante as seis campanhas amostrais e VMP (Valor Máximo Permitido) pela Portaria 2.914/11 do MS para as águas de consumo humano.

	Poços	Al	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Nov	P1	0,013	< LD	<LD	0,002	0,161		0,006	< LD	<LD	<LD
	P2	0,089	< LD	<LD	0,004	0,545		0,009	< LD	<LD	0,013
	P3	0,517	< LD	0,000	0,002	0,326		0,007	< LD	<LD	0,006
	P4	0,083	< LD	<LD	0,000	0,863		0,014	< LD	<LD	0,017
Fev	P1	0,109	0,000	0,003	0,002	0,153	0,001	0,042	0,007	0,005	0,015
	P2	0,274	0,001	0,004	0,003	0,353	0,001	0,010	< LD	<LD	0,013
	P3	0,082	0,001	0,002	0,002	0,253	0,001	0,010	0,006	0,002	0,042
	P4	0,143	0,001	0,003	0,005	0,360	0,001	0,087	0,000	<LD	0,020
Mar	P1	0,182	< LD	0,000	< LD	0,014	0,001	0,014	0,002	< LD	0,003
	P2	0,104	< LD	0,003	< LD	0,134	0,001	0,008	< LD	0,004	0,002
	P3	0,580	< LD	0,001	< LD	0,037	0,001	0,032	0,000	< LD	0,027
	P4	0,078	< LD	< LD	< LD	0,179	0,001	0,015	< LD	< LD	0,005
Mai	P1	0,067	0,000	0,000	0,001	0,022	0,001	0,009	< LD	0,007	0,005
	P2	0,051	0,000	< LD	< LD	0,113	0,000	0,053	< LD	0,008	0,010
	P3	0,262	< LD	0,001	0,004	1,123	0,000	0,037	0,007	0,014	0,023
	P4	0,130	< LD	0,001	0,002	0,302	0,001	0,014	< LD	0,028	0,006
Ago	P1	0,036	0,002	< LD	0,001	0,079	0,000	0,012	0,000	0,130	0,003
	P2	0,044	0,002	< LD	0,005	0,626	0,000	0,005	< LD	0,132	0,002
	P3	0,347	0,000	0,002	0,005	3,091	0,000	0,030	0,004	0,001	0,021
	P4	0,099	< LD	0,001	0,004	0,315	0,000	0,012	0,003	< LD	0,005
Out	P1	0,042	<LD	<LD	<LD	0,068	0,003	0,025	0,004	<LD	<LD
	P2	0,084	<LD	<LD	<LD	0,628	0,001	0,008	<LD	<LD	<LD
	P3	0,145	<LD	0,000	<LD	3,659	0,002	0,073	0,002	<LD	0,008
	P4	0,151	<LD	<LD	<LD	0,494	0,001	0,055	0,006	<LD	0,005
	VMP	0,2 mg L^{-1}	0,005 mg L^{-1}	0,05 mg L^{-1}	2 mg L^{-1}	0,3 mg L^{-1}	0,001 mg L^{-1}	0,1 mg L^{-1}	0,07 mg L^{-1}	0,01 mg L^{-1}	5 mg L^{-1}

*<LD: Abaixo do Limite de Detecção. As concentrações acima do VMP estão em negrito.

De modo semelhante às águas superficiais, os poços apresentaram maiores concentrações dos metais Al e Fe, quando comparado aos demais metais. O poço P3 foi o que apresentou os maiores valores de Al na água, com maiores concentrações no período de chuvas. O Fe apresentou maiores concentrações no período menos chuvoso, momento em que o nível da água dos poços estava bem baixo, e o poço P3 também foi o que apresentou maiores concentrações de Fe. Resultados que reforçam a afirmativa de influência do lixão na qualidade da água subterrânea na região.

Com relação ao Hg, somente os poços P1 e P3 obtiveram valores acima do VMP pela Portaria, com concentrações levemente superiores no período menos chuvoso. Tanto em águas

superficiais quanto subterrâneas o Hg não apresentou diferença entre pontos a montante ou a jusante do lixão, o que sugere que a contaminação venha a ter por origem outra atividade antropogênica, como descarte de lixo eletrônico de modo inadequado (Kemerich et al., 2013), pois não existe coleta de lixo nas comunidades estudadas. Já o Pb obteve maiores concentrações no período menos chuvoso nos poços P1 e P2, ambos a montante do lixão. A alta concentração de Pb a montante do lixão corrobora com a hipótese de dispersão de Pb pelo ar através da incineração de materiais ricos desse metal no lixão.

4. CONCLUSÃO

A avaliação da água superficial demonstrou que os rios e nascentes estudados estão impactados, o fato de os pontos N3, RP2 e RI2 apresentarem mais parâmetros em desconformidade com a Resolução 357/05 do CONAMA comprova a hipótese de influência do lixão, embora outros fatores não possam ser desconsiderados.

De modo semelhante, foi constatado que a água nos poços avaliados se encontra imprópria para consumo, resultado das concentrações de coliformes totais, *E. coli*, Al, Cd, Fe, Hg e Pb acima do VMP estabelecido pela Portaria 2.914/11 do MS. Os poços P3 e P4 apresentaram maior deterioração da qualidade da água quando comparados aos poços P1 e P2, o que reforça o pressuposto de influência de derivados do lixão na composição da água local.

O estudo da sazonalidade da concentração dos parâmetros em águas superficiais e subterrâneas revelou que a maioria dos parâmetros e dos metais apresenta variabilidade sazonal. O período de chuvas se caracterizou pela maior degradação da qualidade da água em águas superficiais, em virtude do carreamento de matéria orgânica, sedimentos, sais e microrganismos para os corpos hídricos. Quanto às águas subterrâneas, o período menos chuvoso contribuiu para o aumento das concentrações de sedimentos e de alguns metais na água dos poços, como Cu, Fe, Hg e Pb. Entretanto, as concentrações de coliformes totais, *E. coli*, Al, Fe, Cr e Zn estiveram mais elevadas durante o período de chuvas.

A avaliação da água e sua sazonalidade em Cuiarana é ponto de partida para a tomada de decisões que visem à melhoria da água na região, uma vez que a água analisada é consumida pela população local. Além disso, a influência da topografia (lixão em cota mais elevada que os corpos hídricos), a alta velocidade de infiltração de água no solo e o regime pluviométrico na área conduzem o escoamento superficial do lixão em direção às águas superficiais e subterrâneas, o que torna a área extremamente vulnerável à contaminação da água pelos derivados do lixão. Desse modo, se não houver a adoção de medidas que mitiguem essa situação, as chances de uma deterioração gradativa da qualidade da água consumida pela população é evidente.

5. AGRADECIMENTOS

Ao CNPq/Edital Universal – n.º 14/2012 e à FAPESPA/Universal 2014, pelo apoio financeiro, indispensável para a realização desta pesquisa. Ao Instituto Evandro Chagas que com grande solicitude realizou as análises de metais pesados na água.

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