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Linking Water Security to Sustainable Development Goals

Marcelo Nolasco, Elvis Carissimi, Ernesto Urquieta-Gonzalez (Eds.)

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CONTENT

PREFACE

Water Security is emerging as a primary sustainability challenge across the globe in the 21st century, and is conceptualized as the capacity of a population to safeguard sustainable access to adequate quantities of acceptable quality of water for sustaining livelihoods, human well-being, and socio-economic development. *Water Security* is a determinant in various societal aspects including food, energy, economy, environment and public health, and thus has a complex political momentum that goes far beyond the traditional water sector.

In this sense, the academia plays an important role in providing new science based knowledge and multidisciplinary approaches in order to deal with water security challenges and its solutions. The collaboration among researchers, stakeholders, governments, non-governmental organizations, and the communities in a systemic way are necessary, as this complex issue requires to be addressed long-term.

Like many other *Developing Regions* worldwide, the *Metropolitan Region of São Paulo, Brazil*, one of largest conurbation and human agglomeration in the world, shows many problems regarding the distribution and availability of fresh and drinking waters, water scarcity, quality and pollution aspects of water, water governance, transboundary water, and other related issues in the context of the climate change. In summary, it faces a cyclic water problem: water comes often too little, sometimes too much, and in general too dirty.

This book presents a contribution to the advancement of knowledge as part of the results of the work performed by the participants of the workshop *"Linking Water Security to the Sustainable Development Goals"* held at the Institute of Advanced Studies of the University of Sao Paulo, Brazil in August, 2018. The workshop aimed to develop a creative co-learning among different experts, and knowledge exchange through experiences from different parts of the world, contributing to produce and to disseminate knowledge regarding water and sanitation.

We are grateful for the financial sponsorship given by Exceed-Swindon and the local support provided by the Institute of Advanced Studies and School of Arts, Sciences and Humanities, University of São Paulo. The International Workshop allowed the attendees a unique opportunity to acquire and to share important know¬ledge regarding Water Security considering the global and regional aspects of water governance and manage¬ment, emerging technological innovation, and nature-based solutions for water conservation to achieve the Sustainable Development Goals proposed by the Agenda 2030 of the United Nations in their regions.

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A TREATISE OF APPRECIATION OF THE RELATIONSHIP BETWEEN THE WATER SECURITY INDEX (WSI) AND THE SUSTAINABLE DEVELOPMENT GOALS (SDG) IN TROPICAL AFRICA

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Keyswords: water security index, sustainable development goals, SDG, Tropical Africa

Abstract

The combined effects of population growth, increasing demands for water to enhance activities, security, development and the challenges of climate change give rise to an urgent need to carefully monitor and to assess trends and variations in aquatic resources. Over 1.7 billion people are currently living in river basins, where water use exceeds recharge, leading to the desiccation of rivers, depletion of groundwater, and the degradation of ecosystems and the services they provide. As countries develop and populations grow, global water demand (in terms of withdrawals) is projected to increase by 55% till 2050. Already by 2025, two thirds of the world’s population could be living in water-stressed countries, if current consumption patterns continue. The economic loss from the inadequate delivery of water and sanitation was estimated to amount to 1.5% of gross domestic product (GDP) of the countries included in a WHO study on meeting the millennium development goals (MDGs). Water is only renewable, if well managed. Water can pose a serious challenge to sustainable development, but managed efficiently and equitably, water can play a key enabling role in strengthening the resilience of social, economic and environmental systems in the light of rapid and unpredictable changes. Water security and the sustainable development goals (SDGs) are key ingredients of *"Our Common Future"*, which is defined as *“development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”* This is the overture of our expression on the relationship between the water security index (WSI) and the Sustainable Development Goals in Tropical Africa.

1 Introduction

Water security is the capacity of a population to safeguard sustainable access to adequate quantities of acceptable quality water for sustaining livelihoods, human well-being and socio-economic development for ensuring protection against water-borne pollution and water-related disasters. It is to for preserving ecosystems in a climate of peace and political stability (UNEP, 2010). Discussions on the sustainable green development to protect environment health enhance earnings, and poor eradication had been conducted**.** The concept of water security index (WSI) had been proposed to monitor the water status, which links to the socio-economic development of the country. The index comprises the securities of rural water, urban water, water for development, water quality in the basin, and disaster, and can be used to measure the overall development and to project implementation together with socio-economic planning of the country. This paper proposes the water security definition and assesses the water security in central Africa by reviewing water use status correlated with population data and gross domestic product (GDP) in various countries of the world while achieving their development goals. CEMAC countries (Central African Economic and Monetary Community) can help to understand the competitiveness and the strength, weakness and potential of water development of Central Africa.

2 Material and Methods

2.1 Localization of study area

The study was carried out in Central Africa in the CEMAC countries, which is one of the oldest regional arrangements in Africa, consisting of Cameroon, Central African Republic, Chad, the Republic of Congo, Equatorial Guinea, and Gabon (Falkenmark, 1990). In 1994, the member countries established a full-fledged economic and monetary union (treaty was ratified in 1999), strengthening the existing customs and monetary union, which originated in the colonial era. Linked partly by geography and partly by history, the economies of the CEMAC zone share a number of distinctive characteristics. They are not populous (a combined total population of 32 million), have experienced low historical growth in per capita incomes, made limited strides in poverty reduction over the last several decades, and are highly dependent on oil and other natural resources' exports. The economies also share common challenges, both internal and external, such as volatility resulting from reliance on commodity exports, conflicts of interest between richer coastal and poorer landlocked countries, very limited intra-regional linkages, and political instability within CEMAC and neighboring countries. Regional integration can be a vehicle for overcoming these challenges and a force for improved economic prospects. It may lock countries into policy reform, achieve economies of scale, and provide a unified forum for international negotiations. Success in this endeavor will depend critically on strengthening the institutional capacity, gaining political consensus, building effective infrastructure as well as developing stronger ties within the region and with the neighbors. Figure 1 shows the CEMAC Zone.

2.2 Water security index concept

Up to now, water resources development process started with project development, implementation, monitoring and system improvement, which aimed to facilitate basic needs to people and society. The other portion of water was used for economic development. In recent years, environmental issues were raised and had to be simultaneously considered during water resources planning, too. The index described sufficiency and risk, and was later developed to water security. The index helped to monitor the development of water management clearer and determined under various aspects, e.g., water sufficiency of both quantitative and qualitative aspects for health, life, ecology preservation, production, disaster relief (UNICEF, 2010), or the accessibility to clean and safe water with sufficient amount and payable cost for hygiene and good quality life with environment protection.

Figure 1: Map of the CEMAC zone in Africa

The planning of each country normally concerned with the development of economics, society and environment. However, the important element for sustainable development is still engaged with water resources. The concept of water security was developed to investigate the actual situations of these basic water developments with socio-economic and environmental development. The security dimensions comprised of water security of household, economics, urban, river health and resilience to disaster. This study determined the water security status from five dimensions: (i) basic water (renewable, supply, sanitation); (ii) sufficient water (water supply, consumption, agricultural water); (iii) development water (irrigation area, industrial water use, water for energy, water for aquaculture); (iv) water disaster (loss from floods and drought), and (v) water for future (population growth, urban population growth, water footprint). The index status' analyzed were correlated with water productivity of the five countries classified by their first capital town. Based on the available data from various sources of the world (Sullivan, 2002; Asheesh, 2003), the index of each country was determined comparatively by weighting equally from each dimensions and marking equally (1-5 points) of each element with ranking from the average (1 = very poor, 2 = poor; 3 = average; 4 = good and 5 = excellent) and standard deviation values.

2.3 Situations in CEMAC Countries

In Gabon, water outages have reached critical levels in the capital Brazzaville. Several neighborhoods, including Mfilou and Moungali, have no access to potable water due to ongoing issues at the National Water Supply Company. The *Water-For-All* program, which has cost some USD 333 million, has yet to reach its goals of significantly increasing potable water access in the country, particularly in parts of rural Congo, where less than 15% of the population has readily available drinking water. Individuals are advised to stock up on bottled water and to collect water in large vessels, when running water is available, and to make sure the water is completely clear before collecting it by running taps for few minutes to flush pipes.

Strict food and water precautions are advised, such as boiling, filtering, and/or chemically treating water before consumption. Water quality in Gabon is abundant, but unevenly distributed and strained by high rates of urbanization. Gabon has one of the highest levels of water availability in the world about 127,825 m^3 per capita and year. 87% of Gabon's 1.8 million people live in urban areas, such as Libreville and Port-Gentil. As the urban population increases, so does the demand for a fixed water supply. Gabon's low capacity for drinking water production and lack of storage and maintenance facilities leads to frequent water shortages in Libreville and other urban areas. Water quality in Gabon is different in urban and rural areas. In 2015, 92% of urban areas and 59% of rural areas had access to improved water resources. 'Improved' drinking sources include piped water on property and other improved sources of drinking water, according to the World Health Organization. Despite its status as an upper middle-income country, 34% of the population lives in poverty. Rural, poverty stricken areas suffer deprivation from drinking water resources in Gabon, and 58% of the population does not have access to improved sanitation facilities. In 2015, sanitation rates in urban and rural areas were 43% and 32%, respectively. Access to sanitation facilities is very low in Gabon. Inadequate wastewater and rainwater networks and deficient solid waste management explain the disparity. Inadequate sewage and waste management led to negative health outcomes. Insufficient sanitation and lack of access to improved water sources are associated with the increased risk of neglected tropical diseases (NTDs), a class of infectious bacterial and parasitic diseases. In Gabon, a large proportion of the population is at risk of infection from soil-transmitted helminthiasis, lymphatic filariasis and schistosomiasis.

RCA The town of Birao, with 10,000 residents, is suffering from its remote location in the north of the Central African Republic and receives little aid. In addition to experiencing long gaps in the provision of public services, residents face an influx of people displaced by the conflict. Birao, over a thousand kilometers from Bangui, is hard to reach by road and almost completely cut off during the rainy season. *"It's a real challenge for those few aid organizations that attempt to reach these people,"* said Marius Cocoa, an official of the International Committee of the Red Cross (ICRC) based in the region. *"Although they have not been directly affected by the fighting, those living here are suffering from a shortage of health services, drinking water and food."*

In BANGUI, Central African Republic (CAR) just ahead of the onset of the rainy season, which increases the risk of water-borne diseases like cholera, UNICEF and its partners have restored safe and chlorinated drinking water for more than 183,000 displaced people across the Central African Republic (CAR). *"Access to safe drinking water remains out of reach to many people who have been displaced by the violence,"* said UNICEF CAR Representative Souleymane Diabaté. *"As the first heavy rains have already begun, standing water and flooding increase the risk of a cholera outbreak."*

In Baney, the sight of children fetching water at the nearest river with buckets on their heads is a common scene, a small town situated in the outskirts of Malabo, the capital of Equatorial Guinea. Running water is scarce in homes. That is, why families must mobilize and organize their daily pilgrimage to a river named Ehola, which means *'the protective spirit of the people'*. *"God has not endowed our people with water,"* said the director of the Papa Bacabo National School in Baney, referring to the river, which is completely dry most of the time. Adding to concerns over its quantity, the water is not of good quality, and the nearest source is far from having the minimal hygienic conditions for use without risks in terms of water quality and children survival. This dramatic situation is prevalent in almost all of Equatorial Guinea; a country, where less than half of the population has access to safe water, and one that has not yet developed a large-scale sanitation program. Around 2 children out of 10 here die before the age of five, often from diarrhea, cholera or other diseases linked to poor water quality. Water is the source of life and must be protected. This leitmotiv is gaining momentum on the world's development agenda. It is of particular interest this date in 2008, which had been declared by the United Nations as the International Year of Sanitation.

In N'djamena, the capital of Chad, bakes in the midday heat, Aisha Adoum uses the harsh sun to dry tomatoes, ochre and berries for the market. It is the dry season there, with dust coating everything. Children find relief playing in the low and polluted lakes and rivers, alongside carpet washers. Clean water is in high demand, but poor neighborhoods, called quartiers, on N'Djamena's outskirts do not benefit from the city's utilities grid. Instead, they rely on shallow wells or, if they can afford it, water vendors. Even then, there is no guarantee that the water is clean. In 2016, over 17,000 people contracted cholera in Chad, with thousands of cases in the capital alone. In the same year, UNICEF started building clean water delivery systems in the poor communities around N'djamena in partnership with the "Secours Islamique France". The wells are 60 meters deep – far deeper and, thus, far cleaner than the open or hand-pumped wells commonly used here. Solar panels fuel the pumps, which suck up and deliver the water to an elevated tank, which in turn feeds two water points.

3 Results and Discussion

The UN analytical brief present a summary of core elements needed to achieve and to maintain water security, synthetized from a broad range of sources access to safe and sufficient drinking water as affordable cost in order to meet basic needs, including sanitation and hygiene, safeguard health and level of well-being. In spite of the importance and the apparent abundance of water, most of Sub-Saharan Africa faces a serious water scarcity problem. Countries of the CEMAC zone are not margin of the situation. These five countries face water crises. Cameroon is crisscrossed by many rivers that run from the countries mountainous north to the south. It is believed to have one of the world's largest reserves of fresh water. But for more than three months, millions in the Cameroon capital have gone without it. The ministry of water and the water utilities corporation, Camwater, says a drop in the water level at major catchments has caused the problem. But it is also clear that over the years, new infrastructure was not built to match the city's rapidly growing population. The unplanned expansion of the sprawling city has left entire neighborhood unconnected to the city's water network. Cameroon plans to increase Yaounde's water supply to 500,000 m^3 in two years by tapping into the Sanaga, one of the country's largest rivers. The move should increase potable water supply from more than 30% to 60% of the population.

3.1 Protection of livelihoods and human rights

This means to reduce inequality within and among countries. One cannot live in a truly developed world without equal opportunities for both countries and their citizens. Equality is at the core of all sustainable development goals. Together, one can empower and promote the social, economic and political inclusion of all people irrespective of age, sex, disability, race, ethnicity, origin, and religion, economic or other status. Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels. One can only look forward to a more equal and sustainable world, if one has more peaceful and inclusive societies. That means one needs to reduce crime, violence, and exploitation. The illegal arms and drug trade will have to stop. Public institutions that one relies on will have to be effective, transparent and accountable. The protection values receive a mark of 3.5/5, which is an average mark for the five countries in CEMAC zone as resumed in Table 1.

3.2 Water for environmental development

Urgent actions must be taken to combat climate change and its impacts. The world's industrialized nations have changed the balance of the earth's carbon cycle over the last 150 years by burning large amounts of fossil fuels. Climate change has the potential to derail other efforts toward sustainable development by altering weather patterns that threaten the food production and increasing sea levels, which will displace coastal communities. One needs to increase awareness and convey urgency to world leaders, so one can begin combating climate change before it is too late. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss. Pressures from the growing global population, urbanization and climate change are causing biodiversity to decline. Most developing countries rely on meat from wild animals for food. Let's work to restore and to protect our planet's biodiversity in order to prevent land degradation, ecosystem imbalance, and food insecurity. The water supplies for socio-economics and environmental development in the CEMAC area receive a mark of 2.5/5.

3.3 Wastewater treatment/sanitation

Ensure availability and sustainable management of water and sanitation for all. More than half of households worldwide have access to clean water in their homes; however, the number of people without adequate sanitation (a safe toilet) is increasing as people move into more crowded cities. Diseases caused by contaminated water kill more people every year than all forms of violence, including war. By prioritizing clean water, one can improve the health and livelihoods of millions of people. Water is essential to life. As populations grow and economies expand, access to clean and safe water is imperative. Isotopic techniques shed light on the age and quality of water. Some countries use this to implement integrated water resource management plans to sustainably use resources and to protect water and water-related ecosystems. For this point, the mark is 3/5.

3.4 Water for economic development

Isotopic techniques provide accurate assessments of soil erosion and help to identify erosion hot spots, providing an important tool to reverse land degradation and restore soils. The IAEA's support in this area helps many countries to gather information using these techniques to shape agricultural practices for more sustainable use of land and, ultimately, to increase incomes, while also improving conservation methods and protection of resources, ecosystems and biodiversity. Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all. Economic recession has taken a toll on both the quantity and quality of jobs around the world. For the 190 million unemployed, job availability is the key not only to economic growth, but also to more equal wealth distribution. Economic prosperity and opportunities for gainful employment are critical for safe, stable societies. This enables the building of an organizational capacity, the bargaining power of inhabitant's people, and achieving sustainable improvements in the prospects for income generating activities of women and young people. The World Bank and other international agencies assist in promoting good governance in public enterprises. The good governance receives a mark of 3/5.

Table 1: Water Security Index WSI of CEMAC Countries

Countries	Cameroon	CAR	Chad	Congo	Guinea Eq.	Gabon	Average
Protection of livelihoods and human rights	4	4	3	3.5	3.5	3	3.5
Water for environmental development	3	2	2	2.5	2.5	3	2.5
Wastewater treatment/sanitation	2.5	3	3	3	3	3.5	3
Water for economic development	3	2.5	3	3	3	3.5	3
Water security index (WSI)	3.3	2.7	3	3	3	3	3

The Water security index (WSI) for CEMAC Countries is 3.3 + 2.7 + 3 + 3 + 3 + 3 = 18/6 = 3, which is above the average of all African countries.

Ensuring access to water is increasingly becoming a challenge in the world in general and in Central Africa in particular. Countries are facing significant threats of water scarcity and increasing volatility of supply, attributable to factors such as climate, geography and demographics (Kalbermatten et al., 1982; Rijsberman, 2006). Limited access to water can *“jeopardize economic growth and social wellbeing”*. The acquisition of modern infrastructures for potable water and wastewater treatment, transmission could improve on the water security index of our community.

4 Conclusions

The objective of this study was to evaluate the water security index in five countries in Central Africa (CEMAC). Water security has recently received attention, but it has been an issue in several regions for decades. Particularly in many urban centers in Sub-Saharan Africa, poor sewage infrastructure and limited access to piped or improved water sources have been a persistent and chronic issue. In such situation, perception of what is normal water access, might be distorted, hence, continuing to use environmental indicators such as common water sources, per capita water use and excreta disposal facilities might provide a clear indicator of water related issues. However, a valid scale to measure water insecurity at the household level is needed, especially to capture anxiety, changes in water intake behaviors and food access issues those families due to water shortage. Also, a scale will be useful to capture opportunity cost and risk of food insecurity due to limited water access.

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SOCIAL FOOTPRINT OF WATER AND SANITATION IMPROVEMENTS
IN LOW HDI COUNTRIES

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Keywords: Life cycle assessment; social LCA; sustainable development goals; water and sanitation services;

Abstract

Investment in water and sanitation is needed to achieve the Sustainable Development Goals (SDG). Improving access to safe water and sanitation facilities has substantial effects on health. This paper aims to assess social impacts of intervention scenarios regarding water and sanitation improvement in five low Human Development Index (HDI) countries. These improvements should result in establishing a better public health and a higher environmental quality, which in turn should result in lower public healthcare expenses, liberating resources for other areas like education and security. Social impacts were assessed combining impacts on productivity and impacts on human well-being according to the social footprint impact assessment, considering characteristics of each country studied. In different levels between the analyzed countries, economic benefits of providing access to safe drinking water and wastewater treatment services to the population would vary from US$ 186,000 to more than US$ 150,000,000 annually, considering just the reduction of diarrheal disease incidence. In this way, sanitation improvements will not be only economically feasible, but also socially affordable from a sustainability perspective according to the SDG.

1 Introduction

With the deadline for the Millennium Development Goals expired in 2015, there has been a call for renewed development targets in the context of the Sustainable Development Goals. These goals include universal access to improved water and sanitation for all by 2030, which still remains a challenge mainly for developing countries, since the ability of governments to expand access is constrained by limited financial resources (Evans, 2005; Whittington et al., 2007; Ndikumana & Pickbourn, 2016; Fuller et al., 2016).

It is remarkable that improving access to safe water and sanitation facilities has substantial spill over effects on the overall wellbeing of the population resulting from better hygienic conditions and improved public health (Ndikumana & Pickbourn, 2016; Garfi & Ferrer-Martí, 2011). Estimates from Ortiz-Correa et al. (2016) suggest that access to water and sanitation services also has a positive and significant effect on schooling, when measured by the completed number of school years.

The main effects of improved sanitation are related to diarrheal disease. Infectious diarrhea includes cholera, salmonellosis, shigellosis, amoebiasis, and other protozoal and viral intestinal infections. These are transmitted by water, person-to-person contact, animal-to-human contact, and food borne, droplet and aerosol routes (Haller et al., 2007). Diarrheal diseases are most common in low-income countries with poor access to clean water, sanitation, and urgent medical care, but are also a frequent cause of hospitalization in high-income countries, making diarrhea an important health problem globally. From 2000 to 2015, the total annual number of deaths from diarrhea among children under 5 decreased by more than 50%, from over 1.2 million to half a million. Thus, better access to clean water, improved sanitation, and fewer cases of malnutrition are likely to be responsible for the reduction in mortality rates for children under 5, while many more children could be saved through basic interventions (UNICEF, 2017). Additionally, a wide range of health problems like infectious hepatitis, trachoma, schistosomiasis and other geo-helminthiases would be reduced by improvements of water and sanitation services.

Additionally, there are many more benefits associated with water and sanitation services. However, the valuation of external benefits is often not accessed because they are not set by the market (Hernández-Sancho et al., 2010). In this way, nowadays social issues have been gaining attention by the LCA community (Guinée et al., 2011). Social footprint is a practical, yet comprehensive approach to accounting the productivity impact by a monetary value for the sum of all productivity-reducing externalities. The term "social" is used as in welfare economics, to signify an accounting that encompasses the entire societal economy, as in "social costs", combining private costs and externalities (Weidema, 2018). In this context, this paper evaluates the social footprint of water supply and sanitation improvements in five countries with low HDI (Afghanistan, Haiti, Ethiopia, Uganda and Tanzania), taking into account health impacts on the population by the reduction of diarrheal disease.

2 Material and Methods

The lack of water and sanitation services in countries with limited or no progress toward the MDG target according to WHO/UNICEF Joint Monitoring Programme was studied in order to estimate social impacts involved in providing universal access to those services in the domestic sector of those countries in 2030. Investment scenarios were drawn up by considering that 100% of the population in each country will get access to improved water supply and sanitation in 2030, according to Figure 1.

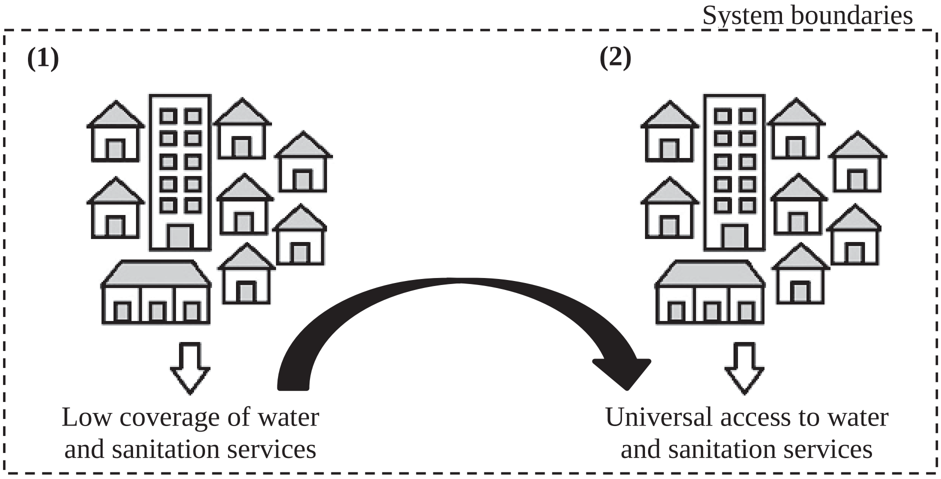


Figure 1: Scope of the study – Access to water supply and sanitation by 2030

Demand analysis

Five countries were selected based on the following criteria: Improved sanitation services covering less than 30% of the population with limited or no progress to meet the MDG as per WHO/UNICEF program; and low HDI, according to UN data (Table 1).

Table 1: General characteristics, HDI and its components of selected countries

	Afghanistan	Haiti	Ethiopia	Uganda	Tanzania
Human Development Index (HDI)[1]	0.465	0.483	0.442	0.483	0.521
Life expectancy at birth (years)[1]	60.4	62.8	64.1	58.5	65
Expected years of schooling (years)[1]	9.3	8.7	8.5	9.8	9.2
Gross national income (GNI) per capita (2011 PPP $)[1]	1,885	1,669	1,428	1,613	2,411
Population, total (Millions)[2]	33.5	10.9	103.9	42.8	55.4
Population, urban (% of total)[2]	27.6	60.9	20.4	16.8	33.0
Improved water access (%, in 2015)[3]	55.3	57.7	57.3	79.0	55.6
Improved sanitation access (% in 2015)[3]	31.9	27.6	28.0	19.1	15.6
Domestic water use (L/cap.d)[4]	13.4	49.2	9.4	23.8	27.9

Source: [1]United Nations (UN). Human Development Indices: A statistical update (2015); [2]United Nations (UN). Population division (2014); [3]WHO/UNICEF (2015); [4]World Bank (2014).

First, the population growth in each country was assessed using data from the UN (2014), considering both urban and rural projections. Additionally, three scenarios were modelled regarding the water user types, as suggested by Koutiva & Makropoulos (2016), in which the change of water conservation attitudes is explored from negative to positive points of view. Then, based on the average baseline scenario of water use for each country (World Bank, 2014), scenarios of water use were projected, considering 30% of variation in consumption, depending on the conservation attitudes. A sensitivity analysis was made considering different water uses projections.

Interventions and scenarios modelled

Interventions were chosen based on the percentage of people with effective access to water and sanitation services for the years 2018 to 2030. The proposed interventions were assessed by moving the population of each selected country to higher exposure categories in a constant rate up to reach 100% of water and sanitation services.

Costs and benefits of modelled interventions are presented on an annual basis in US$ for the year 2018. The analysis assumes a first year of intervention in 2018 and an intervention period of 12 years until the end of 2030. All costs and benefits occurring after 2018 are expressed in 2018 values using a discount rate of 3%.

Following the demand analysis results, the expected investment costs were assessed, which consists of all resources required to put in place and to maintain the interventions, as follows: pumping, storage, transmission, treatment and distribution of drinking water as well as collection and treatment of wastewater, also including costs of negative externalities, as damages imposed by the discharge of treated wastewater.

The estimated investment costs of water supply and sanitation facilities interventions could vary widely due to many reasons, including the selected technologies, level or scale of treatment (the larger the quantity of water or wastewater treated, the lower the per-unit cost), geographic location or even the resource availability, since in regions with abundant freshwater supplies, the opportunity cost of diverting water from existing or potential users may be very low. Thus, cost estimates of expanding water and sanitation services in urban areas were adopted according to Whittington (2011), in which improved water services cost varies from 0.35 US$/$m^3$ to 0.85 US$/$m^3$ and improved sanitation services cost varies from 0.45 US$/$m^3$ to 1.15 US$/$m^3$. Based on these data, it was accepted that rural costs of improving water and sanitation services account about one third of urban expenditures (WHO, 2017; McIntyre et al., 2014). Table 2 shows estimated costs of improving water and sanitation services based on population growth of each country (US$ for the year 2018). A financial discount rate of 3% was used to calculate the present value of the future cash flows.

The lowest estimated costs could represent a situation, in which the population has access to improved water supply and sanitation facilities through low cost technologies, while the highest estimated costs correspond to the situation typically encountered in developed countries with high coverage of high technology services such as in-house regulated piped water supply and sewer connection.

Table 2: Costs of improving water supply and sanitation service based on population growth (US$ for the year 2018)

Countries	Afghanistan	Haiti	Ethiopia	Uganda	Tanzania
Estimated population in 2030, total (millions)[1]	49.6	12.5	149	63.4	79.4
Additional cost of providing universal water and sanitation services, low (US$, millions)[2]	482	742	3,112	1,016	1,815
Additional cost of providing water and sanitation services, high (US$, millions)[2]	2,130	3,280	13,759	4,487	8,069

Source: [1]United Nations (UN). Population division (2015); [2]Estimation based on Whittington (2016).

Assessing the health impacts

Although a full analysis of improved water and sanitation services would consider many water-related diseases, distinguished by different routes of infection (as cholera, typhoid, trachoma, schistosomiasis, malaria, filariasis, dengue and legionellosis), the analysis in this paper has been restricted to diarrheal disease as it accounts for the main disease burden associated with poor water supply and sanitation, in which 90% of deaths are children under five (Haller et al., 2007). Thus, each exposure scenario was assigned a relative risk (RR) of diarrheal. Figure 3 estimates the proportional reduction in disease or death that would occur if exposures were reduced to an alternative baseline level bearing a minimum risk (also referred to as theoretical minimum risk), while other conditions remain unchanged. It is derived from the proportion of people exposed to the conditions of interest and the relative risk of disease related to the exposure.

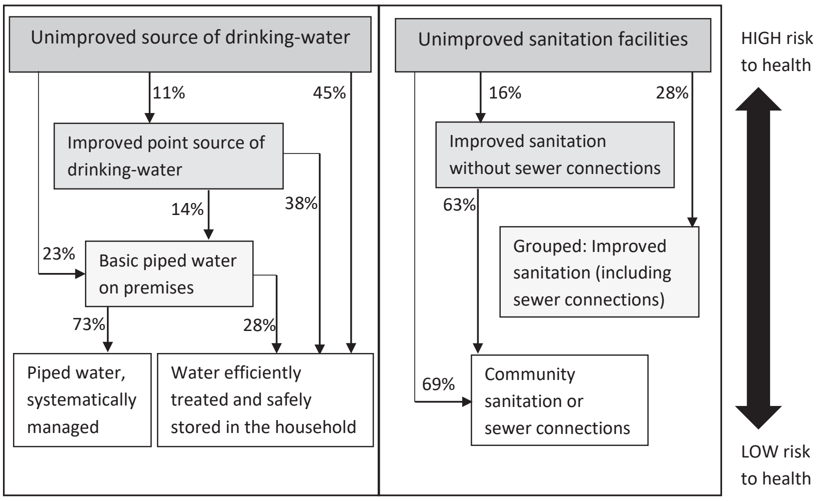


Figure 3: Drinking-water supply and sanitation transitions and associated reductions in diarrhoeal disease risk *(Source: WHO, 2014).*

In general, interventions might change the incidence and duration of different health problems as well as fatality rates. Because interventions to improve water supply and sanitation services are preventive interventions, the main outcome is, first, a reduction in the number of diarrheal episodes and, accordingly, a proportional reduction in the number of deaths. For each intervention in each sub-region, a new incidence rate was calculated based on the number of persons, which were moved to lower exposure categories, and the amount of exposure reduced in that population.

For instance, a reduction of 23% in diarrheal diseases can be observed, when providing basic piped water on premises, and of 45%, when providing water efficiently treated and safely stored in the household. Therefore, for each country, the risk reduction rates was assessed varying from 11% to 73% for drinking water services' improvements, and from 16% to 69% for sanitation services' improvements, corresponding to the absence of transmission of pathogens causing diarrheal through inadequate water, sanitation and hygiene.

Reduced hospital expenses

The lowered hospital expenses according to the WHO-CHOICE model were projected (WHO, 2011), which have developed estimations of the unit costs of a hospital bed-day, outpatient department (OPD) visit and health centre visit in different settings using a regression model. In the model, nation-wide numbers are a function of GDP, ownership (public/private), level of the facility for hospital bed-day and OPD unit costs (primary, secondary and tertiary), the level of capacity utilization and whether or not capital and food costs are included (for hospital bed-days) (WHO, 2011).

Table 3 shows the estimates of child cause of death in the selected countries due to diarrheal for the year 2015, according to UNICEF Data (2015), as well as the unit cost related to health care services as per WHO (2011).

Table 3: Estimates of child diarrhoeal cause of death, 2015

Countries	**Afghanistan**	**Haiti**	**Ethiopia**	**Uganda**	**Tanzania**
Estimates of child cause of death, diarrhoeal 2015 (inhabitants)[1]	525,977	1,860	15,535	7,001	8,000
Cost per bad day (US$)[2]	4.08	4.39	2.07	3.65	3.39
Cost per outpatient visit (US$)[2]	1.86	1.78	0.91	1.39	1.32

Source: [1]UNICEF (2015); [2]WHO (2011), secondary-level hospital (highly differentiated by function with five to ten clinical specialities).

Assessing social impacts

The LCA, as standardised by ISO 14040 (2006) and ISO 14044 (2006), was applied using SimaPro software 8.3. The goal and scope of this LCA is to assess social impacts by expanding the domestic access to water and sanitation services at the selected countries. Thus, through the intervention scenarios modelled, the potential improvement of social conditions raised from the universal access to those services was assessed. The main function of water and sanitation services is to ensure both human and environmental health, promoting hygiene through the prevention of contact with hazardous contaminants. The functional unit is defined as the total volume of water and wastewater demanded by the population of five selected countries until 2030.

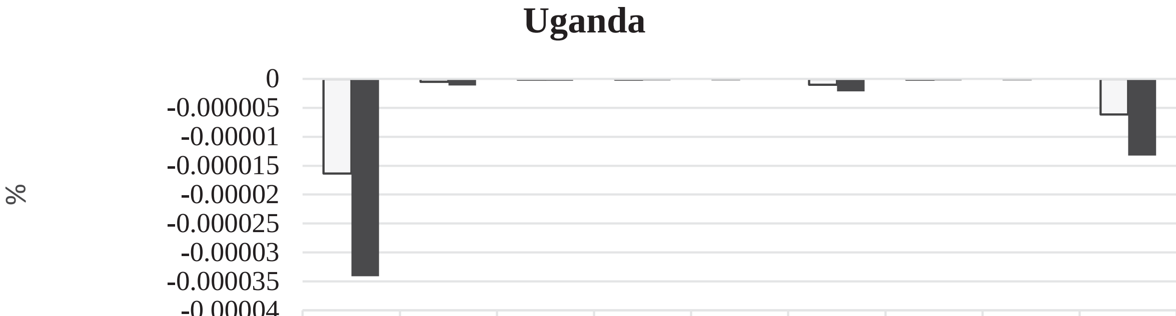
In order to weight social impacts, a novel way of combining impacts on productivity and impacts on human well-being according to Weidema (2018) was applied, showing that inequality implies that an intervention that changes the amount of QALY (quality-adjusted life years) for a population group will always give a larger change in well-being than an intervention of the same monetary value that only affects the level of consumption of the same population group.

The databases of Exiobase v3.3.102c were used for the processes included in the social footprint analysis, in which the following regions were considered to represent the selected countries: Rest of the World Africa (WF), including Uganda, Ethiopia and Tanzania; Rest of the World America (WL), including Haiti; and Rest of the World Asia and Pacific (WA), including Afghanistan.

3 Results and Discussion

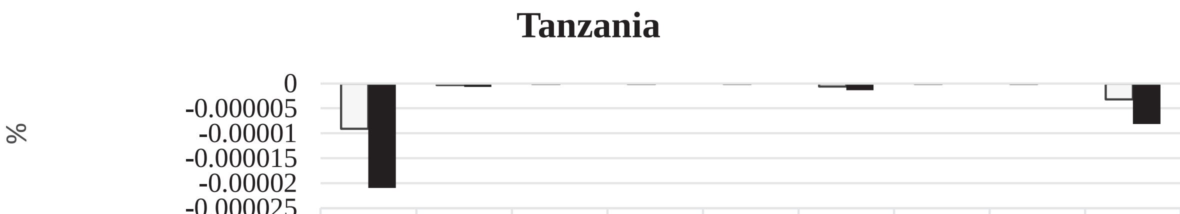
At the global level, the spending required to provide universal access to water and sanitation services would cost more than US$ 20 billion annually (Hutton et al., 2007), while in different levels between the analyzed countries (Uganda, Ethiopia, Tanzania, Haiti and Afghanistan), economic benefits of providing access to safe drinking water and wastewater treatment services to the population would vary from US$ 186 thousands to more than US$ 150 million per year in each country, considering just the reduction in the incidence of diarrheal disease, which means that this benefit can be even higher if it would account for other benefits provided by this intervention as well.

Figures 3 to 7 show social impact benefits from the interventions in each country in the following impact assessment categories: productivity impact (utility-weighted), utility weighted value added (PPP), life cycle costs, work hours, insufficient clean water, insufficient education, insufficient health care, undernutrition and productivity impact.



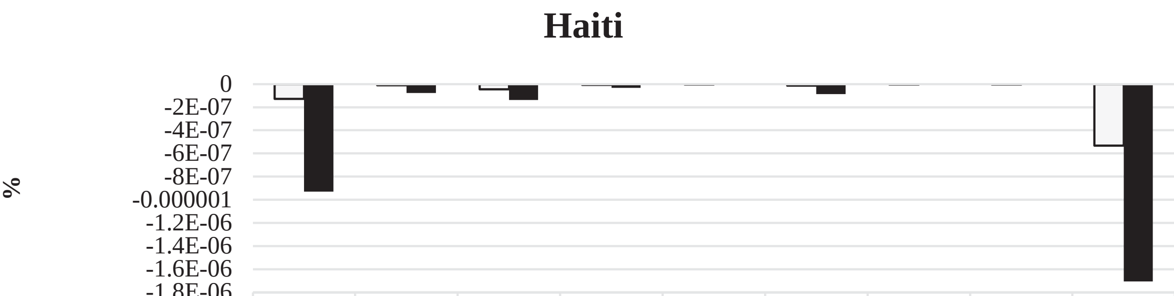
	MEUR, PPP Productivity impact, utility-weighted	MEUR, PPP Utility weighted value added (PPP)	MEUR Life cycle costs	Million h Work hours	MEUR, PPP Insufficient clean water, u.w.	MEUR, PPP Insufficient education, u.w.	MEUR, PPP Insufficient health care, u.w.	MEUR, PPP Undernutrition, u.w.	MEUR, PPP Productivity impact
□ Uganda high cost scenario	-1.63E-05	-5.56E-07	-1.46E-07	-1.2E-07	-2.59E-08	-1.05E-06	-1.29E-07	-5.03E-08	-6.16E-06
■ Uganda low cost scenario	-3.41E-05	-1.16E-06	-3.21E-07	-2.57E-07	-5.38E-08	-2.18E-06	-2.67E-07	-1.05E-07	-1.33E-05

Figure 3: Social impacts of water and sanitation services improvement in Uganda



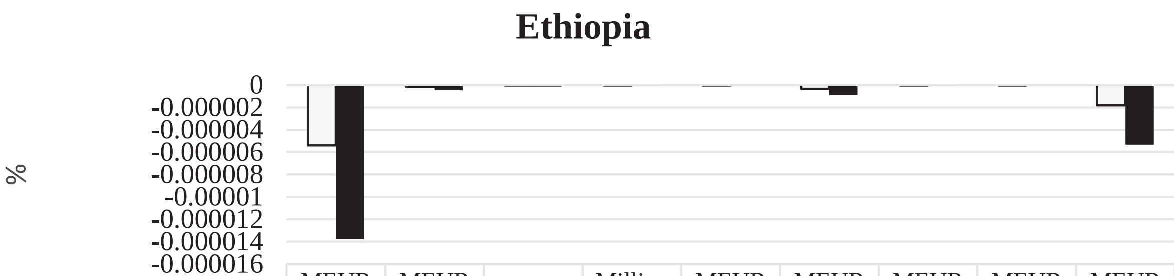
	MEUR, PPP Productivity impact, utility-weighted	MEUR, PPP Utility weighted value added (PPP)	MEUR Life cycle costs	Million h Work hours	MEUR, PPP Insufficient clean water, u.w.	MEUR, PPP Insufficient education, u.w.	MEUR, PPP Insufficient health care, u.w.	MEUR, PPP Undernutrition, u.w.	MEUR, PPP Productivity impact
□ Tanzania high cost scenario	-9.08E-06	-3.09E-07	-7.21E-08	-6.41E-08	-1.45E-08	-5.84E-07	-7.19E-08	-2.82E-08	-3.18E-06
■ Tanzania low cost scenario	-2.1E-05	-7.15E-07	-1.95E-07	-1.57E-07	-3.31E-08	-1.34E-06	-1.65E-07	-6.44E-08	-8.1E-06

Figure 4: Social impacts of water and sanitation services improvement in Tanzania



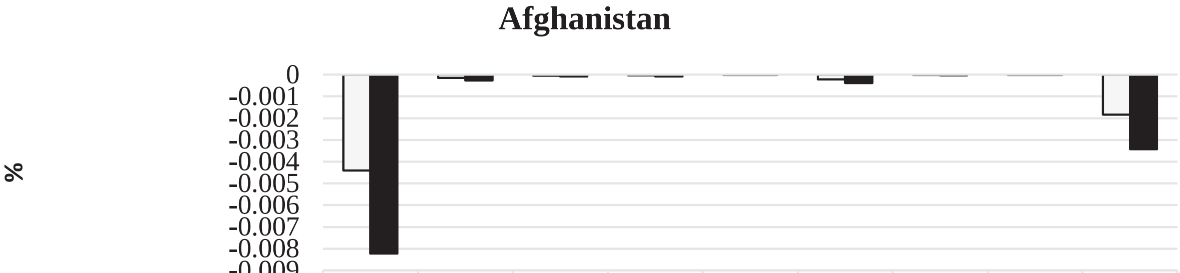
	MEUR, PPP Productivity impact, utility-weighted	MEUR, PPP Utility weighted value added (PPP)	MEUR Life cycle costs	Million h Work hours	MEUR, PPP Insufficient clean water, u.w.	MEUR, PPP Insufficient education, u.w.	MEUR, PPP Insufficient health care, u.w.	MEUR, PPP Undernutrition, u.w.	MEUR, PPP Productivity impact
□ Scenario 2 Haiti high	-1.29E-07	-1.2E-08	-4.41E-08	-8.1E-09	-8.37E-11	-1.36E-08	-9.04E-10	-2.15E-10	-5.34E-07
■ Scenario 2 Haiti low	-9.29E-07	-7.72E-08	-1.37E-07	-3.25E-08	-4.45E-10	-8.7E-08	-5.58E-09	-1.23E-09	-1.71E-06

Figure 5: Social impacts of water and sanitation services improvement in Haiti



	MEUR, PPP Productivity impact, utility-weighted	MEUR, PPP Utility weighted value added (PPP)	MEUR Life cycle costs	Million h Work hours	MEUR, PPP Insufficient clean water, u.w.	MEUR, PPP Insufficient education, u.w.	MEUR, PPP Insufficient health care, u.w.	MEUR, PPP Undernutrition, u.w.	MEUR, PPP Productivity impact
□ Scenario 2 Ethiopia high	-5.41E-06	-1.84E-07	-3.99E-08	-3.65E-08	-8.69E-09	-3.48E-07	-4.3E-08	-1.69E-08	-1.83E-06
■ Scenario 2 Ethiopia low	-1.38E-05	-4.69E-07	-1.28E-07	-1.02E-07	-2.18E-08	-8.83E-07	-1.08E-07	-4.24E-08	-5.33E-06

Figure 6: Social impacts of water and sanitation services improvement in Ethiopia



	MEUR, PPP Productivity impact, utility-weighted	MEUR, PPP Utility weighted value added (PPP)	MEUR Life cycle costs	Million h Work hours	MEUR, PPP Insufficient clean water, u.w.	MEUR, PPP Insufficient education, u.w.	MEUR, PPP Insufficient health care, u.w.	MEUR, PPP Undernutrition, u.w.	MEUR, PPP Productivity impact
□ Scenario 2 Afghanistan high	-0.004401	-0.000144	-4.4E-05	-3.92E-05	-1.95E-06	-0.00021	-1.61E-05	-3.75E-06	-0.001836
■ Scenario 2 Afghanistan low	-0.008228	-0.00027	-8.24E-05	-7.32E-05	-3.64E-06	-0.000393	-3.01E-05	-7.01E-06	-0.00343

Figure 7: Social impacts of water and sanitation services improvement in Afghanistan

It is noticed that the productivity impact category is the most relevant impact category of the social footprint of water and sanitation service interventions. Also, it is possible to note that Afghanistan has the most evident positive benefits compared to other countries due to the high hospital expenses' reduction.

It is worth mentioning that, in the context of the sustainable development goals, an improvement action on water and sanitation issues does not only influence SDG 6 corresponding to clean water and sanitation, but this also influences other SDGs that might be directly or indirectly related. In this sense, for example, life on land (as stated in SDG 15 - life on land) can only be healthy, when all the waste is managed properly, including wastewater. In the same way, high rates of sewage being discharged into rivers and oceans, aquatic life is also drastically influenced (SDG 14 - life below water). Also, without access to quality water, it is not possible for the population of any country to meet the basic requirements that guarantee good health and well-being (and consequently impacting SDG 3 - good health and well-being).

Conceptually, any tariff must be linked to the provision of a service that can be quantitatively measured. The tariff balance method assumes that all costs incurred are covered by a tariff to be applied to consumers, by the polluter pays principle; but this tariff should be within the constraints of affordability and willingness to pay of customers (WHO, 2017). So, households have direct taxes to make feasible access to water and sanitation services (Santos et al., 2011).

On the one hand, there are the total annual costs of each country (financial and operational services), and, conversely, the estimated benefits from the public health improvement and the tariff collection. The relationship between the two represents the amount to be allocated to the unit of volume to achieve the balance between costs and expenses. Finally, there is an annual value to be attributed to each cubic meter of sewage treated. On average, those on low incomes spend a significantly greater proportion of their income on water than the wealthy ones, which affects their ability to invest in other basic needs such as food, shelter, clothing, housing, health and education. The absolute price they pay to water vendors can be ten times or more the price per liter supplied through the pipes" (COHRE et al., 2008). Although charging for water and sanitation is affecting behavior towards conservation and efficient water usage, it is important to know the consumers' willingness to pay for additional investments in water and sanitation services, since it is strongly sensitive to factors as the scope (i.e., the magnitude of improvement in drinking water services) or average household income (Van Houtven et al., 2017; Souza et al., 2017).

In the same fashion, occasionally, the consumers' willingness to pay for improvements in water and sanitation services is far below retail prices, indicating that significant scale-up may need significant subsidies. For example, it has been reported that in regions with low levels of coverage, the willingness to pay for improved drinking water access greatly exceeds the cost of provision (Burt et al., 2017). While it is observed low cost recovery overall, especially in rural areas, it is also clear that cost recovery rates can differ greatly within countries from municipality to municipality. Larger municipalities can better recover costs than smaller municipalities with less capacity (WHO, 2017).

When full cost recovery is not possible by the tariff collection, foreign aid disbursements produce a strong, positive, and significant effect on improved access to water supply and sanitation (Gopalan & Rajan, 2016). However, it is noted that the proportion of aid allocated to water and sanitation has steadily declined since 2012 with respect to other development priorities, such as health, refugees, and humanitarian assistance (WHO, 2017). 85% of the global population without access to improved sanitation or drinking-water from an improved source lives in three SDG regions: Central Asia and Southern Asia, East and South-Eastern Asia, and Sub-Saharan Africa. However, aid commitments to these three regions were only 48% of global official development assistance (ODA) for water and sanitation in 2015 (WHO, 2017).

Nevertheless, foreign aid allocation is not a new issue. Data from Njoh (2013) shows that in Africa, for example, a positive association was uncovered between colonial tenure and the availability of improved water and sanitation facilities. The high cost associated with public infrastructure projects means only national or local governments possess the wherewithal to develop them. This was particularly true during the colonial era, when local non-governmental entities possessed no resources of their own. Thus, the costly nature of such projects meant that colonial powers could only develop them in territories intended for permanent European settlement. The entire colonial project is abhorrent and indefensible. Moreover, its reprehensibility notwithstanding, colonialism laid the foundation for some development initiatives in colonized countries (Njoh, 2013; Njoh & Akiwumi, 2011). Hence, lessons from the past demonstrate that countries severely explored or just disadvantaged, need to be helped by countries, which present capacity to support their own development.

On the other hand, capital subsidies for water supply and sanitation investments require disciplined public-sector resources allocation, demanding attention against corruption and excessive use of water. Such discipline is extremely difficult when subsidies come from outside the community that is to benefit from the investment, thus an intensive supervision of the real improvement would be demanded (Whittington, 2016). In some circumstances, the financed community could provide part of the associated stream of positive benefits as a form of payment to the first world countries, by financial or non-financial terms, as carbon credits for example.

4 Limitations

Estimates of health impacts from the interventions are likely to underestimate the burden, since the analysis was restricted to the effects of diarrheal and not all the potential diseases or risks. Additionally, impacts on the case fatality rate also have not been considered.

5 Conclusions

It is recognized that deficiencies in the water and sanitation services compromise both the environment and public health, triggering environmental damage, which can generate short and long-term effects. Investments in water and sanitation, even based on external funding provided by a cooperative approach between countries, in addition to providing benefits related to health, tend to instigate socio-economic development, leading to new investments in other sectors of the economy. In different levels between the analyzed countries, economic benefits of providing access to safe drinking water and wastewater treatment services to the population would vary from US$ 186 thousands to more than US$ 150 million, considering just the reduction of diarrheal disease incidence.

It is important to put the Sustainable Development Goals at the heart of the developmental policies to underpin the trajectory and the direction, in which sanitation infrastructure need to be designed and developed. The evidence compiled in this paper demonstrates that investing in sanitation is socially, environmentally and economically worthwhile.

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INDICATORS OF WATER ACCESS AND INCIDENCE OF DISEASES IN SLUMS OF THE PROAP PROGRAM

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Abstract

The popular settlement urbanization program (PROAP) aimed to improve the quality of life of residents of low-income informal settlements in the city of Rio de Janeiro. The objective of the program was to equip these settlements with basic urban infrastructure, to develop social programs and to promote land and social regularization. A diagnosis made in the year 2014 identified urban and social infrastructure problems, indicating the basis for the project proposals. The same diagnosis was repeated in 2017 after the works of the program to be able to identify the impacts caused, using a methodology of monitoring and evaluation. The diagnosis has promoted indicators of urban infrastructure, health, environment, housing, family income and others. The present article presents a summary of these indicators that allow crossing data of urban infrastructure with the data of health of the populations of the favelas presented.

1 Introduction

In Brazil, popular settlements constitute a contemporary urban phenomenon associated to the processes of socio-spatial segregation imposed by the absence of wealth redistribution mechanisms and housing policies that guarantee access to housing for the poorest sections of the population. In Rio de Janeiro, these settlements are called “favelas”. These favelas are part of the urban scenario, representing one of the most serious social issues facing the city. These favelas can be generically characterized as settlements informal networks that present precarious urban infrastructure networks, such as accessibility, sewage and drainage, and public services, such as education, health and leisure, as well as the irregular ownership of land.

In the city of Rio de Janeiro, the Land Settlement Program, and PROAP, financed with IDB (Inter-American Development Bank*)* funds and a counterpart from the City Hall, constituted Urbanization Programs for Popular Settlements in Rio de Janeiro. PROAP was based on the guidelines established by the Decennial Master Plan of the City, sanctioned in 1992. The program was set up to run in low-income popular settlements (favelas and irregular settlements), meeting the need for urbanization and land regularization of the popular settlements and its integration into the neighborhoods, and its inclusion in the maps and registers of the city. The program aims to improve the quality of life of residents of low-income informal settlements (slums or irregular settlements) in the city of Rio de Janeiro. The goal is to provide these settlements with urban infrastructure and basic social services.

The main health impact of inadequate sanitation, water, personal hygiene and food is associated with the occurrence of intestinal infections, the most frequent manifestation of which is diarrhea. Chemical poisonings and other infections such as leptospirosis are more associated. Other diseases transmitted to people, who have water reservoirs, such as hepatitis A, dengue, schistosomiasis and malaria, afflict millions of people worldwide and persist despite the fact that their modes of transmission are well known.

This article presents part of a diagnosis based on a descriptive analysis of the field research carried out to assist in the monitoring and evaluation of the Urbanization Program for Popular Settlements of Rio de Janeiro (PROAP III), and the data collected in relation to access to water and incidence of chronic diseases. The objective is to compare two field surveys, carried out in 2014 and 2017, to evaluate the impact of urban interventions that were carried out in the communities and had as objectives (i) to raise the socioeconomic situation of the population and urban development of the favelas, (ii) to allow a common reading of the reality, and (iii) to permit the comparison of the intervention areas before and after the project and among themselves through the application of similar collection instruments.

The 2014 data collection was prior to the project, identifying problems, needs and design of the project. The results and impact indicators were created as a basis for comparing the initial and final situation of the program, in addition to serving and to guide the team responsible for the program in the planning of actions. Segment research has the objective of compiling the same indicators and comparing the situation prior to the implementation of the project in order to assess, whether there was a significant gain with the implementation.

2 Water Security

The scientific community defines water security as the ability to safeguard an availability of water sufficient to sustain lives and livelihoods and protect against threats to and from water. Water security presents water management and protection as an access and availability issue focused on guaranteeing that our needs as humans are met. This concept defines that water must be managed sustainably throughout its cycle through an interdisciplinary approach, contributing to socio-economic development, enhancing society's resilience to environmental impacts and avoiding water-borne diseases without compromising the ecosystem. Achieving water safety requires that allocation among users be fair, efficient and transparent; that water to meet basic human needs is accessible to all at an affordable cost to the user; that water along the water cycle is collected and treated to avoid pollution and disease; and that fair, accessible and effective mechanisms exist to manage or deal with disputes or conflicts that may arise. The concept operates at all levels, from the individual, home and community, to local, subnational, national, regional and international levels, and takes into account the variability of water availability over time.

The management of water security can be divided into some categories:

- National Security ; Sanitation, Health and Hygiene
- Energy Production and Use; Global Markets
- Natural and Manmade Disasters; Natural Resources and Services
- Agriculture; Infrastructure
- Peace and Conflict; Governance and Institutions

The theme of this article is linked to the first category cited: Sanitation, Health and Hygiene. Clean, safe drinking water and adequate sanitation prevent people from getting sick and allow them to be healthy and productive members of society. The World Health Organization estimates that water supply and sanitation costs the world $ 260 billion annually. These costs result from premature deaths, health costs, productivity and time lost through the practice of open defecation. Investing in access to improved sanitation and the best water supply has a rate of return of more than 4 times for every US dollar invested. More than 2 million people die every year from diarrhea, with 90% of these deaths caused by poor hygiene and contaminated water. At least 1.8 billion people drink water contaminated with feces. Adequate water and sanitation help economic development and ensure healthy people.

Improved sanitation is defined as a toilet with discharge or discharge, connected to a sewage system, septic tank or improved well, latrine with slab or bathroom compost. Access to improved sanitation systems can save 30 min a day or 7.6 days a year. This time is spent in finding a safe place to defecate. This time can be spent at school, earning an income, or spending time with family and friends.

Another benefit is the reduced number of cases of waterborne diseases, caused by pathogenic microorganisms. Human waste contains pathogens like *E. coli* that cause infectious diarrhea, cholera, and other diseases. Other bacterial and viral infections use water as a vector or as an incubator for disease-spreading insects or animals, leading to malaria, guinea worm disease, typhoid and trachoma, among others. Exposure to these diseases results in lost income, lost productivity, increased medical and health care expenditures and permanent disabilities, including impaired cognitive ability in children. Improved sanitation reduces diarrhea morbidity by 37.5%.

Access to safe drinking water is essential for healthy people. Improved sources of drinking water include piped water into a dwelling, piped water to a tap in a yard or plot a public tap, a protected dug well, a protected spring, harvested rainwater, or a borehole. These constructions are designed to prevent from contamination. The benefits derived from providing safe, accessible drinking water include:

- More hand-washing and consequently better hygiene,
- Greater menstrual hygiene,
- Fewer visits to health care facilities,
- Fewer lost work days due to water-borne diseases.

Improvement in the quality of water infrastructure, access to potable water and basic sanitation are targets set for the 2030 agenda of Sustainable Development Goal (SDGs). Local policies and governments should seek to align their objectives with global agendas for sustainable development.

3 Material and Methods

The methodology chosen to carry out the monitoring and evaluation of the program consists of researches with a group of communities that was denominated as a treatment group and another one as control. The communities that belong to the treatment group are those served by the program. The communities that belong to the control group are not served by the program. The control group has similar characteristics of population and location with the treatment group. Table 1 shows the two favelas chosen for this article.

Table 1: Favelas chosen for work and classification

Favela	Group	Addresses 2014	Addresses 2017
Barreira do vasco	Treatment	3382	4605
Marechal Jardim	Control	1156	1643

The population surveyed is comprised of those responsible for housing, i.e., the boss or his/her spouse, aged 16 years and older, preferably, who participated in the survey in 2014. The favelas of both groups have an official water supply network, with daily supply 24 hours a day, but there are areas within these favelas, where water supply is clandestine and happens on alternate days with intervals of two days or even longer. In relation to the sewage network in the favelas of the control group, the sewage is released into the official network in a regular way. In the favelas of the control group, they still have sewage released in unofficial networks. In relation to water supply, there was a percentage increase of households that have piped water in at least one room in both groups. The main form of water supply remains the official network. Table 2 shows this growth. This table analyzes the access to water. There was a percentage increase of households that have piped water in at least one room, in both. Due to the fact that most households have access to piped water, it is observed that the main form of supply is through the general network.

Table 2: Distribution of homes according to access to water

Water pipes at home?	2014		2017	
	Treatment	Control	Treatment	Control
At home	3764	1132	4754	1727
On the property	386	166	171	104
Number	16	3	52	14

Both in the Treatment and Control favelas, there is official infrastructure installed for the drainage of rainwater. It is important to point out that we consider as drainage infrastructure lobes, rain gutters, trenches, gutters and gutters built on the sides of stairs and pathways. It is important to note that there is no presence of garbage or other objects in the installed drainage infrastructure.

Table 3: Water supply

Drainage of sewage	2014		2017	
	Treatment	Control	Treatment	Control
Rain gallery	1853	339	2347	573
Sewer collection network	2197	889	2587	1167
Straight to the street	83	33	13	30
Other	1	0	0	39
Don't know	17	22	29	23

Besides access to water, another important factor is the form of sanitary sewage. Table 3 shows how it is the different forms found in communities. Not all households in the treatment group community are connected to the sewage network; just over half of them are connected to the sewage network, and the other type of sewage is the most commonly used storm drainage pipes to eliminate sewage from the home.

Table 4 shows the types of diseases found in both groups. Nausea, vomiting and abdominal pain are the diseases that afflict both groups.

Table 4: Incidence of health dysfunctions

Severe or chronic diseases in the last year?	2014		2017	
	Treatment	Control	Treatment	Control
Nausea	271	149	688	303
Diarrhea	332	95	480	179
Asthma	274	132	325	264
Tuberculosis	16	6	41	82
Hepatitis	32	0	66	25
Verminose	22	12	16	13
Pneumonia	51	25	156	81
Leptospirosis	0	0	5	16

The distribution of serious diseases in the last year follows the same pattern for both moments (2014 and 2017) and also between groups. There was a small increase in serious diseases in the control group. This increase is mainly due to the higher percentage of people with tuberculosis. Pneumonia was the disease that got the greatest and difference in incidence in time.

Table 5 shows the incidence of diseases among the different groups in the period from 2014 to 2017. There has been a considerable increase in population in the treatment and control communities that masks the results, explaining why there was an increase in some diseases between the periods mentioned.

Table 5: Water supply and incidence of health dysfunctions

Disease Trend	**Treatment**	**Control**
Declined	Verminose	
Increased	Nausea, Diarrhea, Pneumonia, Leptospirosis	Nausea, Diarrhea, Hepatitis, Verminose

4 Conclusions

The main objective of the article was to be able to describe the current situation of favelas presented. In this way, the text is descriptive and not conclusive. The cancellation of PROAP may have influenced the information collected as well as the growth of favelas' homes. Overall indicators for water supply are positive, but chronic or serious diseases continue to occur.

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SOCIAL LEARNING AND COMMUNITIES OF PRACTICE – DRIVING WATER SENSITIVE DESIGN IN SOUTH AFRICA?

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Keywords: Water Sensitive Design; Community of Practice; alternative water resources; greywater

Abstract

South Africa (SA) is a water-scarce country facing significant water management challenges, including rapid urbanisation, environmental degradation and fragmented institutional structures. Alternative approaches to conventional water management, which aim to facilitate a change from *'water-wasteful'* to *'water-sensitive'* environments, are required, if serious economic and socio-political threats are to be averted. As one step towards advancing this vision for South African cities, a Water Sensitive Design (WSD) Community of Practice (CoP) programme was established with the aim of highlighting the critical linkages between the various aspects of this new paradigm through engagement with a wide range of stakeholders. The main focus areas are the identification of possibilities for collaborative and participatory interaction between all relevant actors, including awareness-raising and appropriate WSD training activities using the recently-published implementation framework and guidelines for the adoption of WSD in South Africa. The paper focuses specifically on the outcomes of two separate activities that are associated with the CoP programme and which are based in the City of Cape Town – a local-level CoP known as the Liesbeek Life Plan, and the development of guidelines for the use of greywater as a resource. The impact that these activities are having in terms of driving the uptake of WSD in the country and towards achieving the SDGs is discussed. Initial findings indicate that the CoP programme has the potential to generate a new understanding about innovative practices and reflexive learning within WSD in South Africa, and to develop knowledge connected to policy development and change to influence planning and design towards water sensitive cities.

1 Introduction

South Africa (SA) is a water-scarce country facing significant water management challenges, including rapid urbanization, environmental degradation and fragmented institutional structures. The situation is exacerbated by the fact that the country is considered to be one of the most consistently unequal societies in the world, with a Gini Coefficient of 0.68 (0 = equal distribution and 1 = maximum unequal distribution of incomes) (StatsSA, 2017). Basic water and sanitation services do not exist for a large proportion of the population; over 14 million people in the country do not have access to safe sanitation, and only 64% of households have access to a reliable water supply service (DWS, 2018). An opportunity, therefore, exists to introduce alternative approaches to conventional urban water management, which account for water supply and quality constraints and could lower the impacts (through adaptation and mitigation) of extreme weather-related events such as droughts and floods.

New models of water capture, provision, treatment and governance need to be explored and developed to transform *'water-wasteful'* urban environments to those that are *'water-sensitive',* where water is managed and treated in a sustainable manner. One such approach that is gaining recognition in SA, specifically as an enabler that could move the country closer toward meeting national developmental targets as well as the Sustainable Development Goals (SDGs), is Water Sensitive (urban) Design (WSD). WSD is a systems-based approach that is aimed at ensuring that the water cycle is managed more sustainably by focusing on the interactions between the built form and water resources management (Wong, 2006), and in particular**,** between the various actors, who determine water use. WSD integrates water cycle management with the built environment through planning and urban design, providing multiple benefits and opportunities to overcome challenges with water management (Abbot et al., 2013). It promotes water efficiency, reuse and recycling as well as the (re)design of urban area and settlements to include the development of blue-green infrastructure, using techniques such as Sustainable Drainage Systems, Alternative Water Resources and Water Conservation/Water Demand Management.

A paradigm shift such as this, however, requires more than simply publishing frameworks and guidelines; there needs to be an intentional effort to adapt planning processes, adopt new and adjust old technologies, initiate, review and apply new policy and legislation, build capacity, and initiate demonstrations for technology and knowledge transfer with appropriate stakeholders (Armitage et al., 2014). Transforming governance systems needs to include a broader range of actors to establish and to sustain an enabling environment that is characterized by collaborative learning processes. Social learning such as this is characterized by shared interest, joint activities, discussions and sharing of information to enable learning from one another and, where there is potential, to co-create new knowledge through what are known as Communities of Practice.

This paper describes an ongoing research project aimed at facilitating the implementation of WSD in SA through the development and monitoring of a nationally-supported Community of Practice (CoP) programme, the overall aim of which is to strengthen the researcher/stakeholder and implementer interface in order to leverage partnerships and to facilitate, to manage and to document technology transfer opportunities from the planning and design phases through to the piloting and implementation phases. The paper focuses specifically on the outcomes of two separate activities that are associated with the CoP programme and based in the City of Cape Town, currently in the midst of a severe water crisis and thus under increased pressure to start thinking differently about water management, and will discuss the impact that these are having in terms of driving the uptake of WSD in the country as a whole as well as towards achieving the Sustainable Development Goals (SDGs).

Water security and development in South Africa

The South African Department of Water and Sanitation (DWS) recently published a Call to Action in its National Water and Sanitation Master Plan (DWS, 2018), which is focused on addressing the challenges confronting the water and sanitation sector and, in particular, ensuring that by 2030 there is sufficient reserve of water supply to meet SDG 6: *Ensure access to water and sanitation for all.* Owing to the fact that SDG 6 underpins virtually all of the other SDGs, meeting this target would go a long way towards achieving much of the 2030 Agenda. In this regard, the Master Plan is based on five key objectives that define a '*new normal'* for water and sanitation management in SA, and aim to also enable the achievement of the National Development Plan Vision for 2030 of affordable and reliable access to sufficient and safe water and hygienic sanitation for socio-economic growth and well-being, with due regard to the environment: i.e., (i) Resilient and fit-for-use water supply; (ii) Universal water and sanitation provision; (iii) Equitable sharing and allocation of water resources; (iv) Effective infrastructure management, operation and maintenance; and (v) Reduction in future water demand.

SDGs related to water are particularly challenging because of the fragmented nature of water supply, sanitation, flood control, and governance at scales ranging from continent to region to household. History has shown that for South Africa, as indeed for the rest of the world, solutions that are strictly technical can fail in their implementation, while governance and policy options can fail because of lack of technical capability. Research to advance water service provision, therefore, must be collaborative, across research disciplines, but also across a wide range of local and regional stakeholders, ranging from community members to service providers and local/national government departments.

Water Sensitive Design Community of Practice

In 2014, the Water Research Commission (WRC) published the South African framework and guidelines for WSD, with the aim of promoting an approach to the planning of water services for and with communities in a holistic and resource efficient manner (Armitage et al., 2014). At the same time, the WRC initiated a project to develop and to manage a WSD CoP programme as a means of facilitating the implementation of WSD in SA, and specifically at the knowledge sharing and capacity development required to encourage a shift in the water sector. The CoP represents purposeful engagement with a wider (mainly non-academic) group of stakeholders in terms of socio-economic and socio-cultural development challenges (Carden et al., 2016). In this way, it is aimed at applying and disseminating new knowledge and promoting knowledge integration. The main focus areas are the identification of possibilities for collaborative and participatory interaction between all relevant actors, including awareness-raising and appropriate WSD training activities. Another way of raising the profile of WSD amongst national and local government officials, engineers, planners and developers has been the establishment of smaller CoPs or 'Learning Alliances' (LAs) in different geographic locations in order to link the various actors in these urban water systems and to promote shared learning and innovation around sustainable water management practices. These platforms allow researchers, local stakeholders and users to work together to create shared visions, to analyze options and to develop new strategies for the management of diverse forms of infrastructure, including urban water systems.

CoPs are formed by people, who engage in a process of collective learning in a shared domain of human endeavour (Wenger, 1998). ‘Communities’ develop their practice through a variety of participatory activities, which are characterised by co-operation, information exchange, strategic co-ordination, and lived experience. The monitoring of Learning Alliances as part of this programme is aimed at understanding how co-operation is established, how information exchange is facilitated, and how values are framed and processed to enable a network of actors to engage in a lived experience that lends itself to a relational-based approach to nature, biodiversity and the environment in an urban catchment (Carden & Bennett, 2017). This helps to understand, how to form and to sustain a larger Community of Practice in working towards a common cause or purpose, i.e., that of demonstrating a site or project, where WSD is implemented.

Linked to the CoP approach is the concept of ‘shared’ or ‘social’ learning, which draws on concepts of resilience thinking and social-ecological systems to promote learning and the co-production of knowledge, to build networks across scales and sectors, to build stakeholder capacity, and to spark innovative responses to problems (Reed et al., 2013). ‘Shared’ learning is geared towards addressing complex problems under conditions of uncertainty and seeks to engage stakeholders in a structured process of exchanges. The potential role of ‘social’ learning as a mechanism for managing water resources has been frequently highlighted over the past decade (Blackmore, 2010) and is characterized by shared interest, joint activities, discussions and sharing of information and learning within a CoP. A compelling argument for this approach is offered by Pahl-Wostl et al. (2008) and Blackmore (2010), who suggest that the transition towards sustainable strategies in water resources management such as WSD is best achieved by moving from the need to deploy more information through scientific research that feeds into informing policy and expert cycles, to an adaptive management approach that is embedded in social learning processes. The challenge in South African water management is to create an enabling environment first and foremost. This challenge is exceptionally difficult, however, as improved water provision and services need to be provided in an environment of poverty set within a weak and/or fragile institutional domain, where there are limitations in respect of centralized and hierarchical stakeholder participation, inadequate human resources and capacity, and where water pollution and water supply problems are increasing (Berkes, 2006).

2 Methodology

The WSD CoP programme comprises a managed process of multiple social learning case studies, with interested stakeholders throughout SA engaging in WSD awareness-raising, knowledge-sharing and appropriate training activities. The main objectives include: (i) demonstrating the positive influence of coordinating bodies and ‘champions’ in terms of facilitating change; (ii) generating strategic evidence from WSD implementation projects; and (iii) influencing policy to address planning and design. In order to achieve these objectives, several different local-level CoPs have been monitored and assessed over a 5-year period, and various WSD feasibility projects, particularly in respect of the use of alternative water resources (such as greywater) in the context of increasing water scarcity, have been used as dialogue platforms to assess, where and how WSD can be implemented, and the likely associated institutional and policy impacts. Two examples of these initiatives are described as follows:

- *Liesbeek Life Plan (LLP)* – led by the community-based organization, Friends of the Liesbeek River; the LLP is a group of researchers, local residents, officials and practitioners involved in re-conceptualizing the design and form of the Liesbeek River in Cape Town, specifically through planning for the implementation of sustainable drainage system (SuDS) and WSD features along sections of the river. The LLP is being used as a qualitative case study to highlight cross-sector collaboration initiatives that advance learning and improve decision-making for environmentally sustainable urban development – with the overall aim of understanding, how a CoP forms and how values are shared amongst participants through a collaborative learning process. It provides the context for the notions of shared interest or 'common cause' that have the potential to draw on the interests of a wide range of individuals, and private and public institutional members, who see value in the Liesbeek River and desire to see improved conditions along a blue-green corridor flowing through a part of the city of Cape Town.

- *Greywater resource guidelines for South Africa* – greywater is increasingly being included as a resource option in integrated water supply systems around the world, and as part of water sensitive approaches to water management, particularly in terms of relieving pressure on freshwater supplies. There remain uncertainties about the potential health and environmental impacts, however, and the benefits of harvesting greywater need to be carefully balanced with the risks associated with its use and unintentional misuse. A project was thus initiated to develop appropriate SA-specific guidelines to manage these risks. This was achieved by way of an extended review of existing literature on the management and use of greywater worldwide as well as of research that highlighted the unique particularities of the South African context (e.g., informal settlements, Free Basic Services provision, etc.). A series of workshops, dialogue sessions and focus group discussions was held with a broad range of interested stakeholders over an extended (eight month) period to progress the development of the proposed guidelines. A draft guideline document was circulated amongst the participants from all stakeholder meetings as well as several other identified 'experts' around the country for their comments and feedback.

3 Results and Discussion

Liesbeek Life Plan (LLP)

The structured programme based on the Liesbeek Life Plan consisted of a series of interactive experiential events and interventions that presented new opportunities for cross- and inter-sector engagement (e.g., between schools, businesses and NGOs) and learning about, *inter alia*, heritage, ecology, infrastructure, land use and society as well as the required actions for building a water sensitive catchment, including community involvement, river restoration, water quality monitoring, etc. These interventions (executed as LLP educational projects) have included:

[1] Development of fixed public signage along the river – with information on planned WSD activities as well as historical and cultural information.
[2] Strategic workshops using the 'Common Cause' framework (Holmes et al., 2010) to assist in the development of a new vision for the Friends of the Liesbeek River, together with an articulated set of organisational values and implementation strategies.
[3] WSD project for architecture students to develop ideas for greater connection and flow for people working in office complexes alongside the river.
[4] Proposals for river stewardship involving corporates situated along the Liesbeek and involving staff in practical river-based activities.
[5] Learning partnership to upskill Liesbeek maintenance team members.

In this regard, the LLP has contributed to identifying and interpreting the interactive processes at play in collaborative learning networks, and, importantly, in highlighting how the construction of new knowledge is brought about through joint work.

Greywater resource guidelines

The initial stakeholder workshop held in Cape Town served to raise awareness and concerns about greywater use and to discuss, what happens 'on-the-ground', how systems are being managed, and whether they work or not. The research inception report was used as a 'prompt' for the workshop to identify issues/questions (e.g., health risk, impact on sewage systems, incentives for greywater use, legislation, etc.) and link these to relevant sections from existing literature and findings from local and international projects. These were then used as discussion points and to identify and to map thematic areas for further consideration, specifically those pertaining to legal and health issues and to the quantification of the overall risks involved in greywater use and management. The second workshop held in Pretoria was used to concentrate more closely on the institutional framework for the guidelines as well as a discussion of the legislative and health review with participants from different stakeholder groups. Follow-on discussions were also held with specific focus groups as well as representatives of the relevant working groups to consider the incorporation of greywater reuse into National Building standards.

The resulting guidelines report represents a strategic document aimed at providing a South African context for the inclusion of greywater as a viable, alternative, non-potable resource. The guidelines are based on existing knowledge and expert opinion, and are intended to provide background information to national and local government policy makers, so that appropriate legislation and local-level guidelines can be drafted by these authorities, with the oversight and duty of care thus remaining with the policy-makers and legislators. The guidelines were specifically targeted towards household-level and onsite (untreated) greywater use within serviced settlements as well as managed facilities, which could include some form of greywater treatment system in government buildings, office blocks, schools, hostels, etc.

4 Conclusions

Facilitating the implementation of Water Sensitive Design in South Africa requires active, concerned citizens and an institutional system or other form of responsible organisation structure or combinations thereof that are capable of rising to the challenge. Water sensitivity is not a product but rather a pursuit that is driven by a strong moral imperative that becomes tangible, when elements of WSD are seen on the ground and this then offers opportunities for further involvement, education and learning. In this regard, emerging local-level Communities of Practice such as the Liesbeek Life Plan are contributing to an understanding of the way, in which the concepts of social learning can influence the implementation of WSD actions along a river, through three main objectives:

[1] Framing the water sensitive environment – understanding the context, defining its value;
[2] Understanding processes of change – the way in which a CoP contributes to changes in the way people connect with nature and sustainable urban infrastructure; and
[3] Roles and relationships – interpreting exchanges and interactions that shape a CoP in actions that support WSUD.

The development of a comprehensive set of Greywater Resource Guidelines has contributed to addressing and mitigating the risks associated with the management and use of domestic greywater in SA and supporting the wider uptake of this practice such that the diverse benefits that greywater use may offer can be realised. These include building resilience into the water supply system, managing water demand, reducing volumes of greywater to wastewater systems, and reducing diffuse pollution loads from unserviced settlements. Importantly, the project has enabled a further opportunity for driving home the message of water resilience and WSD to a wider audience, including linking with institutions such as the South African Bureau of Standards regarding integrating the guidelines within the National Building Regulations.

The successful incorporation of WSD into water management strategies in SA requires the application of best planning, design and management practices involving a wide range of stakeholders that bring different perspectives, principles and strategies to the process. This is exemplified by the two different social learning processes that helped to shape the CoP examples described in this paper, both of which have acted as effective agents of change in terms of institutionalizing and transitioning towards the ideals of water sensitivity and sustainable urban water management. Through the comprehensive monitoring and assessment of these activities this project has demonstrated the positive influence of Communities of Practice in terms of raising awareness about WSD and facilitating/driving the uptake of WSD in the country, thus contributing to the achievement of the SDGs.

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CHALLENGES OF WATERSHED HYDRO-ENVIRONMENTAL MASTER PLANS (CASE STUDY)

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Abstract

This work aimed to identify the main challenges to the implementation of the water infrastructure actions foreseen in the Capibaribe's Hydro-Environmental Master Plan, also suggesting a methodology for monitoring process optimization. The study was developed through a survey of data in several governmental institutions, internship at the State Agency of Water and Climate and participation in Capibaribe Committee meetings. Thus, the methodology was structured in the stages of documentary research, critical analysis of the data, methodological proposal for monitoring optimization and also characterization of the study area. The results showed that the water infrastructure actions were not implemented in accordance with the hydro-environmental plan, due to lack of coordination between the agencies to monitor the investments, among others.

1 Introduction

Water management has been one of the greatest challenges faced by governments and by society in general over the last few years in view of the serious problems of water scarcity affecting the world. Experiences and past efforts to enhance water security have taken limited perspectives when addressing decision making in a highly interactive approach and holistic view, being too prone to apply analyses based on a single discipline and overlooking interdisciplinary interactions (James & Jood, 2017).

In Brazil, the relationships maintained by stakeholders with water resources and their appropriation modes were greatly responsible for leading the country to the current scenario of environmental degradation and vulnerability (Piccoli et al., 2016). In the semi-arid region of the country, the low water availability due to prolonged drought periods and high evaporation rates has historically caused serious socio-environmental disasters, such as desertification processes and lack of food (Braga, 2016). As a consequence of the repeated droughts since the beginning of the last century, there has been an incentive to implement combined or isolated hydraulic infrastructures to mitigate the effects of water scarcity in the semi-arid areas, such as cisterns, small reservoirs, wells and small dams (Cirilo et al., 2017). Until the early 1990s, many water management measures had proved being ineffective in matching the demand with variable water availability, for example, and the relationships between available infrastructures and natural hazards were fragile or insufficient (Ribeiro et al., 2014).

In this perspective, the National Water Resources Policy, established through the Law 9433/97, represented a major progress in the national scenario by promoting water sustainability and participatory governance. In the State of Pernambuco, Northeast Brazil, the management of water resources is based on State Law No. 12984 from 2005, which created the State Water Resources Policy and the Integrated Water Resources Management System. At watersheds scale, there are hydro-environmental plans developed and being implemented in the Capibaribe and Ipojuca River basins. The Hydro-Environmental Master Plan of the Capibaribe river basin, elaborated in 2010, is an important advance in the state water resources management, constituting itself as a modern and embracing water resources plan (Pernambuco, 2010a). The plan sought, among other actions, to suggest proposals for investment plans, which aimed to solve problems related to the quantity and quality of water available in the basin, analyzing scenarios in terms of sustainability and trend.

This work aims to identify the main obstacles to the implementation of the water infrastructure actions foreseen in the Capibaribe hydro-environmental plan, also suggesting a simplified methodological structure for optimize monitoring process.

2 Material and Methods

Capibaribe River Basin Hydro-Environmental Master Plan

In the last decade, it is possible to observe a significant advance in Pernambuco State water resources scenario regarding laws formulation and strengthening of the institutional arrangement for water management. From 2007 to 2009, the National Water Resources Development Program (PROágua Nacional) was implemented in all Brazilian regions. This program, developed by Brazilian government and financed by the World Bank, was of great importance for the northeast region and for Pernambuco itself, having as one of the objectives the expansion and optimization of water infrastructures.

In 2010, through State Law No. 14028, the Pernambuco State Agency of Water and Climate (APAC) was created, with the purpose to execute the State Policy of Water Resources and, in this way, to control water use in the level of state and federal water resources under delegated terms. The agency is also responsible for hydro-meteorological monitoring, weather and climate forecasts in the state, and operation of the Integrated Water Resources Management System (Gouveia & Pedrosa, 2015).

In the same year, the Capibarive River Basin Hydro-Environmental Plan (PHA) was completed. This plan is a result of Contract No. 004/2009 signed between Pernambuco Government, through the Water Resources Secretary, and a Consortium with resources from PROÁgua Nacional and World Bank. The Capibaribe River Plan received investments of approximately R$ 740,000 (= US$ 200,000), with financing from the World Bank (Bird). The National Water Agency (ANA) and the

Integration Ministry provided technical support for the document preparation process (Pernambuco, 2010a).

The hydro-environmental plan was based on the Capibaribe River Basin Water Resources Master Plan (PDRH Capibaribe), completed in 2002, with reference to the State Water Resources Utilization Plan, prepared in 2005, as well as other state and federal Plans related to the theme. The Capibaribe River Plan elaboration process included the critical participation of a River Basin Committee Technical Chamber, which contributed with content evaluations and suggestions in several formulation stages (Pernambuco, 2010b). In what refers to the documentary structure, the Plan provided for technical reports publications and informational database construction, distributed according to Figure 1.

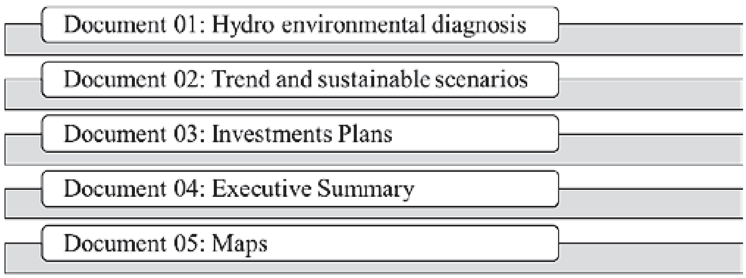

Figure 1: Hydro-Environmental Plan documentary structure

Document 03 (Investment Plans) was formulated as a response to different problems and potentialities identified in the Hydro-Environmental Diagnosis (document 01). The diagnosis provided basis for the establishment of document 02 (Trend and Sustainable Scenarios for 2015 and 2025), indicating interventions and necessary reforms for the sustainable basin development (Pernambuco, 2010c).

The Investment Plans (document 3) were presented as complementary actions to those already implemented, in implementation phase or planned for the Capibaribe River Basin. They were focused on structural and non-structural actions according to three thematic topics in order to broaden the scope of these actions as well as the access to their results: Topic I - socio-environmental; Topic II - water infrastructure, and Topic III - water resources management.

Topic II (Water Infrastructure) has as synthesis of the proposed actions with the focus on environmental sanitation, looking for improving living conditions in diffuse rural areas, and contemplating simplified alternatives for water supply and sewage system. This topic also predicted actions to revitalize the Capibaribe River gutter in order to reduce floods (Pernambuco, 2010c). Table 1 presents a summary of the Investment Plans in the basin under thematic topic II.

With regard to the investment plan 1, its implementation is justified by the precarious water supply scenario for dispersed populations in the basin rural area. In 2010, approximately 80% of this population still did not have a regular water supply for family consumption, and there was an urgent need for investment programs capable to progressively meet basic human needs and providing other supports.

Table 1: Water infrastructure investment plans

Investment Plan	General objective	Goals	Deadline	Costs (R$)
1. Use of simplified alternatives for water supply (diffuse population)	Universalize basic sanitation services to dispersed population in the rural area of the basin and permanent supply of quality water.	Universalize basic sanitation services to dispersed population in the rural area of the basin until 2025.	15 years	83,990,320
2. Use of simplified alternatives for water supply (diffuse population)	Universalize basic sanitation services to dispersed population in the rural area of the basin with investments to implement sanitary sewage systems.	Implementation of sanitary sewage simplified models for diffuse communities in the rural area of the basin.	8 years	74,383,080
3. Critical stretches recovery of the Capibaribe river channel for flood attenuation	Reduce flood risks in the basin and improve the Capibaribe river banks and channels conditions.	Application of technical solutions at the Capibaribe river channel critical points to reduce floods risk.	1 year	1,110,288

Three supply models were proposed for the upper, middle and lower river courses, with average value per family of R$ 3,712 (US$ 1000). For the universalization, all the diffuse communities of the rural area populations were considered (22,360 families). The execution of action 2 is also justified by the sanitary sewage deficiency in the basin, with more than 3/4 of municipal offices and almost the whole rural area without adequate solution for domestic effluents discharge in 2010.

Two models were proposed for individual sewage systems (wet and dry) and one model for collective services with an average value of R$ 3,303 per family. For the universalization, all the diffuse communities of the rural area populations were considered, estimated in 22,360 families (Pernambuco, 2010c).

The historical floods in Capibaribe River Basin, especially in its mid and low courses, reaching the capital and other riverside cities, led to the adoption of measures to solve the problem, especially after the 1975's flood. Although the dam constructions for floods control contribute to a significant reduction of its effects, extravasation possibilities continued to persist. These facts reinforce the importance of plan 3, which aimed to reduce flood risks in the basin with a deadline for conclusion in one year (Pernambuco, 2010c).

The document 3 also suggests an integrated monitoring of the actions proposed in the Investment Plan through a Performance and Results Monitoring Program. This program was detailed in the document in order to avoid cost dualities foreseen in several plans, to optimize projects schedules and to guarantee the desired results in the Capibaribe Basin. The program considers the following macro activities: program execution management, financial monitoring, and Investment Plans management (Pernambuco, 2010c).

Study Area

The Capibaribe River Basin (CRB) has a drainage area of approximately 7,454 km², and is located in the Pernambuco State – Northeast Brazil, running in west east direction to the Atlantic Ocean. The west portion is characterized by shallow soils, Caatinga vegetation (thorn scrub, cactus, and bunch grasses), and a semi-arid climate with 550 mm/yr of rainfall and mean air temperatures between 20 and 22 °C. Periodically, this region suffers from the consequences of drought events, whereas the eastern part of the basin is characterized by deeper soils, Atlantic Forest vegetation, and a humid/sub-humid climate with 2400 mm/yr of rainfall and mean air temperature between 25 and 26 °C (Ribeiro Neto et al., 2014).

The CRB can be divided into three macrozones: MZ-1, MZ-2 and MZ-3, easily identified as Upper, Middle and Lower Capibaribe. The Upper and Middle Capibaribe suffer from water deficit. As a result, in addition to the imperative need to conserve water in the sandy beds of intermittent watercourses, it is essential to import this natural resource, particularly from São Francisco River through channels and water conduits.

At Lower area, there is a positive water balance, since the needs can be met by the water production in the macrozone itself, only needing a good water resources management regarding the recharge of aquifers areas, pollution control and demand orientation (Braga et al., 2015). The basin extends for about 280 km until the river mouth in the state capital Recife. On this route, the CRB cuts 42 cities, of which 15 are totally inserted in the basin and 26 have their headquarters in it. Figure 2 shows the CRB regions.

Documentary Research

In this phase, it was made a documentary survey of several relevant documents to the theme, including legislation, water resources plans, minutes of meetings, Watershed Committee publications, scientific articles, and internal monitoring spreadsheets from competent institutions. From the survey, it was made a documentary analysis to identify the investments progress in water infrastructure proposed in the CRB Hydro-Environmental Plan, identifying the main challenges to implement the actions. The survey was carried out through an internship at the State Agency of Water and Climate in the responsible sector for monitoring the investment plans as well as the participation in Watershed committee events and managers meetings. In this way, it was possible to identify the main monitoring obstacles, and a simplified methodological structure was proposed to help monitor actions more effectively.

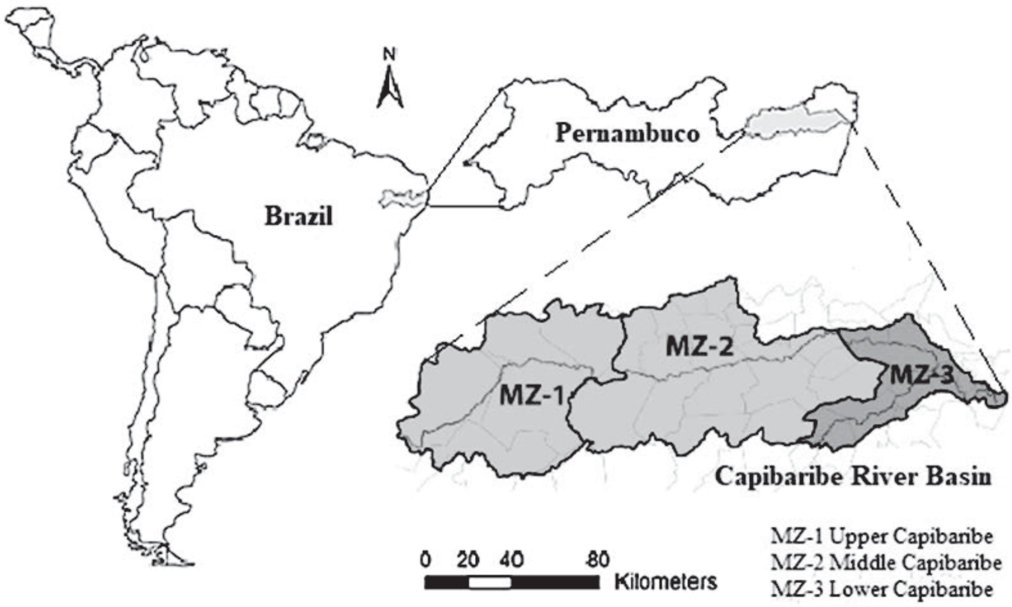

Figure 2: Capibaribe River Basin

Methodological Proposal

Despite the existence of a Performance and Results Monitoring Program foreseen in the Hydro-Environmental Plan (document 3), the macro activities suggested for the Investment Plans management are presented in a generic way with little detail of the methods to be executed. In this way, after completing the documentary analysis and identifying the main challenges to the water infrastructure actions implementation, this work suggested a methodological proposal for optimize monitoring process. In order to develop the proposal, the monitoring methods data used by the Pernambuco Agency of Water and Climate (APAC) were initially collected, consisting of internal spreadsheets for monthly follow up the actions and meeting minutes from the watershed committee. The spreadsheets data feed depends on technical and operational responses and other information provided by several agencies and entities (such as the State Sanitation Company, Ministry of the Environment, City Halls, among others), and APAC being responsible for contacting and collecting information with such agencies.

Based on the information provided by APAC managers and professionals responsible for monitoring the Investments Plans and other information obtained at a Seminar on Methodology for Monitoring Investments in the Ipojuca River Basin (held in Gravatá city-Pernambuco State), a simplified methodological proposal was developed with a view to optimize the process. The proposal was based on the monitoring indicators suggested in the Hydro-Environmental Plan Document 3 (Table 2) and in other methodologies and article contents related to water security in the developed world (James & Shafiee Jood, 2017; Siska & Katara, 2015; Petelet Giraud et al., 2018).

Table 2: Infrastructure actions monitoring indicators

Investment Plan - Thematic Topic II	Indicators
Use of simplified alternatives for water supply (diffuse population)	number of cisterns built; number of wells drilled; number of fountains built; number of supply networks and systems installed
Use of simplified alternatives for sewage system (diffuse population)	number of systems built; number of families attended
Critical river reach recovery of the Capibaribe river channel for flood attenuation	number of recovered river reaches; number of channel overflow occurrence

3 Results and Discussion

Critical Analysis of the Dat

In general, the actions and targets follow-up of the Capibaribe Investment plans take place jointly between the Watershed Committee (COBH Capibaribe), through its Technical Chamber of Plans, Programs and Projects (CTPPP), and the Pernambuco Agency of Water and Climate (APAC). The analyses for assessing the investments actions progress foreseen in the Plan have been basically consisted of the following stages:

a. Information extraction from the Plan and adequacy to the APAC database;
b. Articulation to prepare an action plan for follow-up;
c. Identification of those responsible involved in the proposed actions execution;
d. Articulation with those responsible and information collections regarding status;
e. Actions progress monitoring with those responsible.

These steps were materialized in Excel spreadsheets by APAC and COBH along with meetings minutes. During March to November 2016, eight meetings were held periodically to discuss the PHA goals implementation and to elaborate a monitoring framework. Representatives of COBH Capibaribe, APAC, Economic Development Secretary (SDEC), Water and Energy Resources Secretary (SERH), and State Environment and Sustainability Secretary (SEMAS) participated in these meetings. In June 2016, APAC's Management of Plans and Information Systems department surveyed the status of actions that were directly related to investments in water infrastructure impacting the Capibaribe basin. Table 3 presents actions in the municipalities that are part of the basin, the global investment, status and conclusion forecast.

Table 3: Capibaribe water infrastructure actions 2016

Action	Investment (R$)	Status	Conclusion*
Sewage system implantation in Tacaimbó city (MZ-1).	15,670,340	In execution	January/2017
Expansion of water supply and sewage systems in Gravatá city- (MZ-2).	35,000,000	In execution	April/2018
Expansion of water supply and sewage systems in Santa Cruz do Capibaribe city (MZ-1).	77,000,000	Bidding in progress	October/2019
Expansion of water supply and sewage systems in Surubim city (MZ-2).	78,880,354	Stopped	-
Desalination systems implantation and maintenance in Jataúba, Pesqueira, and São Caetano (MZ-1) cities; and Caruaru and Riacho das almas cities (MZ-2).	10,195,216	In execution	September/2016
Implementation of the Agreste adduction System.	2,300,000,000	Stopped	-
Expansion of supply systems in Vitória de Santo Antão and Pombos cities (MZ-3) through the Tapacurá Dam.	21,842,051	Stopped	-
Construction of Engenho Pereira dam Moreno city (MZ-3)	54,483,004	Stopped	February/2018
Complement of the Minerva Sewage Treatment Station in the cities of Recife (MZ-3) and Olinda.	18,623,919	Bidding in progress	May/2018
Sanitary sewage system implantation in the neighborhoods of Imbiribeira, Boa Viagem and Porta Larga (Recife city- MZ-3).	70,505,868	Bidding in progress	-
Water supply system implantation in Ibura neighborhood (Recife city MZ-3)	Not informed	In execution	-
Water supply system implantation in Iputinga, Caxangá, Dois Irmãos, Apipucos and Monteiro neighborhoods (Recife city- MZ-3)	11,868,766	In execution	July/17
Extension and adequacy of the Cabanga sewage treatment station (city of Recife MZ-3)	81,538,369	Stopped	-

Despite the collection of information and status definition, after the meetings in the year 2016 the table has not been updated. After this year, an action that deserves to be highlighted is the Jucazinho Dam recovery (R$ 52,000,000 in investments), the third largest reservoir in the state and having a capacity for 327 million m^3 of water (Pernambuco, 2017). Although they do not have a direct interface with the water infrastructure monitoring indicators suggested by the hydro-environmental plan, the actions reported in Table 3 reveal a Government's desire to increase storage capacity and to improve the spatial distribution of water in the Capibaribe basin.

The Monitoring Barriers
The documental analysis, together with the information collection from stakeholders, allowed to identify four main obstacles to the investment plans monitoring process in the Capibaribe River Basin, as shown below on Figure 3.

Figure 3: The monitoring process barriers

The four obstacles presented in Figure 3 are directly connected, leading to a monitoring methodology proposal that can include all of them and adjust the actual monitoring methods to a new one that can also be implemented to monitor other water resources plans actions. A first obstacle identified that affects the monitoring process is the staff turnover at the state public agencies involved in the hydro-environmental investment plans. The main difficulties around this problem are related to the missed information not properly shared or stored. The follow-up done by a certain employee ends up not being adequately passed on to the new managers during the staff transition processes.

The lack of a system to carry out the monitoring through documental and data storage is another problem that also impacts the access to important information for a continuous monitoring. Several documents as laws, budgets, schedules, meetings minutes, and the hydro-environmental plan itself could be digitally stored in folders for each investment plan foreseen.

The follow-up of the actions foreseen in the investment plans thematic topic II is complex due to the dependence of several institutions. In this way, the fourth obstacle identified reveal that the connection between the agencies is of fundamental importance and must be sufficiently strong, so that information exchange is improved and data can be constantly updated. Without proper dialogues and articulation between the agencies, the monitoring will not occur even with a solid documental and data storage.

The integration of decision-makers to establish priorities and policies compatible with each other is of extreme importance for the adequate planning of water resources' uses in response to the increasing demands for multiple uses (Montaño & Souza, 2016). This fact reinforces that efficient articulation and dialogues are also important to monitor the real impacts of historical deliberations, so that decision-making processes can be evidence-based and anticipate potential impacts for different future scenarios (Siegmund-Schultze, 2017).

Challenges to the Water Infrastructure Actions Implementation

Based on the documental analysis it was not possible to precisely measure, which investment plans actions were actually executed or which are in execution process or not initiated. Despite the suggestion of monitoring indicators to measure the water infrastructure actions implementation, the lack of a specific methodology and the fragile arrangement between organizations only allow a superficial analysis of the Investment Plans compliance.

For each one of the three Water Infrastructure investment plans the document defines: general methodology and project details to be executed; indication of institutional arrangement (responsibility matrix for implementation, operation and actions maintenance); general schedule and implementation period; costs estimation (general, education and environmental awareness costs estimative); sources of financing and physical financial schedule.

Use of simplified alternatives for water supply and sewage system for diffuse population

For these investment plans implementation, the hydro-environmental plan suggests the following project models to be executed according to the basin region (Table 4).

Table 4: Water supply and sanitary sewage suggested models

Macrozone	Water supply model
MZ1	Tank 16 m³ + 60 m deep tubular crystalline well + fountain
MZ2	Tank 16 m³ + 60 m crystalline well + desalinator + distribution network
MZ3	60 m crystalline well + Distribution network + Dam 51,000m³
	Sanitary sewage model
MZ1/MZ2	Toilet with individual septic tank and soak pit
MZ1/MZ2	Ecological dry toilet
MZ3	Toilet + collecting network + sewage treatment station

Due to the lack of mapping details in the rural area, all models considered as basis for the costs involved communities constituting of 100 families, obtaining the unit cost per family in order to allow sizing for population clusters with different composition (Pernambuco, 2010c).

Although the plan presents the project details and guidelines for the execution, the main implementation challenges identified are related to institutional arrangement and dimensioning the technical and support staff. The document does not specify precisely, which organization are responsible for each step, as these definitions and staff dimensioning should have been defined by common agreements in strict articulation with involved decision makers and city halls.

Through consultation with public agencies and documental research it was possible to observe that many water supply and sanitary sewage measures were in fact implemented in the Capibaribe River Basin region, but they were not necessarily in accordance with the plan guidelines. After the plan conception there were not enough dialogues to define a consolidated responsibility matrix and attributions division. In this way, many agencies were not properly informed about their possible roles in the actions' execution, resulting in its non-implementation in accordance with the document premises.

Critical stretches recovery of the Capibaribe River gutter for flood attenuation
This investment plan had as principal objectives to minimize flood risks in the basin and to improve the river gutter and banks conditions. The main goals were to reduce the stretches pike discharges and to open, to adjust or to construct dikes in some stretches of the river gutter. It was also suggested that the actions were elaborated in parallel with the project: implantation of urban municipal parks "windows to the river". There were no available data related to the purposed indicators regarding this plan on the monitoring spreadsheets. Through documental consultation it was possible to notice that, as occurred with the water supply and sewage system actions, the government made investments in drainage of the Capibaribe Basin with view to flood attenuation, but the actions were not directly following or related to the plan instructions.

In 2010 and 2011, projects supported by the State Water Fund (FEHIDRO) for recovery and conservation of riparian forests and river springs in the Capibaribe Basin were executed in some basin cities (Silva & Silva, 2014). From 2016 to 2018, the basic and executive projects of the "Windows to the river" in Vitória de Santo Antão and Taquaritinga do Norte cities were developed. It was verified that the main difficulty in the execution of FEHIDRO basin recovery projects was the limited institutional capacity of the cities in the land use management and low environmental awareness in municipal management issues. Another problem was the initial operational structure of APAC (created in 2010) to deal with the whole complex process to implement the Water Resources Policy in Pernambuco (Silva & Silva, 2014).

Simplified Methodological Structure for Optimize Monitoring Process

The methodological structure proposed aims to cover the monitoring obstacles identified and to optimize the current process made through spreadsheets. To this end, the following topics were considered as simplified steps to optimize monitoring process:

a) Monitoring system software develop and documental storage
b) Rearrangement of monitoring team and macrozones sectorization
c) Indicators, set goals and reprogram deadlines
d) Direct interaction between the competent agencies and the decision makers

The monitoring system must be designed to be the key of the whole process, with available functions to make possible or to facilitate the execution of topics (b), (c) and (d). It is important to point out, however, that the system collected data must be focused on useful information regarding the investment plan actions' accomplishment, also solving three important issues: (1) which relationships to cover in data gathering, (2) how to limit data gathering to manageable levels delivering important information, and (3) how to proceed from current management practices to a future management system for multi-party, multi-dimensional decision making. To promote well communication, big data systems need to address issues faced by the wide range of decision makers and thus deserve reviewing in more detail (James & Shafiee Jood, 2017).

Since the suggested investment plans models vary and follow the peculiarities of each macrozone, it is important to define a multidisciplinary team with representatives in each competent institution. To stimulate monitoring managers and to create a more direct connection network with city halls managers and other agencies must be one of the systems major tasks, besides functions related to documental data storage and projects status.

The use of the indicators suggested in the plan as parameters for monitoring the proposed actions is fundamentally necessary for measure real progresses. However, the document does not define exact numbers as targets, requiring numerical definition to be sought for a given period as well as a schedule reprogramming, especially for plans 2 and 3 that already have expired deadlines. Figure 4 shows the simplified methodological structure for the optimized monitoring process.

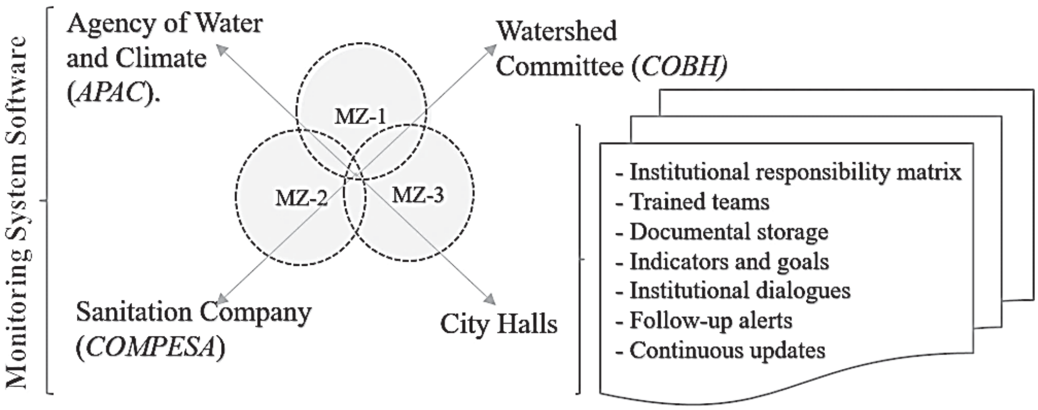

Figure 4: Simplified methodological structure

4 Conclusions

In Brazil, the water policy for participatory planning and management has been materialized through the Water Resources Plans, elaborated at national, state and watershed scales. Such plans become particularly important in arid/semi-arid and low water availability regions, such as the Capibaribe River Basin, located in the State of Pernambuco, Northeast Brazil.

It could be observed that the Government made important investments to ensure water security in Capibaribe River Basin. However, it was also noticed that the hydro-environmental plan has not been a guide for these investments, highlighting the necessity to develop a methodology for restructuring actions and optimized monitoring.

The administrative continuity and discontinuity issues present themselves as a major obstacle to the development of public policies for water security. The interruption of programs, projects and actions due to fragile institutional capacities has been a reality in water resources management, and these problems were also identified in the Capibaribe Basin. Despite the legitimacy of the hydro-environmental plan and its water infrastructure investment plans, to prioritize the environmental agenda and to put it above political interests has been one of the biggest challenges regarding water security in the basin.

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WATER QUALITY OF BEYSEHIR LAKE AND IRRIGATION AND DRAINAGE CHANNEL BETWEEN BEYSEHIR LAKE AND SALT LAKE

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Keywords: Beyşehir Lake; drainage channel; water quality; irrigation channel; Konya basin.

Abstract

The aim of this study was the assessment of water quality of Beyşehir Lake, and irrigation and drainage channel between Beyşehir Lake and Salt Lake; the determination of pollutants and their sources; to establish measures necessary for the conservation and control of water quality. For this purpose, surface water samples were taken from 10 different quality observation points in Konya Closed Basin, Turkey. The results obtained were evaluated according to water resources classes in Water Pollution Control Regulation (WPCR) and Surface Water Quality Regulation (SWQR) of Turkey. Surface water sources in the basin are generally classified as class I in terms of temperature, pH, sulphate, sodium, and nitrate, class I and II in terms of dissolved oxygen, chloride, EC, and ammonium, and class III and IV in terms of color, nitrite, boron, COD and BOD_5. Class II water can be used for irrigation purposes. In this case, only two surface water sources are suitable for irrigation according to the WPCR. Surface waters that could be used for irrigation purposes were evaluated according to Turkish regulations. It was generally found to be suitable in terms of EC and chloride but not of sodium and boron. Sources causing pollution in the basin have been defined as domestic wastewater discharges, industrial discharges, agricultural activities, irregular solid waste repositories, drought, animal husbandry activities, and rapid population growth. As a solution recommendation, new urban wastewater treatment plants (WWTPs) should be built, improvement of treatment of existing WWTPs should be ensured, a Water Quality Monitoring Network should be established, new regular solid waste sites should be constructed, and good agricultural practices should be introduced.

1 Introduction

Urban expansion, landscape modification, population growth and atmospheric deposition affect surface water quality in basins, and the wastes and pollutants transported into surface water cause a series of environmental problems. Today, many basins do not have enough water in order to meet all demands. Especially, water scarcity is very severe in arid or semi-arid zones such as Konya in Turkey. Anthropogenic and natural effects such as urban, industrial and agricultural activities increase consumption of water. Global Climate Change reduces precipitation, and depletion of surface water sources also effect surface water quality. The deterioration of water quality threatens human health and aquatic ecosystems. Konya Closed Basin (KCB) is located at the Central Anatolia Region and covers an area of 44,841 km^2 corresponding to 7% of the total area of Turkey, and has a water capacity of 4.52 billion m^3 (BCM). The only water source of KCB is precipitation. Intensive agricultural activities are carried out in the basin, whilst water resources are limited in the region. Beyşehir Lake is the largest water source in the basin, and there is no outlet to the sea. After completing the circulation from underground and the surface in the basin the water reaches Salt Lake. Due to its large grassy steppes, biological diversity and wetlands, it is one of the 200 most important ecological regions in the world. KCB is under pressure and negative effects occur especially in recent years. Lack of rainfall and water sources, climate change and drought, development of industry, untreated domestic and industrial wastewater discharges, non-efficient water consumption for agricultural purposes, drainage water from agriculture, drop in groundwater level, and solid waste disposal problems are the main sources of negative impacts.

Several studies were conducted on the surface water quality in KCB. Some heavy metals in 32 surface waters in KCB were investigated. Cd, Pb, Cu, Cr, Ni, Mn, Al and Se measured in surface water samples used for drinking water were complying with the limit values given by Turkish Regulation, USEPA and WHO, except for As and Fe. Konya surface water falls in 1st or 2nd class inland water according to WPCR. Heavy metals and toxic element contents in surface water of KCB were determined below the threshold values for continuous irrigation for any type of soil, and for less than 24 years irrigation for any type of land (Aydin et al., 2010). The water quality of the Main Drainage Channel (MDC) used for agricultural irrigation in KCB was investigated. It was found that high salinity and toxicity of boron could deteriorate the soil (Bahçeci, 1993). Heavy metal analyses of 50 water samples taken from Konya and its districts were carried out. While the concentration of Pb exceeded the limit value, the other metals (Ag, Al, Ba, Cd, Cr, Cu, Mn, Ni, and Zn) were below the limit values (Yalcin, 2005). Zengin et al., (2002) carried out analyses on 90 irrigation water samples collected from various places of KCB in the irrigation period June to August 1999. The results showed that one surface water sample (May Dam) was found not suitable due to its high pH of 8.70. The other surface waters were found suitable for irrigation related to their EC, B, sodium absorption ratio (SAR) and residual sodium carbonate (RSC) values. The pH and B values of surface waters were higher, whereas EC, total cations, total anions, SAR, RSC and quality classes were lower than those of underground waters. Muhammed et al., (2018) investigated the circulations and hydrodynamic conditions inside the Beyşehir Lake and in the vicinity of the stream's inlet, and calibrated the hydrodynamic model and water quality in terms of dissolved oxygen. Hydrodynamic measurements showed that there is a decrease of water surface level of Beyşehir Lake. The measured water quality readings showed a deterioration of the water quality. Climate change scenarios generally predict decreased nutrient loads from the catchment of Beyşehir Lake, decreased water level, and minor changes in chlorophyll a (Chl-a). Reduced nutrient loading may balance the effects of warming the lake water. However, total Phosphorus (TP), temperature and hydraulic loading data show a risk for increased cyanobacteria formation in Beyşehir Lake (Bucak et al., 2018). Beyşehir Lake has a mesotrophic characteristics according to TP, Chl-a and secchi disc depth. Due to high level of nutrients in the Lake, algae are growing. Heavy metal pollution of the lake was lower than recommended by WHO and the Turkish WPCR for drinking waters (Muhammed et al., 2018).

KCB has no other water sources than precipitation. The basin resources are limited and the basin is one of the areas, where the demand for water is the most intense. Also, Beyşehir Lake is the most important drinking and irrigation water source for Central Anatolia. In order to control pollution and to maintain water quality, it is necessary to determine the change of the water quality over time. The purposes of this investigation was (1) to assess the water quality of Beyşehir Lake, and of the irrigation and drainage channel between Beyşehir Lake and Salt Lake; (2) to determine pollutants and their sources; and (3) to establish measures necessary for the conservation and control of water quality.

2 Materials and Methods

Konya is a city with a population of 1,300,000 and is the largest province of Turkey with a surface area of 38,183 km^2. The annual mean temperature of the city is 11.5 ^oC, and average precipitation is about 325 mm. The city has a semi-arid climate and limited water sources. This is especially a problem for wide agricultural land and the irrigation water demand. Konya Closed Basin with an area of 53,850 km^2 is located in Central Anatolia and occupies 7% of Turkey's total area. The basin is a flat plain with an altitude changing from 900 m to 1,050 m. KCB has been under many pressure and adverse effects especially in recent years. The factors that cause significant environmental pressure in the basin can be listed as follows: agricultural and livestock activities, which are intensive in the basin, domestic wastewater discharged without treatment, industrial wastewater discharged untreated along with the development of the industry, the lack of rain and water resources, irregular landfills, climate change, unconscious water consumption for agricultural purposes, illegal wells, and erosion around dam reservoirs and rivers.

The lack of water in KCB has caused great problems for centuries. During the arid periods, especially in 1844, 1854, 1874 and 1878, there were water shortages that forced the residents of these basins to migrate. For this reason, in the beginning of the twentieth century, a project was prepared for provision of water for the Konya plain from Beyşehir Lake, and the Konya Plain Irrigation Network was constructed between 1907 and 1914. In rainy periods, there is a flooding problem in the basin due to excess water. Because of the large flood events between 1967 and 1970, the main drainage channel was taken into operation in 1974. The most important water sources of Konya Basin are Beyşehir Lake, Suğla Lake and Çarşamba Stream. Beyşehir Lake is the largest of the natural freshwater lakes in Anatolia. The surface of the lake is 73,000 hectares at 1125 m altitude, 64,700 hectares at 1122 m altitude. The maximum surface area is 74,500 ha and the maximum capacity is 5,549 hm^3. Beyşehir Lake is of high economic value in terms of aquatic products. Beyşehir Lake is an important bird breeding, orchard, nutrition and accommodation center. With this respect, it is also important for tourism. The length of the lake in the northwest-southeast direction is 45 km. The lake is feed from various creeks and streams from 9 different sub basins. The rainfall basin of Beyşehir Lake is 4,086 km^2. While the lake is fed with surface flows, groundwater and rainfall, the lake water is taken for irrigation.

Surface water samples were taken from 10 different quality observation points in Konya Closed Basin, Turkey. Five streams were selected in order to examine the effects of the rivers feeding to Beyşehir Lake on the lake quality. Five sampling points were chosen to examine the changes in total surface water quality along the 343 km line starting from Beyşehir Lake and ending at the Salt Lake (Tuz Gölü). Names, resource type, sampling number and time per year of sampling points are given in Table 1. Sampling points are divided in various sources such as stream, irrigation, and drainage channel. These waters are used for different purposes such as drinking and irrigation.

Table 1: Names, resource type, sampling number and time per year of the water sampling points

No	Sampling point name	Resource type	Sampling number and time
1	Çeltik Channel, Beyşehir Lake Input	Stream	4/year, Feb, May, Aug, Nov
2	Sarısu Eylikler, Beyşehir Lake Input	Stream	4/year, Feb, May, Aug, Nov
3	Soğuksu Yeşildağ Bridge, Beyşehir Lake Input	Stream	4/year, Feb, May, Aug, Nov
4	Ulu Irmak Yeşildağ Bridge, Beyşehir Lake Input	Stream	4/year, Feb, May, Aug, Nov
5	Üstünler Bridge, Beyşehir Lake Input	Stream	4/year, Feb, May, Aug, Nov
6	BSA Channel, Seydişehir Kumluca Bridge, Suğla Input	Irrigation channel	4/year, Feb, May, Aug, Nov
7	BSA Channel, Seydişehir Suğla Output	Irrigation channel	4/year, Feb, May, Aug, Nov
8	BSA Channel, Apa Dam Output	Irrigation channel	3/year, Feb, Oct, Dec
9	Apa Drainage Channel, 1. pump inlet	Drainage channel	3/year, Feb, Oct, Dec
10	Apa Drainage Channel, Gölyazı Bridge	Drainage channel	3/year, Feb, Oct, Dec

All samples were collected free of air bubbles in glass bottles and stored in the dark at 4 ^{o}C. Water samples were analysed for temperature, pH, electrical conductivity (EC), sodium, chloride, sulphate, boron, ammonium, nitrate, nitrite, dissolved oxygen (DO), BOD_5, COD, organic matter (OM), color, and turbidity. Analyses of the water samples were carried out according to the methods given in Table 2. The results obtained were evaluated according to water resources classes in WPCR and SWQR of Turkey.

Table 2: Methods used for analysis of water samples

Parameter	Method	Parameter	Method
Temperature (^{o}C)	-	Nitrate	EPA, Method 352.1
pH (25 ^{o}C)	TS 3263 ISO10523	Nitrite	APHA Method 4500-NO_2
EC (25 ^{o}C)	TS 9748 EN 27888	DO	TS 5677 EN 25814
Sodium	TS 4530	BOD_5	APHA Method 5210
Chloride	TS 4164 ISO 9297	OM	TS 6288 EN ISO 8467
Sulfate	TS 5095	COD	TS 2789 ISO 6060
Boron	TS 3661	Color	TS 6392 EN ISO 7887
Ammonium	EPA, Method 350.2	Turbidity	TS 5091 EN 7027

3 Results and Discussion

Water quality classes according to WPCR and SWQR are given in Table 3. According to regulations, 1st class water is very good, 2nd class water is good, 3rd class water is medium, and 4th class water is weak.

Table 3: Water quality classes according to WPCR and SWQR

Parameters	Water Quality Class			
	I (very good)	II (good)	III (medium)	IV (weak)
Temperature (^oC)	25	25	30	>30
pH	6-9	6-9	6-9	6-9
EC (µS/cm)	<400	1000	3000	>3000
DO (mg/L)	>8	6	3	<3
Na^+ (mg/L)	125	125	250	>250
Cl^- (mg/L)	<25	200	400	>400
SO_4^{2-} (mg/L)	200	200	400	>400
NH_4-N (mg/L)	<0.2	1.0	2.0	>2.0
NO_2-N (mg/L)	0.002	0.01	0.05	>0.05
NO_3-N (mg/L)	<3	10	20	>20
BOD_5 (mg/L)	<4	8	20	>20
COD (mg/L)	<25	50	70	>70
Color (Pt-Co)	5	50	300	>300
Boron (mg/L)	1	1	1	>1

Mean, Min- Max, temperature, pH, EC, DO, color, OM, BOD_5, COD, SO_4^{2-}, NH_4-N, NO_2-N and NO_3-N values of water samples between 2006 and 2014, and water quality classes are given in Table 4. Similar results were obtained in terms of temperature during the years examined. Seasonal changes of air temperature affected water temperature. While the lowest temperature was detected in February, the highest temperature was detected in August. According to WPCR, surface waters with temperature up to 25 °C were in 1st and 2nd class water quality. When waters were evaluated in terms of temperature, they were in the 1st class water quality. pH values of the samples changed between 6.8 and 9.2. According to mean pH of the samples, all surface water samples can be regarded as 1st class water in terms of water quality.

Stream waters feeding the Beyşehir Lake (sampling points 1, 2, 3, 4, 5) and irrigation channel waters (sampling points 6, 7,8) were determined as 1st and 2nd class water qualities in terms of EC. EC valuse of sampling point 9 and 10, which are from drainage channel, were found being higher than of the other samples. According to mean EC values, these waters are in the 3rd and 4th quality. Generally, the concentrations of DO in waters taken from stream and irrigation channel are determined between 6 and 8 all the year. These waters were classified as 2nd class according to regulation. DO value of the sampling point 10 is between 3 and 6 mg/L. This water is identified as 3rd class water quality. DO value of the sampling point 9 is below 3 mg/L, that is, the water is in the 4th class. The highest mean colour value was measured as 51.4 Pt-Co in sampling point 9; it varied between 5-43.8 Pt-Co in other sampling points. The waters in the KCB were determined as 2nd quality class (5-50 Pt-Co) in terms of colour. Generally, the BOD_5 concentration of sampling points

1, 9, 10 was high for all years. Surface waters in the KCB were generally classified as 3rd and 4th class in terms of BOD_5. Drainage channels were classified as 4th class in terms of COD. While, in terms of SO_4^{2-}, drainage channel waters were determined as 2nd and 4th class waters, stream and irrigation waters were classified as 1st class water. In terms of NO_2-N, the surface water quality in the Konya Closed Basin is generally classified as 3rd and 4th class water. In terms of nitrate, the surface water quality is generally identified as 1st class water in the basin. However, water is clasified as 3rd and 4th class in terms of nitrite in the basin.

Table 4: Mean, Min-Max for temperature, pH, EC, DO, color, OM, BOD_5, COD, SO_4^{2-}, NH_4-N, NO_2-N and NO_3-N values of water samples between 2006 and 2014, and related water quality classes

Sampling point	Mean (Min-Max)	Class	Mean (Min-Max)	Class	Mean (Min-Max)	Class	Mean (Min-Max)	Class
	Temperature (°C)		pH		EC (µS/cm)		DO (mg/L)	
1	16.1 (6.4-26.1)	I	8.0 (7.5-9.2)	I	590 (370-803)	II	7.2 (4.3-12.1)	II
2	16.3 (5.9-26.2)	I	7.9 (7.1-8.5)	I	700 (400-838)	II	6.6 (4.1-9.2)	II
3	16.3 (7.9-26.4)	I	8.0 (7.5-8.5)	I	370 (259-831)	I	7.5 (6.0-9.1)	II
4	16.2 (7.2-26)	I	7.8 (7.2-8.4)	I	340 (260-590)	I	7.4 (4.9-9.1)	II
5	16.9 (6.2-26.3)	I	7.9 (7.3-8.4)	I	450 (268-660)	II	7.1 (4.9-9.0)	II
6	18.2 (10.7-32)	I	7.8 (7.1-8.3)	I	390 (277-460)	I	7.0 (5.7-8.1)	II
7	19.2 (10.5-36)	I	8.0 (7.4-8.6)	I	410 (240-860)	II	7.0 (5.6-9.4)	II
8	15.8 (3.0-24)	I	7.9 (7.6-8.7)	I	340 (230-420)	I	7.7 (6.5-9.7)	II
9	16.7 (9-24)	I	7.2 (6.8-7.7)	I	2300 (344-3040)	III	0.29 (0.0-2.1)	IV
10	14.9 (3.2-22)	I	7.9 (6.8-8.2)	I	3120 (1900-5050)	IV	5.9 (0.0-7.8)	III
	Color (Pt-Co)		OM (mg O_2/L)		BOD_5 (mg/L)		COD (mg/L)	
1	43.8 (3-609)	II	9.7 (2.7-85.4)	-	20.3 (4.0-130)	IV	50.6 (12.4-221)	III
2	11.9 (0-53)	II	6.9 (1.3-33.2)	-	14.1 (2.0-57)	III	39.7 (5.0-147)	II
3	5.0 (0-25)	II	4.9 (0.86-22.1)	-	10.5 (1.0-42)	III	34.0 (5.0-113)	II
4	15.9 (0-176)	II	3.8 (0.9-11.8)	-	6.9 (2.0-19)	II	26.3 (5.0-57)	II
5	6.7 (0-50)	II	3.9 (1.1-9.5)	-	8.9 (3.0-41)	III	30.2 (5.0-83)	II
6	20.0 (2.5-200)	II	3.9 (1.2-9.5)	-	12.9 (3.5-25.6)	III	18.6 (9.0-45)	I
7	11.3 (0-101)	II	3.8 (1.4-11.2)	-	11.8 (2.5-49)	III	30.2 (6.3-90)	II
8	9.7 (0-25)	II	4.2 (1.8-10.2)	-	8.2 (2.8-20.1)	III	28.1 (5-114)	II
9	51.4 (10-250)	III	286 (79.2-693)	-	469 (158-1170)	IV	760 (220-1734)	IV
10	13.3 (0-40)	II	48.1 (3.7-331)	-	79.7 (8.0-653)	IV	145 (17.4-964)	IV
	SO_4^{2-} (mg/L)		NH_4-N (mg/L)		NO_2-N (mg/L)		NO_3-N (mg/L)	
1	27.2 (14.9-47)	I	0.39 (0.01-3.7)	II	0.07 (0.013-0.24)	IV	1.00 (0-3.35)	I
2	51.1 (14.4-142)	I	0.29 (0.01-2.9)	II	0.04 (0.008-0.31)	III	0.80 (0.1-2.07)	I
3	12.7 (5.8-24.0)	I	0.05 (0.004-0.25)	I	0.01 (0.001-0.06)	II	0.48 (0-1.45)	I
4	13.1 (4.8-28.8)	I	0.08 (0.006-0.46)	I	0.02 (0.002-0.07)	III	0.38 (0-1.32)	I
5	15.7 (6.1-24.0)	I	0.28 (0.002-2.7)	II	0.09 (0.006-0.73)	IV	0.64 (0.1-2.4)	I
6	12.0 (4.8-24.0)	I	0.22 (0.004-1.3)	II	0.07 (0.003-0.24)	IV	1.35 (0.2-3.93)	I
7	18.7 (4.8-81.6)	I	0.21 (0-2.6)	II	0.04 (0.006-0.48)	III	0.89 (0-6.69)	I
8	12.0 (4.8-30.2)	I	0.09 (0.004-0.78)	I	0.03 (0.008-0.09)	III	1.36 (0.1-13.3)	I
9	349 (19.2-681)	II	4.7 (0.157-17.9)	IV	0.18 (0.012-0.60)	IV	2.01 (0.1-13.7)	I
10	532 (148-1200)	IV	0.63 (0.009-6.7)	II	0.04 (0.005-0.16)	III	1.03 (0.1-3.7)	I

Mean, Min-Max, turbidity, Na^+, Cl^-, and boron values of water samples between 2006 and 2014, and water quality classes are given in Table 5. There is no water quality classification in terms of turbidity as parameter according to the SWQR. Sodium values of waters taken from sample points 9 and 10 were identified as 3rd and 4th class water quality. Chloride concentrations of sampling points 9 and 10 were found to be higher than of the other points. While surface water at sampling points 9 and 10 were found to be 3rd class quality water in terms of chlorine, 2nd class quality water was generally found for chloride at other sampling points. While drainage channel and one stream water in the basin were in 4th class (>1.0 mg/L) in terms of boron, other sampling points were in 1st class (<1.0 mg/L).

Table 5: Mean, Min-Max, for turbidity, Na^+, Cl^-, and boron values of water samples between 2006 and 2014, and water quality classes

Sampling point	Turbidity (NTU)		Na^+ (mg/L)		Cl^- (mg/L)		Boron (mg/L)	
	Mean (Min-Max)	Class	Mean (Min-Max)	Class	Mean (Min-Max)	Class	Mean (Min-Max)	Class
1	11.5 (2.5-31)	-	13.3 (5.7-36.8)	I	50.3 (12.4-99.4)	II	0.77 (0.1-2.8)	I
2	14.7 (1.8-60)	-	16.8 (6.9-41.4)	I	53.1 (11.3-106)	II	1.08 (0.1-3.4)	IV
3	5.90 (1.5-15)	-	6.3 (1.7-15.4)	I	29.9 (3.6-56.8)	II	0.92 (0.1-1.8)	I
4	8.35 (2.5-20)	-	5.5 (0.37-15.6)	I	29.8 (3.1-63.9)	II	0.90 (0.1-2.1)	I
5	8.49 (2.0-80)	-	6.7 (1.6-11.5)	I	36.6 (4.2-63.)	II	0.70 (0.1-2.0)	I
6	14.1 (3.0-50)	-	7.1 (4.6-9.2)	I	42.3 (28.4-56.8)	II	0.51(0.15-0.9)	I
7	12.2 (2.0-80)	-	9.1(2.7-32.2)	I	36.4 (7.1-92.3)	II	0.55 (0.1-1.4)	I
8	16.9 (4.0-80)	-	6.2 (2.3-10.3)	I	26.4 (8.5-46.2)	II	0.54 (0.3-0.8)	I
9	82.9 (30-300)		233 (6.9-362)	III	322 (53.3-518)	III	2.03 (1.6-5.8)	IV
10	22.3 (5.0-60)	-	274 (92-570)	IV	470 (262-878)	III	3.74 (1.7-6.5)	IV

Irrigation water quality classes were evaluated according to Wastewater Treatment Plant Technical Procedures Regulation (WWTPTPR). 1st class water is "no damage", 2nd class water is "low-medium damage", and 3rd class water is "hazardous" for irrigation purposes. Irrigation water quality class of Konya surface waters are given in Table 6. EC is an important parameter for determining the irrigation water quality since it is an indicator of salinity. Highly saline irrigation waters cause an increase of salinity levels in soil. High salinity in irrigation water and soil has toxic effects on plants. Drainage channel waters were determined as 2nd class water, while stream and irrigation channel waters were classified as 1st class for EC.

SAR is an indication of the Na^+ amount adsorbed by soil. These values also place Konya surface waters in 2nd class useable water category according to irrigation water quality criteria. According to irrigation water class, surface waters contain very high sodium and high salinity, therefore, it is in the 2nd and 3rd irrigation water classes that should be used with precautions. Careful plant type selection and salt control of soil should be done, when these waters are used for irrigation. Chloride content of stream and irrigation channel waters were below 140 mg/L, and according to irrigation water quality criteria, they were in the good quality irrigation water class.

Table 6: Irrigation water quality class of Konya surface waters

Sampling point	EC	SAR	Class	Irrigation water class	Na^+		Cl^-		Boron
					Surface irrigation	Drip irrigation	Surface irrigation	Drip irrigation	
1	I	2.03	II	C2-S1	III	I	I	I	II
2	I	2.34	II	C2-S1	III	I	I	I	II
3	I	0.72	II	C2-S1	II	I	I	I	II
4	I	1.11	II	C2-S1	II	I	I	I	II
5	I	1.17	II	C2-S1	II	I	I	I	II
6	I	1.34	II	C2-S1	II	I	I	I	I
7	I	1.64	II	C2-S1	III	I	I	I	I
8	I	1.21	II	C2-S1	II	I	I	I	I
9	II	22.34	III	C4-S4	III	II	II	II	II
10	II	21.40	II	C4-S4	III	II	III	II	III

Boron is an essential trace element for plant growth with optimum concentrations of 0.1-0.2 mg/L. However, boron is toxic around 1 mg/L for a number of sensitive plants. It reduces production yield by reducing the growth rate. Usually, there are sufficient quantities of boron in reclaimed water in order to correct soil deficiencies. Some lawn types and most grasses are tolerant to boron concentrations between 2 and 10 mg/L. Generally, boron concentrations in surface waters of Konya basin are between 0.7 and 3 mg/L. This boron concentration makes stream waters grouped in 2nd class irrigation water for sensitive plants such as chestnut, lemon, fig, apple, grape, and beans as well as 2nd class irrigation water for medium level tolerant plants such as wheat, barley, corn, oat, olive, and cotton. Finally, irrigation channel waters were classified as 1st class irrigation water for highly tolerant plants such as sugar beet, clover, bean, onion, lettuce, and carrot.

4 Conclusions

Water at sampling points were determined generally being 1st class water in terms of temperature, pH, sulphate, sodium, and nitrate, 1st and 2nd class water in terms of EC, DO, chloride, and ammonium, and 3rd and 4th class water in terms of color, nitrite, boron, COD and BOD_5. According to irrigation water regulation, only 2nd class water can be used for irrigation purposes provided that irrigation water criteria are met. In this case, water taken only from 2 points is suitable for irrigation. According to the irrigation water criteria, they are generally found to be acceptable for EC and chloride but not for sodium and boron. The main causes of water pollution problems observed in Konya Closed Basin are coming from discharges of untreated municipal or industrial wastewater, discharge waters from agricultural irrigation and drainage channels, irregular solid waste landfills, drought, rapid population growth, surface water pollution caused by animal husbandry activities, erosion, agricultural activities in the fields resulting from the fall of the water level, and aquacultural activities on surface water resources. There are unhealthy storage areas and mine establishments in the areas close to 5 different quality observation points located at the entrance of Beyşehir Lake.

In order to overcome the water pollution problems in the KCB, new regular solid waste sites should be constructed in this area. Agricultural activities should be avoided in areas exposed to the withdrawal of lake water. In the study area around Beyşehir Lake, pollutants originating from domestic wastewater discharges and agricultural activities were also detected. Nitrate pollution should be reduced, pesticide use should be reduced, and good livestock practices should be carried out by implementing good agricultural practices. Sampling point 9 (drainage channel) receives domestic wastewaters and organized industrial district wastewater from Konya. According to the results of this point analysis, domestic and industrial wastewater treatment plants should be operated regularly and regular maintenance measures should be made. Pollution reduction programs should be implemented for polluters originating from industrial facilities. A common wastewater treatment plant should be constructed for the wastewaters of Gölyazı, Yapalı, Günyüzü, Kırkışla, Akıncılar and Akköy settlements along the Apa Drainage Channel, Gölyazı Bridge. A joint wastewater treatment plant should be constructed for Çengilti, Egribayat, Karaömerler, Yazıbelen domestic wastewaters. Sewerage network must be established in residential areas, where water resources pass. A joint treatment facility should be built in Belkuyu, Alanköy, Apasarayçık settlements located in Apa Dam. If the wastewater treatment plant cannot be constructed, sewerage system should be provided, maintained or repaired. A joint treatment plant should be constructed for the wastewaters of Kesecik, Kuran, Kumluca and Balıklava settlements, located at the BSA Canal Seydisehir Suğla Exit. According to WPCR and SWQR, protection areas need to be established. Monitoring programs for water quality should be established and regular monitoring activities should be carried out.

5 Acknowledgements

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IMPACT ASSESSMENT OF BAHR EL-BAQAR DIVERSION PROJECT ON WATER QUALITY STATUS IN LAKE MANZALA, EASTERN NILE DELTA, EGYPT

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Keywords: Bahr El-Baqar Drain; Lake Manzala, MIKE21; Water Quality Management

Abstract

Lake Manzala is the largest Egyptian coastal lake, which lies on the eastern north coast of Egypt. It is considered as one of the most valuable fish sources in Egypt. In the last decades, water quality status of the lake has been dramatically degraded due to the rapid increase of industrial, municipal and agricultural wastewater discharges from the six main drains of Eastern Nile Delta. Bahr El-Baqar drain is the largest and highest polluted contributor that disposing its pollution load into the southern part of the lake. An ambitious project is under planning to treat the total discharge of Bahr El-Baqar drain and to divert it to Sinai for land reclamation purposes. In this work, MIKE21 Model is used to develop and to calibrate a hydrodynamic and water quality model for Lake Manzala. Eight water quality parameters in addition to three hydrodynamic parameters are simulated to investigate the lake water quality status. The calibrated model shows good agreement between the simulated and the observed water depth, water temperature, salinity and water quality records. The model is used to investigate the impacts of diverting Bahr El-Baqar Drain on the hydrodynamic and water quality characteristics of the lake. Significant improvements in the lake water quality status are noticed; about 12% increase in Dissolved Oxygen concentration, while all the other investigated water quality parameters are significantly decreased by a percentage between 43% and 67% comparing with their original records. The developed model can be used to investigate other water quality management scenarios for the lake.

1 Introduction

Among the Egyptian coastal lakes, Lake Manzala is the largest shallow coastal lake on the fringe of the Mediterranean Sea (Figure 1). The lake is located in the Northern-Eastern region of Egypt and is surrounded by five provinces. The lake is an important source of inexpensive fish as it contributed by about 35% of the total country yield during the 1980's (Assar et al., 2015). Recently, it is considered as the most productive lake in Egypt and contributed by about 44% in 2004 and increased to about 56% in 2013 from the total annual production of the northern Delta lakes. In addition to its economic importance, the lake is of a great importance to ecology, as it provides important habitats for wildlife including birds, and as a feeding area for migrating birds and some of rare and endangered bird species.

In recent years, the aquatic health of the lake has substantially deteriorated due to increased contamination by polluted inflows and over intensive aquaculture. The lake receives about 5.5 BCM/year (billion cubic meter per year) of fresh water through the five main drains of Eastern Delta: Bahr El-Baqar, Hadous, Mataria, Serw, and Faresquer drains. These drains are collecting agricultural, industrial and municipal wastewaters from 6 governorates: Cairo, Qalubia, Port Said, Demietta, El-Daqahlia, and El-Sharqia. Bahr El-Baqar drain is considered the main contributor source of polluted water to Lake Manzala, as it discharges about 49% of the total fresh water disposal into the lake (Daly et al., 2015).

The lake has only 3 outlets: two to the Mediterranean Sea (El-Gamil and New El-Gamil Outlets) and one to Suez Canal (Qabuty Canal) (Figure 1). The discharge of untreated wastewater into the lake caused severe contamination due to heavy metals and other toxic materials, which contaminate the whole aquatic environment. These toxins appear at high concentrations in water, sediment and fish, leading to major health problems in the lake area (El-Moghazy, 2018).

Lake Manzala has gradually transformed with time from a brackish environment to eutrophic fresh water in response to increased fresh water inputs, nutrient loading associated with agricultural land reclamation processes, and urban waste disposal (Elshemy et al., 2016). All previous studies admit that the major problems of the lake are as follows:

- The increase of nutrients loading into the lake especially from the input drains that accelerate the eutrophication process occurring within the lake.
- The increase of heavy metal concentrations through the lake including Cu, Cd, Pb, Hg, Zn and Mn in water, sediments and fish.
- The lake is contaminated with high amount of TVB (Total Viable Bacteria) and FCB (Fecal Coliform Bacteria).
- Fish are contaminated in surface and internal tissues with a very high amount of TVB and FCB, and recent studies admit that “the fish is highly polluted and dangerous for human health” (Flower, 2001).

Lake Manzala was selected to be one of nine wetland lakes in North Africa to be studied for biodiversity within the CASSARINA Project (Flower, 2001), and one of three studied cases in the southern Mediterranean region, for the MELMARINA Project (GAFRD, 2014). MELMARINA Project aimed to establish an integrated hydrological and ecological monitoring at the selected lagoons to improve the understanding of its ecological functions and to investigate the impacts of environmental and management changes through hydro-ecological models. Thompson et al. (2009) investigated the hydrological and water quality status of Lake Manzala through MELMARINA

Project and reported that the tidal oscillations of water levels are not extending throughout the lake due to the vegetated islands within the lake.

MIKE21 Model was used to develop a hydro-ecological model for Lake Manzala (Hamed et al., 2013). The developed model was used to identify the required magnitude of nutrients, which reach the lake to an acceptable water quality conditions. Some reduction scenarios of drains' nutrients (relative to the nutrients amount in 2003-2004) were investigated. In 2010, FVCOM Ocean Model was used to develop a hydrodynamic model for the lake to assess a range of sustainable water management strategies (Rashad et al., 2010). For one of the studied scenarios, a 40% reduction of the polluted drain water inflows to the lake, the authors concluded that an improvement of the water circulation at the north-western sector of the lake and salinity increasing in the southern part will happen. Elshemy et al. (2016) developed a hydrodynamic model, based on MIKE21, to investigate the impacts of future climatic changes on the lake characteristics. The results revealed severe impacts of climate changes on water depth, water temperature, and salinity of the lake.

The main objective of this work was to develop a hydrodynamic and water quality model for the lake that can be used to evaluate the impacts of different water quality management scenarios on the status of the lake water quality. The developed model is used to study the impact of one of these scenarios that is the diversion project of Bahr El-Baqar Drain.

2 Material and Methods

Study Area

Lake Manzala, the largest Egyptian Lagoon, lies on the eastern boundary of the Nile Delta. It is about 47 km long and 30 km wide. It is classified as a shallow lake, as its water depth ranges from 0.7 to 1.5 m, and the water salinity is fluctuated from low salinity in the South and West, to brackish water over the most of its area, to saline water in the extreme North East (Khalil, 1990). The lake has a large number of islands, which covers about 23% of its total area (Rashad, 2010). A very narrow canal (El-Qabuty Canal) connects the lake to Suez Canal (saline water) to the East (Figure 1). The northern boundary of the lake is the Mediterranean Sea with two outlets (El-Gamil and the New El-Gamil) from the lake. These outlets improve the water quality status of the lake. Along its eastern and southern boundaries, Lake Manzala receives agricultural, industrial and domestic wastewaters through Bahr El-Baqar, Hadous, Mataria, Serw, and Faresquer drains. The polluted inflows beside other human activities, such as land cultivation and human settlements, transformed the status of the lake water quality from a marine estuary environment to an eutrophic freshwater system composed of about 30 basins, which are varying in their hydrological and water quality characteristics (Khalil, 1990).

Bahr El-Baqar Drain

Bahr El-Baqar drain is the main contributor to Lake Manzala. This drain serves about 640,000 acres (= 260,000 ha) in 6 governorates along 160 km and discharges from 4 to 7 Mm^3/day into Lake Manzala (Daly et al., 2015). The Egyptian Ministry of Water Resources and Irrigation (MWRI) is planning a project to enhance Lake Manzala water quality status and to increase the available water budget for land reclamation in Sinai by diverting Bahr El-Baqar drain to Sinai. The project includes the construction of a water treatment plant to treat the drain discharge (Figure 2).

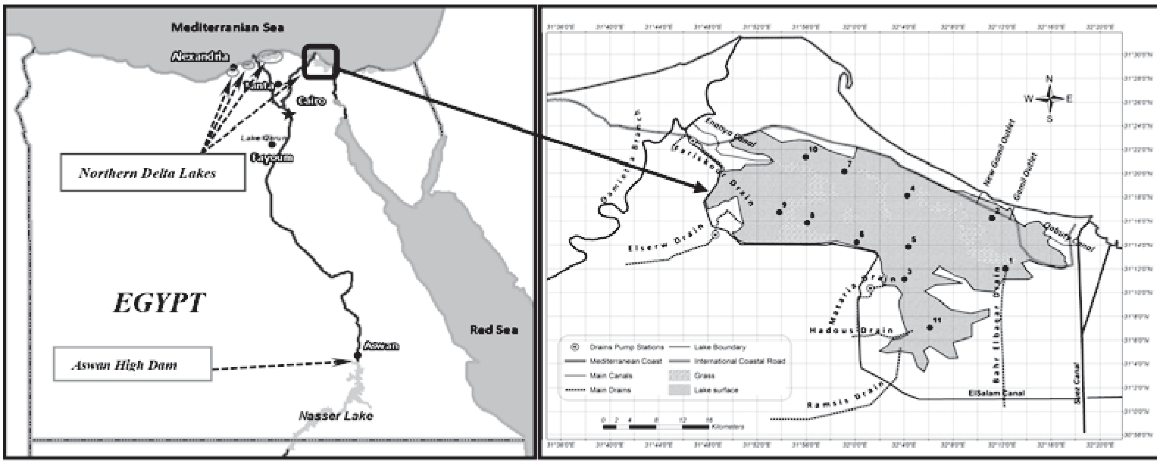

Figure 1: Lake Manzala Location and its Water Quality Sampling Stations

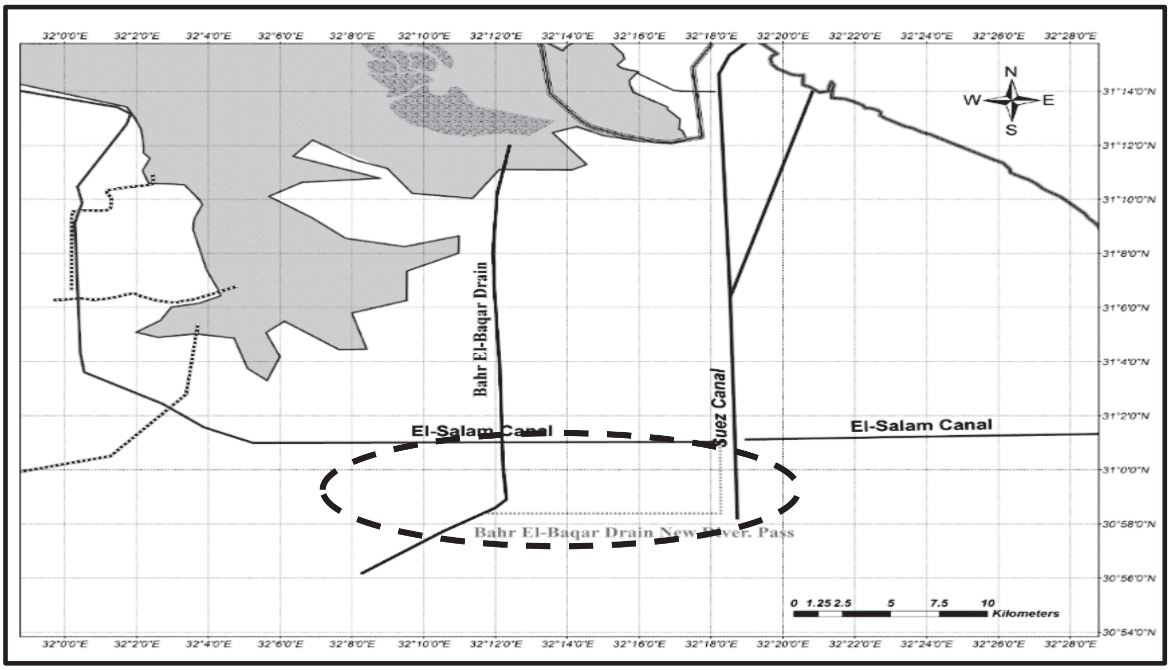

Figure 2: New Diversion Channel of Bahr El-Baqar Drain

Data Collection

Physical, chemical and biological records were collected by the Egyptian Environmental Affairs Agency (EEAA) from eleven stations in the lake and four stations at the outlets of the four main drains (Figure 1). Twelve parameters were seasonally measured for two years (from August 2010 to August 2012). Statistical summaries of these records are presented in Table 1, Table 2 for lake drains, and Table 3 for Bahr El-Baqar drain. Meteorological data were obtained from Port Said

Airport Meteorological Station that lies at the north eastern corner of the lake. Water depths and levels were collected from five stations, as shown in Figure 3. Hydrological records and drain discharges were collected by the National Water Research Centre (NWRC) as shown in Figure 4 (Daly et al., 2015).

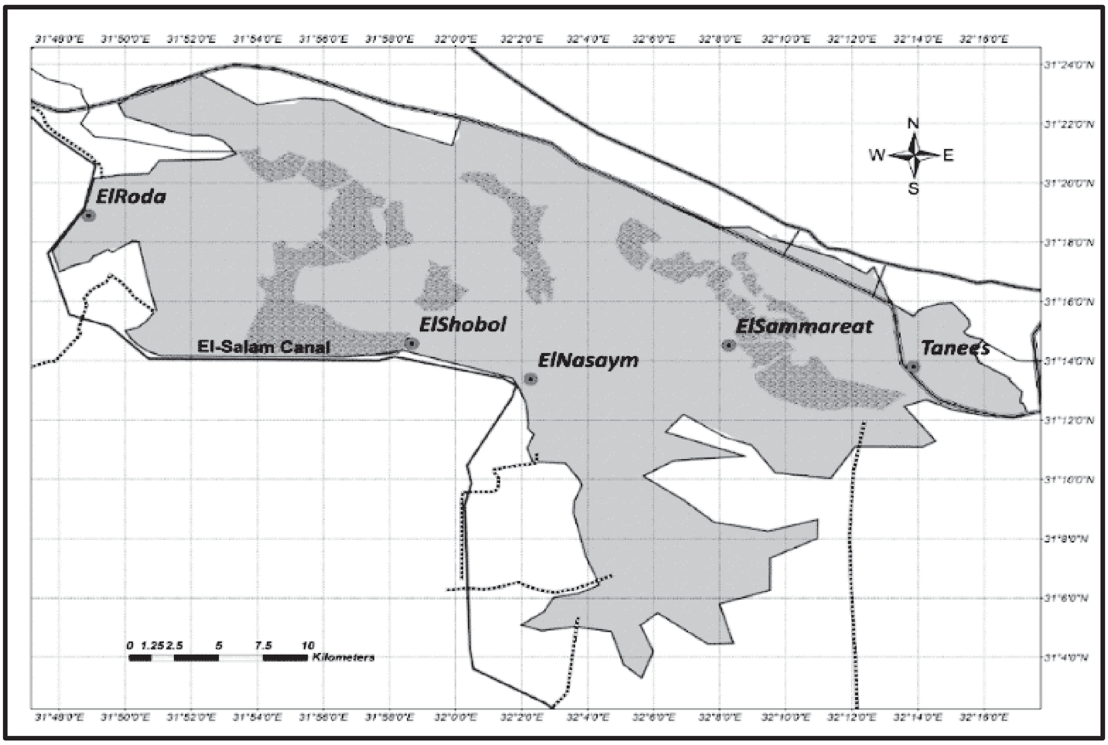

Figure 3: Water levels recording stations in Lake Manzala

Table 1: Statistical summary of water quality data for Lake Manzala (Aug 2010 - Aug 2012)

Parameter	Min	Max	Mean	Parameter	Min	Max	Mean
Temp. *(°C)*	12.7	30.6	23.1	**COD** (*mg/L*)	6.40	660	136
EC (*µS/cm*)	1.50	30.3	7.23	**TN** (*mg/L*)	0.57	19.6	4.56
TSS (*g/L*)	1.24	18.8	4.10	**TP** (*mg/L*)	0.024	2.01	0.49
pH	7.00	9.40	8.30	**NO_2** (*mg/L*)	0.001	0.33	0.051
DO (*mg/L*)	0.00	26.5	6.61	**Phosphate** (*mg/L*)	0.005	0.90	0.22
BOD (*mg/L*)	0.58	219	21.8	**Chll-a** (*mg/L*)	0.002	0.39	0.045
NO_3 (*mg/L*)	0.01	1.29	0.20	**Ammonia** (*mg/L*)	0.02	9.21	1.14

Table 2: Statistical summary of water quality data for Lake Manzala Drains (Aug 2010 - Aug 2012)

Parameter	Unit	Min	Max	Mean	SD
Temp	*°C*	12.7	29.9	23.0	5.26
EC	*µS/cm*	0.85	5.69	2.18	1.40
TSS	*mg/L*	23.2	137	62.3	27.9
pH	-	7.05	8.39	7.99	0.35
DO	*mg/L*	0.00	7.28	2.00	1.79
BOD	*mg/L*	4.09	214	49.6	52.5
COD	*mg/L*	4.35	448	96.4	118
TN	*mg/L*	2.05	17.4	6.30	3.31
TP	*mg/L*	0.37	2.10	0.92	0.45
Nitrate	*mg/L*	0.07	2.08	0.53	0.45
Phosphate	*mg/L*	0.16	1.08	0.44	0.23
Chll-a	*µg/L*	1.74	99.9	24.1	26.5

Table 3: Statistical summary of water quality data for Bahr El-Baqar Drain (Aug 2010 - Aug 2012)

Parameter	Min	Max	Mean	Parameter	Min	Max	Mean
Temp. (*°C*)	13.7	29.0	22.9	**COD** (*mg/L*)	18.0	660	229
EC (*µS/cm*)	3.7	4.8	4.05	**TN** (*mg/L*)	4.42	19.6	9.42
TSS (*g/L*)	1.94	2.55	2.17	**TP** (*mg/L*)	1.04	2. 1	1.52
pH	7.43	8.55	7.94	**NO_2** (*mg/L*)	0.03	0.33	0.12
DO (*mg/L*)	0.00	2.56	0.94	**Phosphate** (*mg/L*)	0.46	1.08	0.67
BOD (*mg/L*)	18.1	214	87.5	**Chll-a** (*mg/L*)	0.02	0.10	0.053
NO_3 (*mg/L*)	0.07	0.89	0.42	**Ammonia** (*mg/L*)	1.82	8.34	4.36

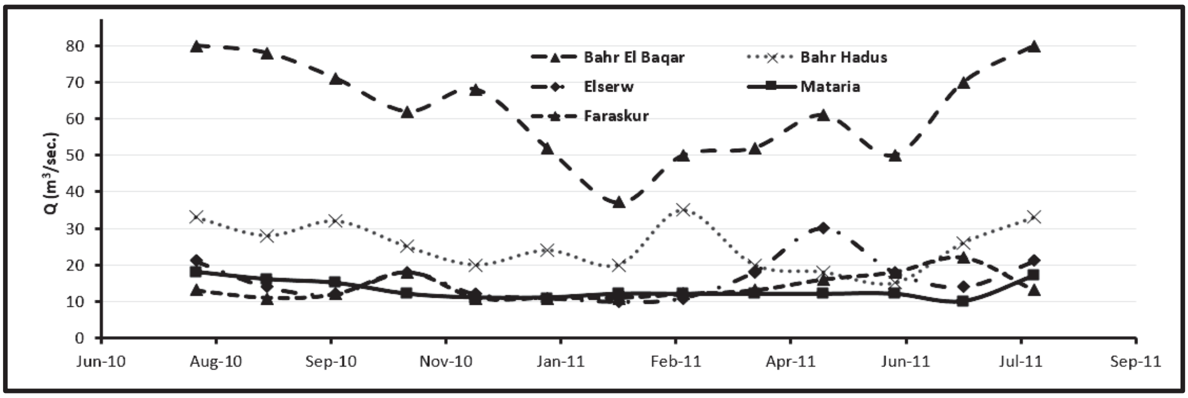

Figure 4: Drains inflow into Lake Manzala for a typical year

MIKE21 Code Description

MIKE21 Model is a general numerical modelling system for two-dimensional free-surface flows. It is applicable to the simulation of hydraulic and environmental conditions in lakes, estuaries, bays and coastal areas. It simulates unsteady two-dimensional flows in one layer (vertically homogeneous). This code contains three modules, hydrodynamic module (HD) for velocities and water levels, advection-dispersion module (AD) for thermal and conservative simulation, such as water temperature and salinity, and ECO-Lab module for water quality simulation (Rasmussen et al., 2009; Thompson et al., 2009).

Model Development for Lake Manzala

The basic input data for the model include: lake topography (bathymetry), water levels and water quality records at the beginning of simulation (initial conditions) and for all the simulation period for the drains and outlets as well as meteorological information. The model grid, as shown in Figure 5, consists of 37,500 cells; each cell has a resolution of 200x200 m. The bathymetry of the lake was developed using UTM-36 map projection of the study area. The five main drains were considered as point sources, while the three outlets were considered as boundary conditions. The lake simulation was run for a typical year (August 2010 to July 2011).

The lake model development has been done on three dependent stages. First stage, a hydrodynamic model (HD) was developed and calibrated using the water level field records at five water level stations. The second stage, an AD model was developed based on the calibrated HD model. The developed AD model was calibrated using the records of water temperature and salinity at eleven record stations for water quality of the lake. The third stage, the Eco-Lab model was developed, based on the developed HD and AD models. Eight water quality variables were simulated: Biological Oxygen Demand (BOD), Dissolved Oxygen (DO), Nitrite (NO_2), Nitrate (NO_3), Ammonia (NH_3), Phosphate (PO_4), Chlorophyll-a (Chll-a) and Total Phosphorus (TP). The seasonal measured records of these water quality variables were used to calibrate the Eco-Lab model.

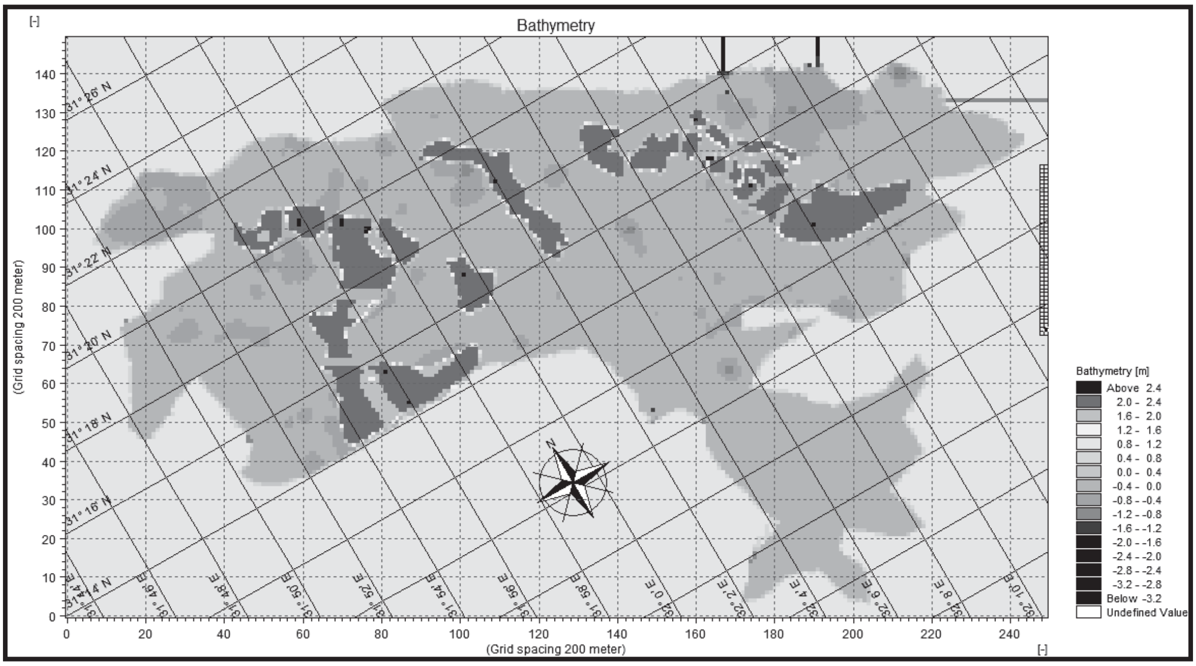

Figure 5: Developed bathymetry for Lake Manzala Model

Model Calibration

The three modules (HD, AD and ECO-Lab) were calibrated by comparing simulated results with the measured values at different monitoring stations for the simulation period. Two statistical measures were applied to quantify the accuracy of the developed model. These statistical measures are the Absolute Mean Error (AME) and the Root Mean Square (RMSE), which are computed according to the following equations:

$$\text{AME} = \frac{\sum|\text{Observed value} - \text{Simulated value}|}{\text{Number of Observations}} \tag{1}$$

$$\text{RMSE} = \sqrt{\frac{\sum(\text{Observed value} - \text{Simulated value})^2}{\text{Number of Observations}}} \tag{2}$$

A list of non-default coefficients for the HD and AD modules of MIKE21 Code are shown in Tables 4 and 5, while for ECO-Lab module, default coefficients were used.

Table 4: List of non-default calibration coefficients of MIKE 21 for the Hydrodynamic Module

Coefficient	Value	Coefficient	Value
Time step interval	150 sec.	**Total time steps**	210,240 sec.
Warm-up period	600 sec.	**Courant number**	4.07
Drying depth	0.05 m	**Flooding depth**	0.3 m
Eddy viscosity (flux based)	0.2 m^2/s	**Chezy bottom friction factor**	50 $\sqrt{m}/s$

Table 5: List of non-default calibration coefficients of MIKE 21 for AD Model

Coefficient	Value	Coefficient	Value
Constant in Dalton's law	0.5	**Wind coefficient in Dalton's law**	0.9
Sun constant *a* in Ångstrom's law	0.295	**Sun constant *b* in Ångstrom's law**	0.371
Displacement (summer time)	1	**Standard meridian for time zone**	30
Integration method for heat exchange	RK4	**Update frequency**	5
Standard meridian for time zone	0	**Displacement (summer time)**	0
Dispersion coefficient for Y- dir.	2	**Dispersion coefficient for X- dir.**	2

3 Results and Discussion

Hydrodynamic (HD) Model Calibration

Figure 6 shows the water depth profiles (measured and simulated) for El-Roda and El-Nasaym stations as examples. The results show a good agreement between the measured and observed profiles. For the five stations, the average AME and RMSE were 0.061 m and 0.078 m, respectively.

Advection Dispersion (AD) Model Calibration

Figure 7 shows the water temperature profiles (measured and simulated) for the stations No. 4 and No. 11. The results show a good agreement between measured and observed profiles for all parameters at all stations. The average AME and RMSE for all recording stations were 0.56 °C and 0.72 °C, respectively.

Figure 8 shows the salinity profiles (measured and simulated) at the stations No. 8 and No. 11. The average AME and RMSE for all recording stations are 1 ppt and 1.4 ppt, respectively. Scarcity of salinity data (only four records per year) may lead to that unsatisfactory result of AME and RMSE values.

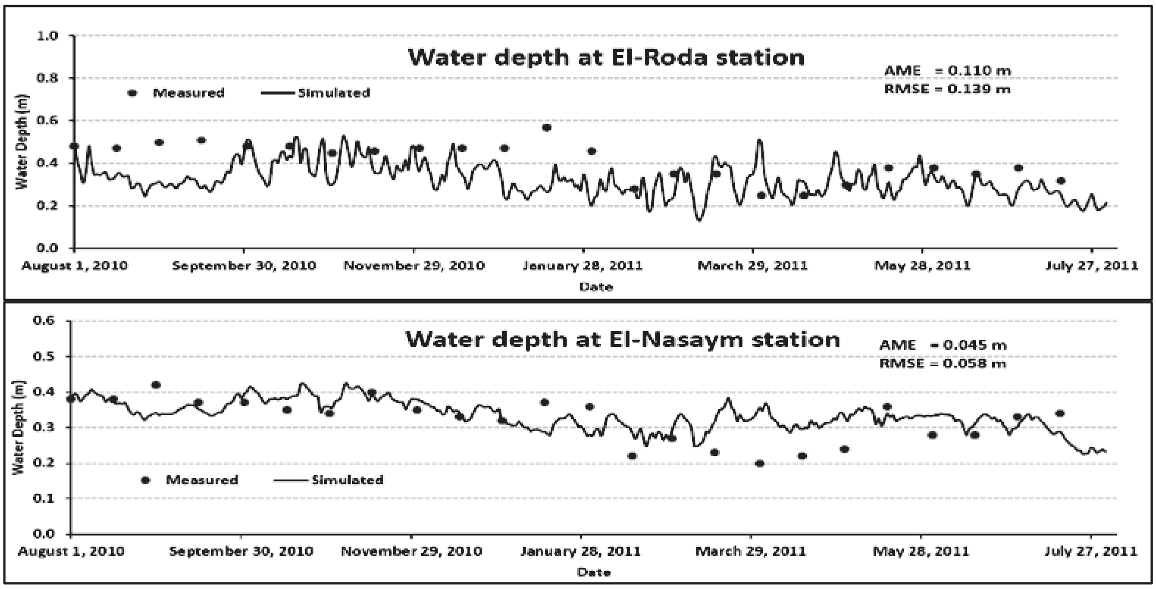

Figure 6: Simulated and measured water depth profiles at El-Roda and El-Nasaym Stations

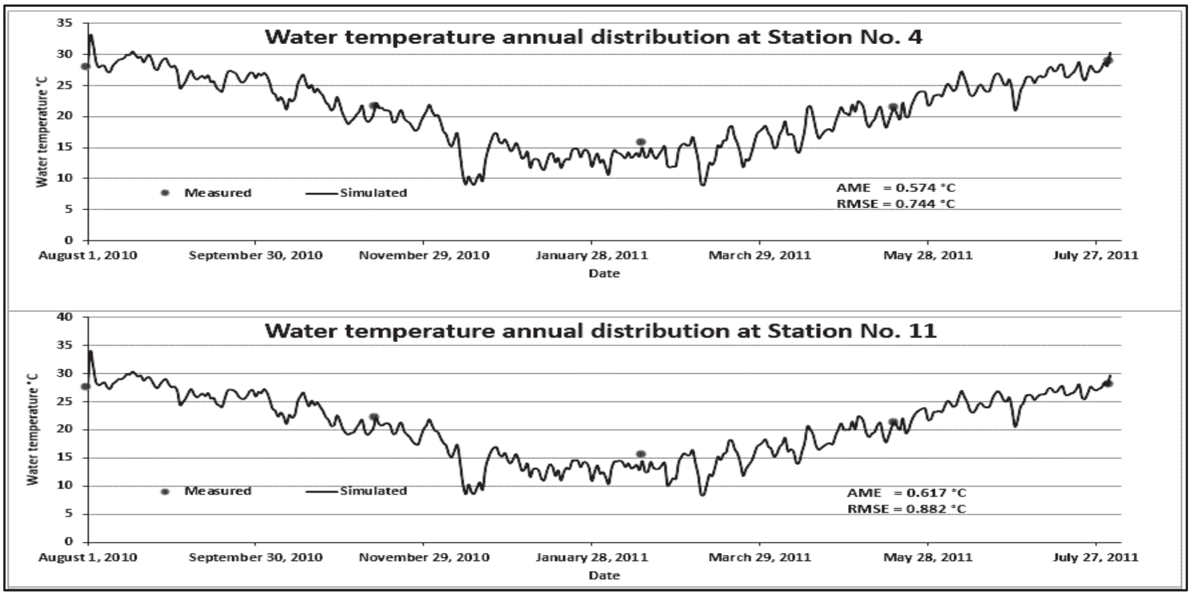

Figure 7: Simulated and measured water temperature profiles at the stations No. 4 and 11

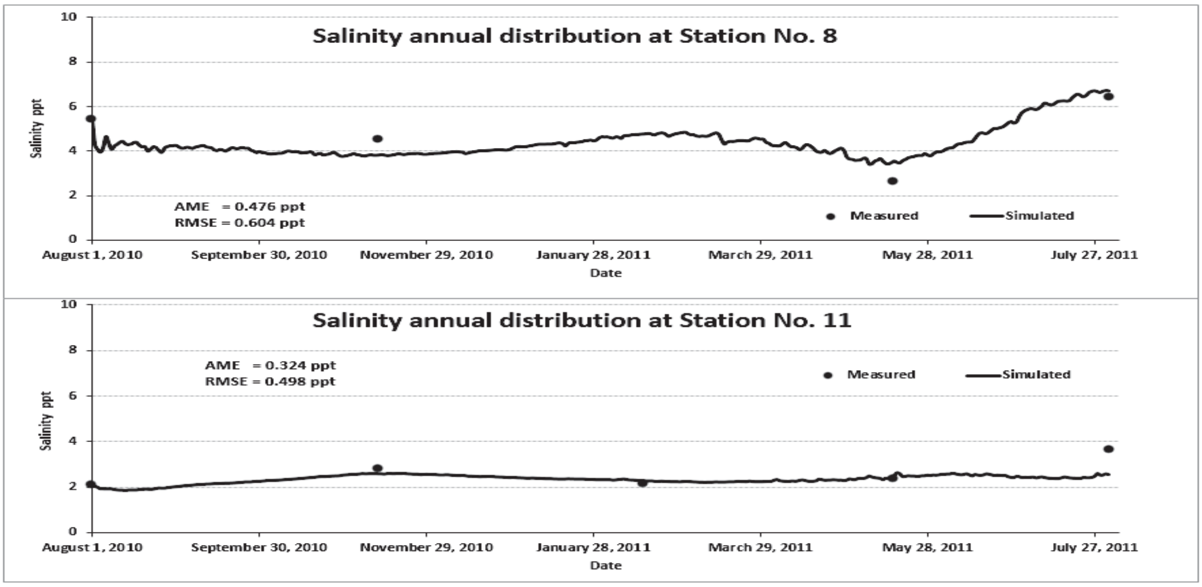

Figure 8: Simulated and measured water salinity at the stations No. 8 and No. 11

Eco-Lab Model Calibration

The ECO-Lab Model for Lake Manzala has been calibrated for the same period and for 8 water quality parameters. The model results closely mimic the measured profiles of the simulated parameters. Figure 9 shows the profiles (simulated and measured) for DO, BOD and Chll-a for stations 1, 4 and 8. The average AME for DO, BOD and Chll-a are 0.052 mg/l, 0.04 mg/l and 0.024 mg/l, respectively. The average RMSE for DO, BOD and Chll-a are 0.09 mg/l, 0.059 mg/l and 0.032 mg/l, respectively.

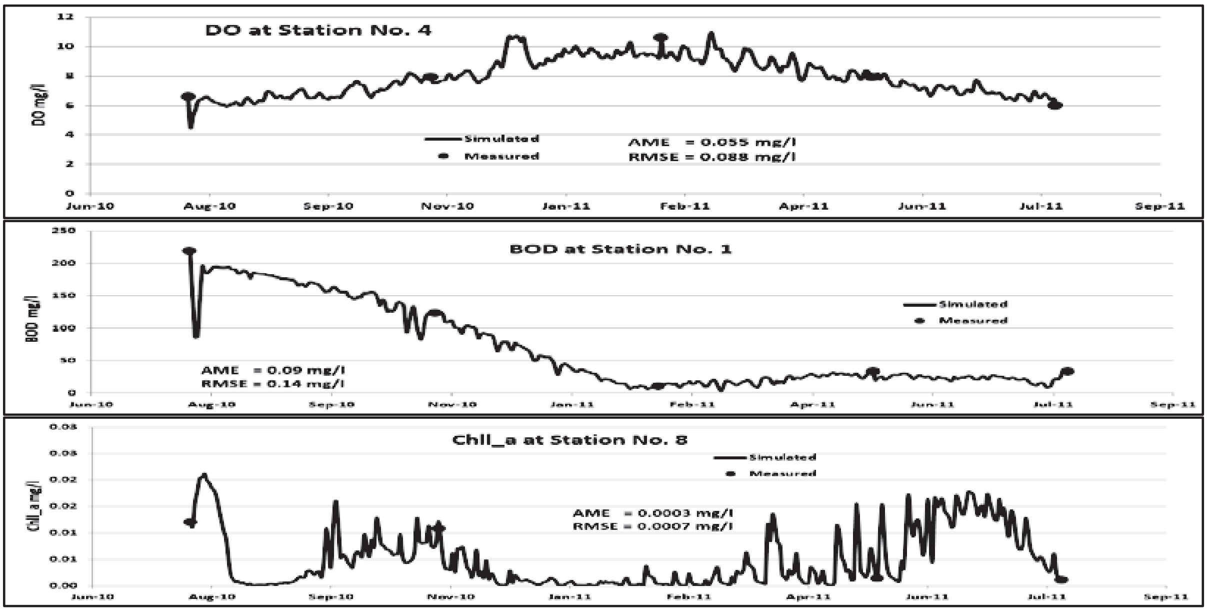

Figure 9: Simulated and measured DO, BOD and Chll-a at the stations No. 1, 4 and 8

Figure 10 shows the nutrients (NO_3, NO_2, NH_3, PO_4 and TP) profiles at some selected stations, as examples. The average AME for NO_3, NO_2, NH_3, PO_4 and TP are 0.044 mg/l, 0.02 mg/l, 0.053 mg/l, 0.032 mg/l and 0.022 mg/l, respectively. The average RMSE for NO_3, NO_2, NH_3, PO_4 and TP are 0.073 mg/l, 0.031 mg/l, 0.095 mg/l, 0.055 mg/l and 0.032 mg/l, respectively.

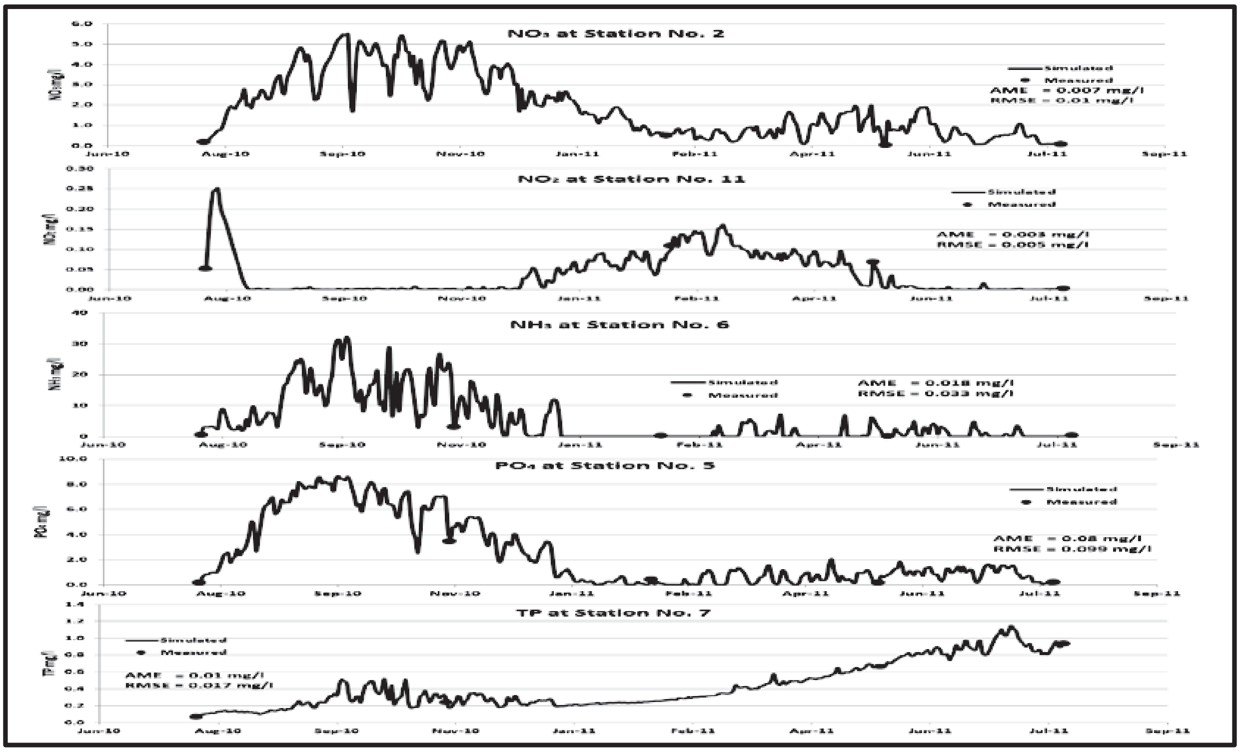

Figure 10: Simulated and measured nutrient profiles at the stations No. 2, 5, 6, 7 and 11

Diversion of Bahr El-Baqar Drain

The calibrated model can be used to evaluate the impacts of water quality management scenarios on the water quality status of Lake Manzala such as the diversion of Bahr El- Baqar project. In order to simulate the diversion of Bahr El-Baqar drain discharge, the calibrated Eco-Lab water quality model was modified by neglecting the effluent of Bahr El-Baqar drain.

Accordingly, the model boundary and initial conditions were modified. To quantify the change in each water quality parameter profile due to the investigated scenario, a percentage change ratio (Δ) has been calculated using the following equation:

$$\Delta = \frac{\text{average simulated} - \text{average calibrated}}{\text{average calibrated}} * 100 \qquad (3)$$

Figure 11 shows the DO, BOD and Chll-a profiles at stations No. 2, 7 and 9, and Figure 12 shows the nutrient components profiles at stations 1, 3, 6, 10 and 11. Figure 13 shows the percentage change ratio for the considered water quality parameters at all recording stations.

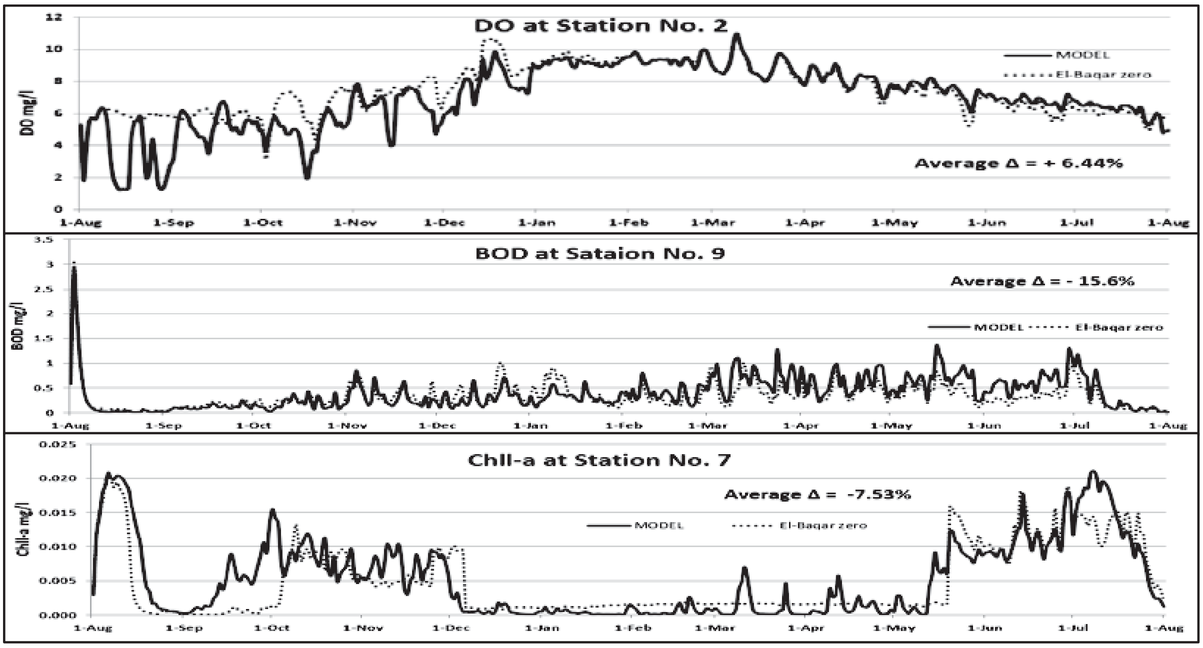

Figure 11: Calibrated and simulated DO, BOD and Chll-a profiles at different stations after diversion of Bahr El-Baqar Drain

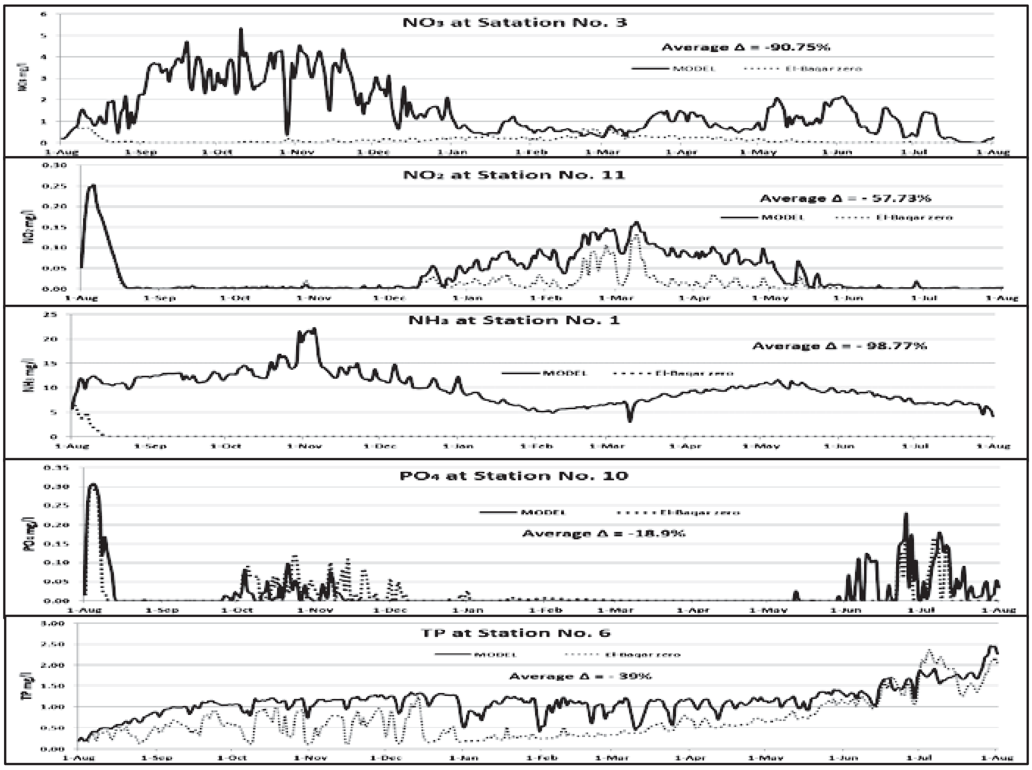

Figure 12: Calibrated and simulated nutrients components profiles at different stations after diversion of Bahr El-Baqar Drain

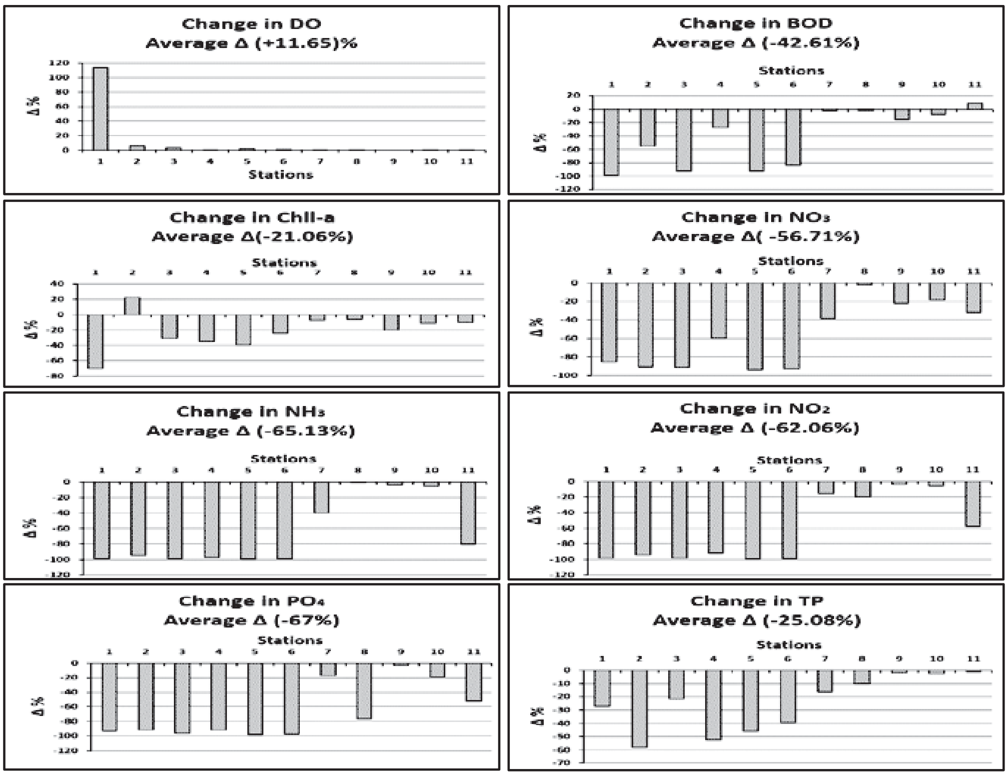

Figure 13: Percentage change ratios for different water quality parameters at different stations after diversion of Bahr El-Baqar Drain

The results show that a significant improvement can be noticed in the water quality status of the lake, particularly in the eastern zone near the outlets to the sea and Suez Canal. The maximum percentage change is noticed at the Station No. 1, and it gradually decreases towards the western zone. The average increase of DO concentration is about 11.6%, where the maximum is about 113% at the Station No. 1. It is also illustrated that other considered water quality parameters have a significant decrease of their concentrations. The average decrease ratios are about 67%, 65%, 62% and 57% for PO_4, NH_3, NO_2 and NO_3, respectively. Additionally, the average decrease of BOD concentrations is about 43%. These results reveal the enhancement impact of diverting Bahr El-Baqar drain effluent on the water quality status in the lake.

4 Conclusion

A hydrodynamic and water quality model was developed and calibrated to investigate the impacts of the diversion project of Bahr El-Baqar drain on the water quality status in Lake Manzala. The model results show that the diversion of the drain significantly improved the water quality status of the lake particularly in the eastern zone near the outlets to the sea and to Suez Canal. The diversion of the drain effluent enhanced DO concentration by an average increase of about 11.7%. Similarly, the concentrations of BOD, Chll-a and nutrients components were decreased by about 42.6%, 21% and 55%, respectively. The developed model can be used to investigate other water quality management scenarios.

5 Acknowledgement

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PERFORMANCE OF BIOLOGICAL INDICES IN COMPARISON TO A WATER QUALITY INDEX IN ASSESSMENT OF AQUATIC ECOSYSTEMS HEALTH OF ZIO BASIN (TOGO)

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Keywords: Biological indices, macroinvertebrates, water quality, watershed, human activities

Abstract

Water quality indices are important tools for ecosystem health assessment and potential water security indicators, but still missing in Togo. To fill this gap, biological and water quality indices performance in a basin of Lake Togo watershed were investigated. Fifty sampling sites were selected in three sections of rivers/streams (upstream, middle stream, downstream) through the basin. To test performance of biological and chemical water quality indices in Lake Togo context, one biotic index, Family Biotic Index (FBI), two metrics (number of taxa in the insects' order of *Ephemeroptera*, *Plecoptera* and *Trichoptera* (EPT), number of taxa in the insects' order of *Ephemeroptera*, *Trichoptera* and *Odonata* (ETO), and one chemical water quality index, Prati's Index (WQI) were used. The biotic index and metrics were calculated using macroinvertebrates features (number of taxon, diversity index and abundance) of Zio River basin. The chemical-based water quality index was derived from measurements of water physicochemical parameters. The result showed that all biological indices were sensitive to a set of organic pollution and bacteriological indicators, which correspond to a set of human pressures affecting the ecological integrity of all basin waterbodies ($r > 0.60$; $p < 0.05$). A factor analyses show three types of sites, which characterize three degree of water quality and ecological conditions. This study reveals that biological indices are complementary methods of classic chemical methods and may be integrated in management of hydrosystems health including riparian human health. This work highlights a method for monitoring and decision making in water management of Lake Togo watershed.

1 Introduction

Of all natural resources, water is unarguably the most essential and precious because life began in water and life is nurtured with water. The crucial role of water as the trigger and sustainer of civilizations has been witnessed throughout human history. But until as late as the 1960s, the overriding interest in water has been *vis-â-vis* its quantity. Except of manifestly undesirable situations, the available water was automatically deemed utilizable water. Only during the last three decades of the twentieth century the concern for water quality has been exceedingly felt so that, by now, water quality has acquired as much importance as water quantity (Abbasi and Abbasi, 2012).

In Africa, despite the potential of water resources for some parts of Sub-Saharan and tropical regions, rivers are subject to strong negative impacts due to human activities, which deteriorate water quality, limiting water availability for drinking and other uses (Everard and Powell, 2002; Tampo et al., 2015a). Furthermore, the increasing demand on water contributed to the change in ecosystems directly through human activities and indirectly by the non-point source pollution that is discharged into the rivers (Voelz et al., 2005). In many countries, this is one of the main national issues, and the governments spent extensive efforts and budget allocation to manage and to rehabilitate the rivers, especially polluted rivers located in urban areas (Wan Abdul Ghani et al., 2018). As an example, Singapore as a developed country has started to clean their urban river (Singapore River and Kallang Basin) since 1977, and it was estimated that until 1998, the Singapore government had invested S$ 200 million (US$ 159.8 million) for the river restoration project (Joshi et al., 2012). South Korea decided to spend US$ 19 billion earlier in 2010 to restore four rivers in the country following their success to restore the Cheonggyecheon River (Normile, 2010). Noticeably, the cost to restore the polluted urban rivers requires huge sum of money. Therefore, it is important for every urbanization process of the countries to be done properly to rivers as the main source of water as well as creating awareness and responsibility among the people of keeping the good health of their rivers.

The river pollution problem, confounded by human disturbances through anthropogenic activities and urbanization (Azrina et al., 2006; Al-Shami et al., 2011; Faridah et al., 2012), has many adverse impacts on river ecosystems that intensify water assessment efforts (Tafangenyasha and Dzinomwa, 2005). Among the river components, aquatic macroinvertebrates are the most impacted by the anthropogenic activities (Nessimian et al., 2008). Their response to the impairment of river ecosystem has been manipulated to assess the river water quality. Therefore, several biotic indices based on these macroinvertebrates were developed across the world. SingScore, one of the latest index developed in 2010 in order to assess urban rivers of Singapore, utilizes the effect of various environmental parameters including heavy metal contents in the water to generate the score (Blakely et al., 2014). From the results of their study, Gonçalves and Menezes (2011) suggested that the use of biotic indices as a tool for river quality assessment was more useful in evaluating river health than the conventional national water assessment standards practiced in many countries such as Malaysian Water Quality Index that focused on the physical and chemical indicators only (Zaki, 2010). Furthermore, Metcalfe (1989) and Alba-Tercedor (1996) pointed at the disadvantage of the physicochemical assessment, which measures the water quality only at the time of sampling.

Henceforth, the rise of biotic indices for river quality assessment triggers the question of how effective are these biotic indices in evaluating the water quality in comparison with water chemical assessment of the rivers especially in polluted rivers. Because many biotic indices that were developed in different areas and localities are specifically adapted to the areas examined (Semenchenko and Moroz, 2005). On another note, the rise of tools for water quality assessment triggers another question of how to express water quality. Indeed at the question: What is water quality? It is immensely more complex than the question: What is water quantity? Whereas water quantity is determined by a single parameter like the water mass, water quality is a function of anything and everything the water might have picked up during its journey from the clouds to the soil and to the water body. One way to describe the quality of a given water sample is to list up the concentrations of everything that the sample contains. Moreover, such a list will make little sense to anyone except well-trained water-quality experts. How to compare the quality of different water sources? It cannot be done easily by comparing the list of constituents each sample contains (Abbasi and Abbasi, 2012), but this kind of comparison is ambiguous. For example, a water sample, which contains six components 5% higher than permissible (hence objectionable) levels: pH, hardness, chloride, sulfate, iron and sodium may not be as bad for drinking as another sample with just one constituent like mercury 5% higher than permissible. Water quality indices seek to address this vexing problem because it aims at giving a single value to the water quality of a source on the basis of one or the other system, which translates the list of constituents and their concentrations present in a sample into a single value.

The combination leads to a single ordinal number that facilitates understanding and interpretation of the overall import of the facts that have contributed to that number. Environmental indices of which water quality indices form a major component are used as communication tools by regulatory agencies to describe the “quality” or “health” of a specific environmental system, and to evaluate the impact of regulatory policies on various environmental management practices (Song and Kim, 2009; Pusatli et al., 2009; Sadiq et al., 2010).

As a result, many recent scientific investigations are focused on the comparison of the biotic indices (Ravera 2001; Semenchenko and Moroz, 2005) in order to adopt the indices into local river assessment program (Zamora-Munõz and Alba-Tercedor 1996; Capitulo et al. 2001; Mustow, 2002; Czerniawska-Kusza, 2005). Above all, Allan (1995) and Metcalfe (1989) suggested that an accurate assessment of the rivers’ health is only possible with the use of an integrated approach for water quality assessment, taking into account the anthropogenic activities around the rivers as well as the influence of urbanization towards water quality.

In Togo, the only and first study linked to water quality assessment of whole basin rivers/streams were undertaken in 2014 and funded by the European Union (SIIeau project, 2014), and until now there is not any monitoring program of surface water. Having that in mind, this study was focused on the comparison of the reliability and suitability of the biological and water quality indices in order to assess the water quality of rivers in Togo. The objective of this study was to determine whether the available biological indices could be applied effectively out of their development ecological settings, and to identify the most reliable biological index for assessing the water quality and the most integrated water quality index for rivers ecosystem health assessment in Togo.

2 Material and Methods

Study area and sampling sites

This study was conducted in Zio River basin, whose catchment is oriented North-West; South-East with an area of 3,400 km^2. It is located between the latitude 6°5’ and 7°18’N, and the longitude

0°15’ and 1°40’E, and drained by several streams coming mainly from Togo Mountains (Figure 1). The upstream with humid tropical climate is characterized by mountain forests and low human activities. In the middle, there is a tropical climate with dry forest and Guinean savanna. At downstream, there is a tropical climate zone with savanna vegetation and many human activities. The agriculture and other human activities described previously (Tampo et al., 2015a, 2015b) are increasing from upstream to downstream. Fifty sites were sampled from downstream to upstream according to the impairment in the basin. Because of South Togo climatic anomalies and overall climate change effects, some years the two short seasons or one of them can be absent or mixed up to one of the long seasons. Therefore, four sampling campaigns were conducted according to flow regime of rivers. The first campaign was conducted in December; this period corresponds to transition between high water flow and low water flow; the second campaign was conducted from March to April, corresponding to low water flow; the third campaign was performed in July, corresponding to transition between low water flow and high water flow; and the last campaign was conducted from September to October and corresponds to high water flow. The surface water of Zio River basin is the major source of water for domestic and agricultural purposes in rural and semi-urban areas in the basin. Moreover, the main activity in the basin is agriculture (maize, cassava, bean, yams, rice, etc.). Fishing and few industrial activities such as gravel washing and sand extraction are noted (Bawa et al., 2018). Zio River basin is composed of many rivers as tributaries. Some rivers have permanent running and others have intermittent running during the year. The water samples were collected only in permanent rivers.

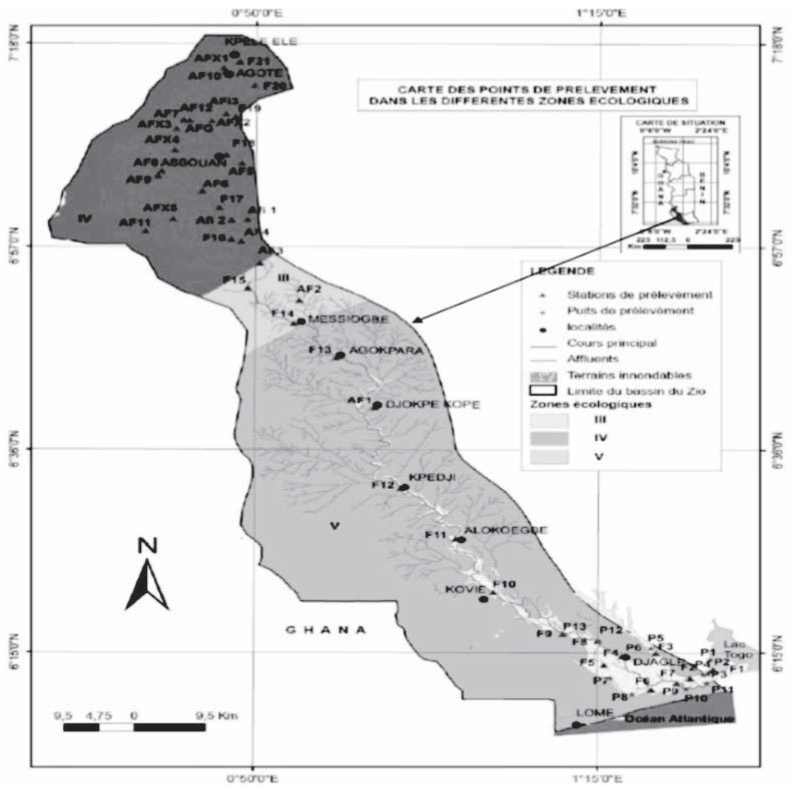

Figure 1: Study area and sampling sites localization map

Sampling and water analyses

Water samples were collected from 50 sampling sites in the basin during four campaigns for physicochemical and microbiological analyses. After the measurement of *in situ* parameters, the water samples were collected in 1.5 L polyethylene plastic bottles for physicochemical analyses. For microbiological analysis, samples were collected in borosilicate glassware of 500 mL. All samples were stored in an icebox during transport to the Laboratory and were analyzed according to the standard procedure NF EN25667-1 (AFNOR, 1997).

Sampling of macroinvertebrates

Macroinvertebrates were sampled using a dip net (circular opening: 33 cm of diameter, mesh size: 320 µm) in lentic habitats and a Surber Sampler (rectangular opening: 20 cm × 25 cm, mesh size: 320 µm) for lotic habitats. At each site, substrate samples were taken and combined to one composite sample following protocol described by AFNOR (1997) and Rodier et al. (2009). The animals were identified using taxonomic manuals and keys (Durand and Levêque, 1981; Merritt and Cummins, 1996; Tachet et al., 2010) as well as taxonomic expert support (see acknowledgements).

Data analyzes

In this study, three biological indices were selected to compare their performances in evaluation of rivers/streams water quality. One biotic index, Family Biotic Index (FBI), two metrics (number of taxa in the insects' order of *Ephemeroptera*, *Plecoptera* and *Trichoptera* (EPT), number of taxa in the insects' order of *Ephemeroptera*, *Trichoptera* and *Odonata* (ETO) and one chemical water quality index, Prati's Index of (WQI) were used. The biological indices were calculated using macroinvertebrates features (number of taxon, diversity index and abundance) of the basin. The selection of the biological indices was based on their simplicity and reliability for assessing the water quality of river as well as the ability to generate quantitative value for water quality. The chemical-based water quality index was derived from measurements of water physicochemical parameters (pH, Biological Oxygen Demand (BOD), Chemical Oxygen Demand by Permanganate (CODMn), Dissolved Oxygen (DO), Total Suspended Solids (TSS), Ammonium (NH_4), Nitrate (NO_3), Electrical Conductivity (EC), Chlorine (Cl), Iron (Fe) and Manganese (Mn). A mathematical expression was formulated to transform each of the values of pollutants into sub-indices (I_i). This transformation took into account the polluting capacity of the parameters related to a selected reference parameter. The resulting functions (sub-indices) are given according to Prati et al. (1971). The final index (WQI) was computed as the arithmetic mean of the sub-indices following formula (1):

$$\mathrm{WQI} = \frac{1}{11}\sum_{i=1}^{11} I_i \tag{1}$$

Furthermore, water quality data usually exhibit the following characteristics: non-normal distribution, presence of outliers, missing values, values below detection limits (censored), and serial dependence. It is essential to apply an appropriate statistical methodology when analyzing water quality data to draw valid conclusions and hence to provide useful advice for water management (Fu and Wang, 2012). As a result, in this study after exploratory analyses, univariate methods like descriptive statistics, and multivariate methods like Principal Component Analysis (PCA) and Factor analysis (FA) were used. These analyses provide scatter plots, which are a very useful summary of a set of bivariate data. They were used to detect the relationships between two variables, and aids the interpretation of the correlation coefficient or a regression model. All data treatment and statistical methods were done using EXCEL and STATISTICA for Windows.

3 Results and Discussions

Macroinvertebrates community

Table 1 shows an overview of the macroinvertebrates community in the Zio River basin. Number of families and total abundance are shown for each benthic macroinvertebrate order. Insects are the most abundant and diversified class recording 49 families. Gastropods are the second group in terms of diversity and abundance. Except crustaceans, about 90% of arthropods were collected at larval stage.

Table 1: Overview of macroinvertebrates community

Phylum	Order	Number of Family	Number of gender	Abundancy
Arthropods	*Hetroptera*	9	18	2,698
	Coleoptera	5	18	2,073
	Odonata	8	19	1,634
	Diptera	11	20	3,032
	Ephemeroptera	8	21	2,087
	Trichoptera	6	15	659
	Lepidoptera	1	NI	97
	Plecoptera	1	1	239
	Decapoda	3	4	925
	« Hydracarians »	1	NI	115
Mollusca	*Pulmonates/Prosobranchs*	6	11	5,224
	Eulamellibranchs	4	NI	330
Annelids	*Tubificina*	2	NI	797
	Hirudinea	1	NI	34

Spatial distribution of benthic macroinvertebrates

A Factorial Correspondence Analysis (FCA) was performed on presence-absence data of the four campaigns (Figure 2). This analysis allowed to classify sites according to distribution of taxa. According to the first axis (A1), which contributes about 46.6% of variance, sites can be divided into three groups, which are characterized by a group of taxa, respectively. Table 2 shows the characteristics of the three groups. According to this result, the first axis can be seen as translation of the “water quality” or “sites degradation gradient” going from less impacted sites to impacted ones. The least impacted sites are associated with intolerant/sensitive species, while the impacted ones are associated with tolerant species. Downstream sites with anthropogenic impacts and degraded water quality recorded mainly *Syrphidae, Hirudinae, Naididae, Tubificidae, Lymnaeidae*, and *Chironomidae*. These taxa are indicators of impaired sites or indicators of bad water quality. This result shows some agreement with Morais et al. (2004), who related that more tolerant taxa such as some *oligocheata, gastropoda* and *diptera* tended to be associated with samples taken at the impaired sites in temporary streams. According to Mary (1999) and Tampo et al. (2015), *Diptera* larval (*Chironomidae, Syrphidae*) and *Oligocheata* (*Naididae* and *Tubificidae*) are taxa, which characterize polluted biotopes receiving very high organic discharges. Upstream sites with a good water quality recorded mainly *Ephemeroptera, Trichoptera, Plecoptera* families and a lot of *Odonata* families. These taxa characterize unimpaired sites or good water quality status. Indeed, *Ephemeroptera, Trichoptera* and *Odonata* are sensitive to human disturbance (Samways and Steytler, 1996; Hornung and Rice, 2003). They reflect the diversity of aquatic organisms and are linked with the health of aquatic ecosystems (Baptista et al., 2007 and 2011). In the present study, the results show that the above-mentioned taxa can be used for bio-assessment of freshwater. According to some authors such as Arimoro and Muller (2010), *Ephemeroptera* is an order of aquatic insects commonly used in bio-assessment and biomonitoring of freshwater ecosystems all over the world. *Trichoptera* is recommended for detecting short-term impacts (Kashian and Burton, 2000). *Odonata* are relatively sensitive to pollution and can be used as a good indicator of water quality. However, there is some variation in tolerance to pollution of the taxa belonging to this group (Mereta et al., 2013). The larval *Odonata* community has been successfully used as an indicator of habitat and water quality in both lentic and lotic systems (Foote and Hornung, 2005).

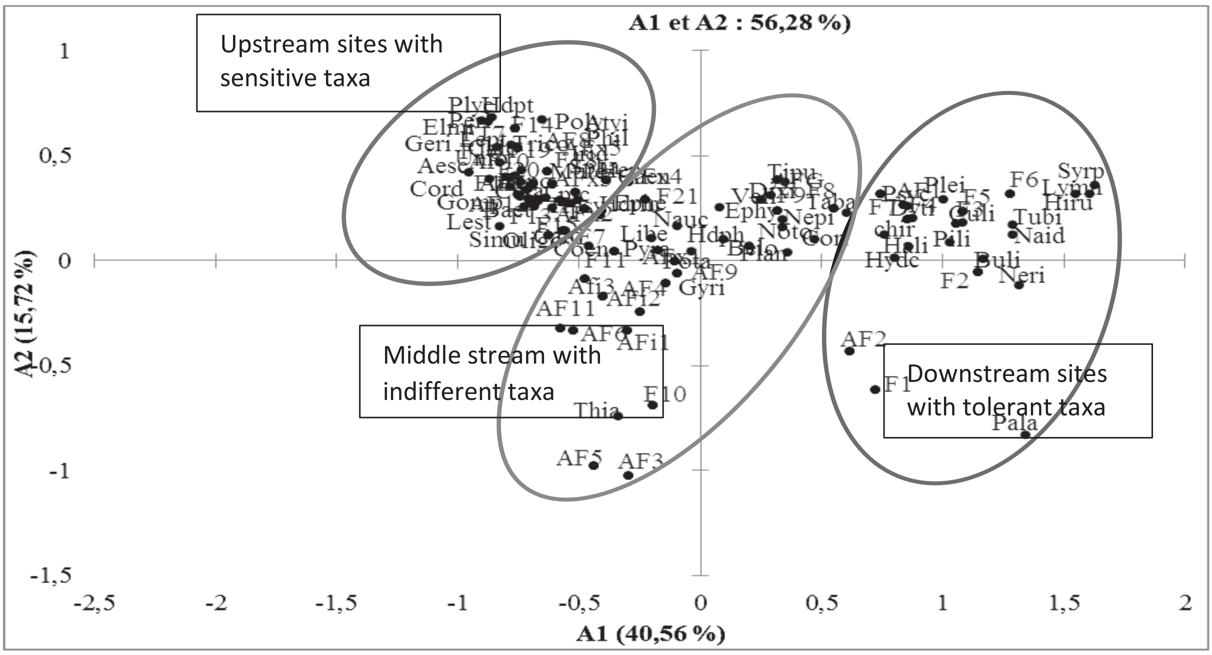

Figure 2: Distribution of macroinvertebrates in Zio River basin

Table 2: Characteristics of sites' groups

	Group 1	**Group 2**	**Group 3**
Sites	F1 to F8, AF1 and AF2	F9, F10, F11, AF3, AF4, AFi1, AFi2, AFi3, AFG, F21, AF5, AF11, AF9, AFX1 to AFX5	F12 to F20, AF10, AF12, AF8, AF6, AF7
Characteristics of sites	Downstream sites Important human impacts Degraded water quality	Middle stream sites in majority Moderate human impacts, Acceptable water Quality	Upstream sites Very few human impacts Good water quality
Indicator taxa	*Syrphidae, Hirudinae, Naididae, Tubificidae, Lymnaeidae, Chironomidae*	*Gyrinidae, Geriidae, Naucoridae, Baetidae Hydrometridae, Coenagriidae, Libellulidae*	*Ephemeroptera, Trichoptera, Plecoptera and Odonata*
Indicator taxa Sensitivity	Tolerant taxa	Moderate Tolerant taxa	Sensitive taxa

Physicochemical characteristics

The summary of main measured variables in the sites during the four campaigns is provided in Tables 3. Data analysis gives an overview of the variations in water quality during the four campaigns in Zio River basin. There are some extreme values especially on Electrical Conductivity showing a point and spot pollution.

Turbidity and Electrical Conductivity are characterized by high standard deviations indicating that the data are widely spread due to the presence of temporal and spatial variations caused likely by natural and/or anthropogenic polluting sources (Ahmed et al., 2016). The measured turbidity is characterized by low to moderate values. The highest turbidity can be caused by soil erosion of the prepared agricultural fields with loose top layer. Regarding pH values, they ranged from 6.4 to 7.8 with the mean value varying to neutral toward alkaline. The mean pH values of water samples were within the pH standards for drinking water (6.5 - 8.5) according to WHO limits.

Concerning Electrical Conductivity (EC), all its values in the basin water were below the WHO maximum guideline limit (1,500 µs/cm) except of some water samples related to mixture of Atlantic Ocean water with Lake Togo water sometimes mostly during the low water flow. In this area, EC varies from 238 to 32,200 µS/cm, showing the temporary influence of the sea water as indicated in Figure 1 (Bawa et al., 2018).

The chemical Oxygen Demand (CODMn) is a parameter used to quantify moderate organic contamination loads, easily oxidized by $KMnO_4$ (Rodier et al., 2009). CODMn shows contents between 1.9 and 13 mg/L. The high values could be linked to the leaching and transport of natural material, domestic sewage, agricultural and industrial pollutant. Biological Oxygen Demand (BOD) presents a similar trend of its variation in the basin. Dissolved Oxygen (DO) content is an essential parameter that maintains the equilibrium of aquatic ecosystems. It is commonly used to assess water quality and aquatic ecosystems' health (Sanchez et al., 2006). DO values vary from 3.4 to 14.6 mg/L and are similar to those obtained by Tampo et al. (2015b). Many values measured are high or close to 7 mg/L showing that water in Zio River basin can be qualified as good to excellent quality according to surface water standards (AFNOR, 1997; Rodier et al, 2009).

The concentrations of other dissolved ions, cations (Na^+, K^+, NH_4^+) and anions (NO_2^-, NO_3^-, SO_4^{2-}, and Cl^-) vary in the magnitude different to previous parameters, with NH_4^+ and NO_2^- being under detection limits and very low values for NO_3^- (0.5 to 2.4 mg/L). The concentration ranges of Na^+ (4.5 to 6,600 mg/L), K^+ (1.2 to 268 mg/L) and Cl^- (0.8 to 13,415 mg/L) are similar to Electrical Conductivity and exhibit similar distribution like EC, showing clearly that these parameters contribute greatly to the conductivity of Zio River basin water. Standard deviations of these parameters confirmed a temporary intrusion of sea water as mentioned above. The presence of Fecal Coliforms and mostly *E. coli* is an indicator of the bacteriological contamination of water and conditioned water use for drinking or domestic purposes (De Troyer et al., 2016). The concentrations of Fecal Coliforms and *E. coli* ranged from 28 to 850 cfu/100 mL and from 0 to 66 cfu/100 mL, respectively. These results do not satisfy the standards of WHO for drinking water and are similar to those obtained by De Troyer et al. (2016) in streams and wetlands of Ethiopia. Metallic elements' analyses show that the total iron (FeT) and Mn concentrations are very low (0.1 to 3.1 mg/L) and (0.05 to 1.2 mg/L), respectively, or under detection limits in water samples of Zio River basin.

The exploratory and summary results of water quality in Zio River basin reveal that some parameters present very low values or are under detection limits (DL). These parameters had a very slight standard deviation (SD) showing their slight variability.

Table 3: Descriptive statistics of parameters summarizing the results:

Parameters	**Mea**	**Med**	**Min**	**Max**	**25P**	**75 P**	**SD**
Turbidity (NTU)	38.46	40.7	0.3	152	4.4	59.1	35.9
pH	7.23	7.27	6.39	7.8	7.03	7.45	0.33
T (°C)	27.16	27	24	30	26	28.5	1.69
EC (µS/Cm)	2,699	186	63.3	32,200	127	322	7,537
Alkalinity (°f)	8.52	7.5	1.5	24.5	5.5	10	5.08
Hardness (°f)	32.9	6.6	2.2	430	4.8	10.8	88.9
Transparence (cm)	35.6	25	1	168	5	35	43
Sodium (mg/L)	512	17.2	3.8	6,600	8	29.6	1,521
Potassium (mg/L)	24.3	3.7	1.2	268	2.4	7.2	62.1
Chlorine (mg/L)	992	15	0.8	13,415	9	36	3,035
CODMn (mg/L)	5.31	5.2	1.9	13	4.15	6.2	2.28
BOD (mg/L)	4.8	4.1	2	12	3.7	6.4	3.4
DO (mg/L)	6.66	6.6	3.4	14.6	5.6	7.4	1.83
Total Germ (cfu/mL)	14,314	3,900	250	203,000	605	10,700	40,246
Total Iron (mg/L)	1.13	1	0.1	3.1	0.7	1.4	0.62

Nitrates (mg/L)	1.75	1.3	0.5	15	0.5	1.5	2.83
Sulfates (mg/L)	16.4	1	1	2.6	1	13.25	5.49
Manganese (mg/L)	0.4	0.1	0.05	1.2	0.08	1	0.5
Total Col. (cfu/100 mL)	554	160	2	9,000	40	260	1,776
Faecal Col. (cfu/100 mL)	84.1	28	0	850	6	50	178
E. coli (cfu/100 mL)	7.8	1	0	66	0	8	16.8
WQI	5.8	5.1	0.94	12.7	2.6	8.53	2.3

Mea: Mean value, Med: Median value, Min: Minimum value, Max: Maximum value, 25P: 25 percentile value, 75P: Percentile value, SD: Standard Deviation value

Physicochemical parameters' distribution

After exploratory analyses, only 14 parameters in 42 sites were used for PCA analyses. The first axis A1 (70.8% of total variance) translates gradient of disturbance indicated by physicochemical features in Zio River basin (Tampo et al., 2015). According to PCA1, sites can be divided into three groups linked to physicochemical quality of water. Table 4 shows the group of sites and their pattern in the basin. The examination of these results in comparison to Figure 2 and Table 3 seem to show that physicochemical and biological features can indicate or translate the same information or complementary information about the health of Zio River basin ecosystem.

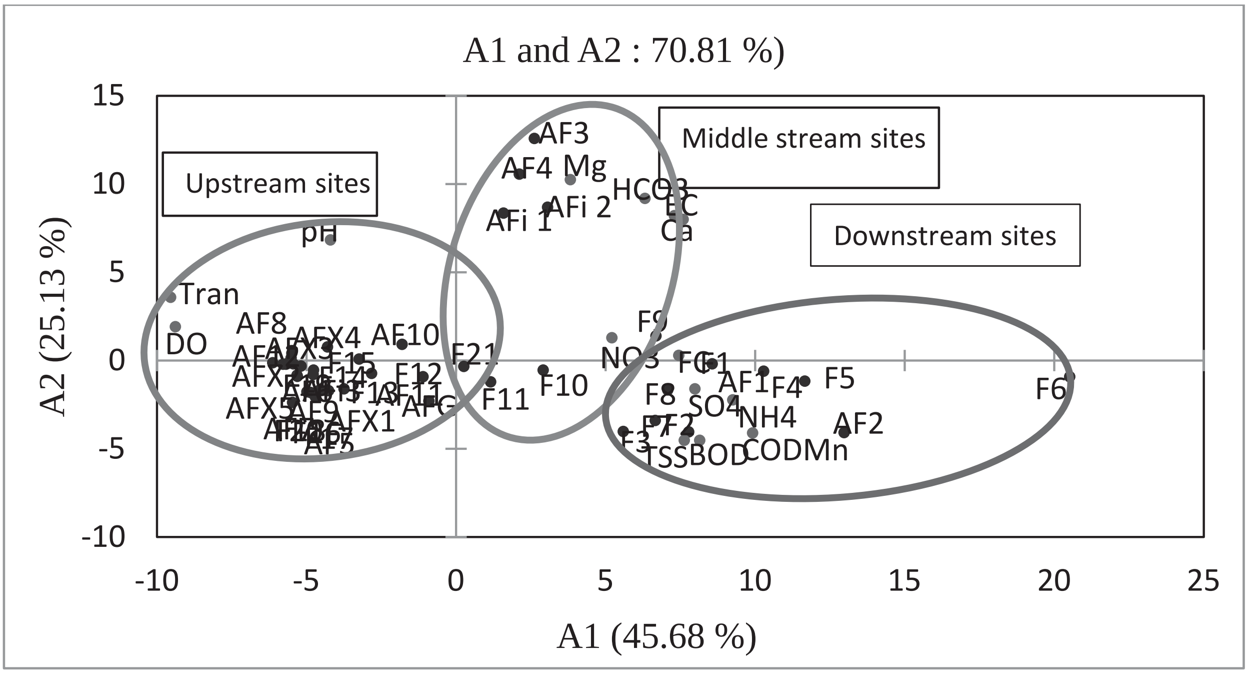

Figure 3: Distribution of physicochemical parameters in Zio River basin

Table 4: characteristics of groups

	Group 1	Group 2	Group 3
Sites	F1 to F9, AF1 and AF2	F9, F10, F11, AF3, AF4, AFi1, AFi2, F21, AF5, AF11	F12 to F20, AF10, AF12, AF11, AF9, AF8, AF6, AF7, AFG, AFX1 to AFX5
Characteristics of sites	Downstream sites Important human impacts Degraded water quality	Mean Course sites and upstream sites Moderate human impacts, Acceptable water Quality	Upstream sites Very few human impacts Good water quality
Indicator parameters	NH_4, CODMn, BOD, Col, TSS, SO_4, K, NO_3	EC, HCO_3, Mg, Ca, NO_3	DO, Transparency, pH

Relationship between physicochemical parameters and biological indices

Table 5 shows values of Spearman correlation between biological indices and water quality index. There is significant positive correlation ($r > 0.5$; $p < 0.05$) between WQI and Family Biotic Index (FBI). This WQI presents a significant negative correlation ($r < -0.5$, $p < 0.05$) with ETO and EPT. The linear regression (Figure 4A, 4B and 4C) shows the trends of evolution of WQI according to biological quality expressed by ETO, EPT and FBI. Examination of Figures 4 combined with Table 6 translates that biological indices can contribute at least 50% of WQI variation. These results reveal that FBI and WQI can be considered as pollution indicator, because their values increase when water pollution increase. ETO and EPT can be considered as water quality indicators because their value increase when water quality increase. These results confirm previous studies on sensitivity of biological indices according to water quality or ecosystem health variation (Tampo et al., 2015).

Table 5: Correlation between WQI and biological indices (Spearman r significant at $P < 0.05$)

	EPT	ETO	IBGN	FBI	Total Taxa	WQI
EPT	1					
ETO	**0.85**	1				
IBGN	**0.71**	**0.75**	1			
FBI	**-0.57**	**-0.53**	-0.41	1		
Total Taxa	**0.67**	**0.69**	**0.89**	-0.35	1	
WQI	**-0.77**	**-0.74**	**-0.63**	**0.61**	-0.45	1

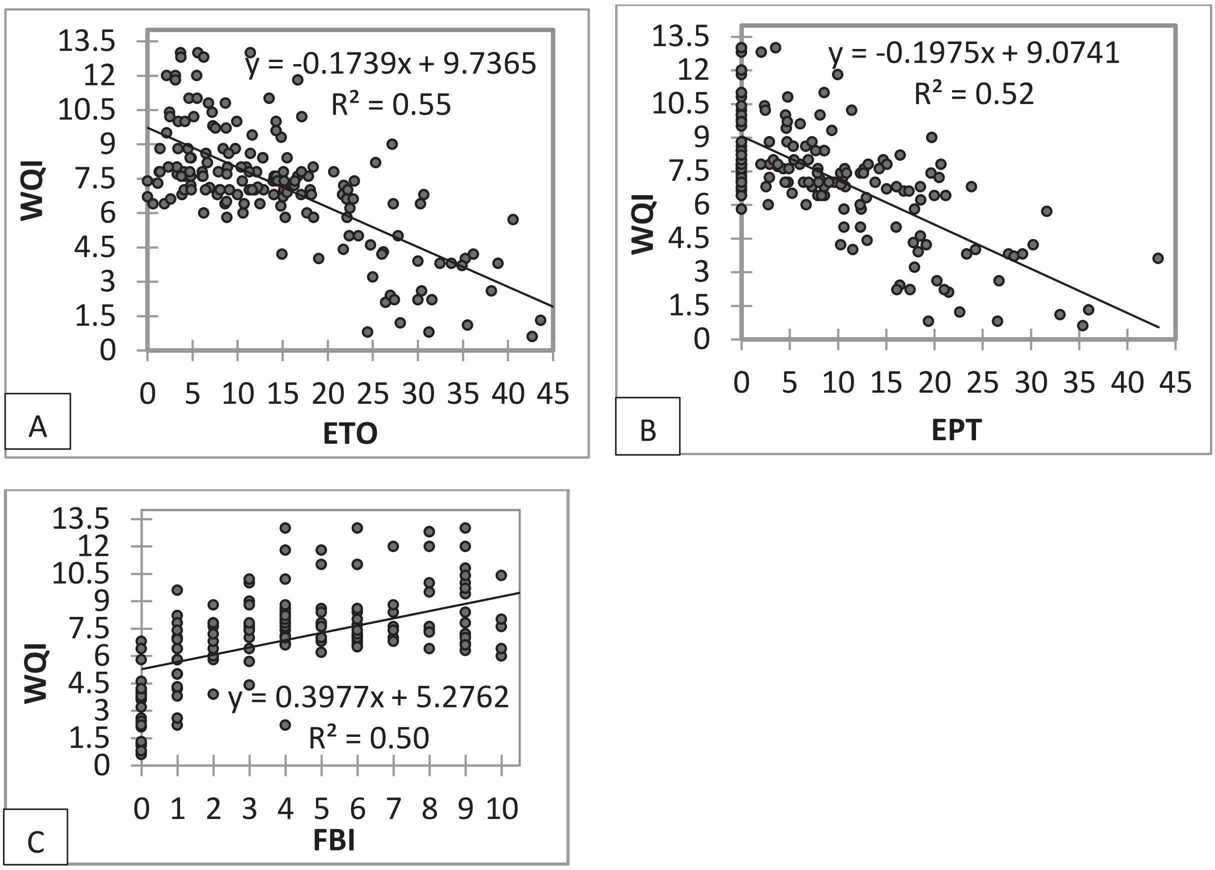

Figure 4: Evolution trends of WQI in relation with Biological indices simple linear regression (A) WQI # ETO; (B) WQI#EPT; (C) WQI#FBI

4 Conclusion and Perspectives

This study revealed that different sections of the rivers were inhabited by some taxa, whereby a majority of the intolerant taxa were more diverse in the upstream sections, meanwhile the middle to downstream sections of rivers/streams were dominated by tolerant taxa. It was found that the biological indices that were used in this study were suitable to evaluate the water quality of rivers/streams with good sensitivity. Physicochemical parameters and biological indices confirmed the presence of three groups of sites, which represent downstream sections, middle stream sections and upstream sections, respectively. Water Quality index formulated using physicochemical features is significantly correlated with biological features and indices. The linear regression showed that biological indices (FBI, ETO, EPT, IBGN) can account for more than 50% of the variation in WQI. This study showed that biological indices are a complementary assessment method of rivers water quality and can be used as most suitable and reliable indices along with WQI in order to obtain the complete spectrum of water quality during the rivers health assessment.

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ENDOCRINE DISRUPTORS: EFFICIENCY OF REMOVAL BY DIFFERENT TREATMENT SYSTEMS AND CONCENTRATIONS FOUND IN WASTEWATER, SURFACE AND GROUND WATERS AROUND THE WORLD

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Keywords: constructed wetlands; macrophytes; ethynilestradiol; bisphenol A; levonorgestrel.

Abstract

Endocrine disruptors are increasingly found in water bodies and in the environment, which may come from industrial, pharmaceutical, or cosmetic origin. Among these substances, one can highlight the drugs, hormones, triclosan (bactericide used in cosmetics), pesticides, and insecticides, among others. These substances may interfere and cause adverse effects on the endocrine system of humans and animals, and can cause feminization of the male fish, early menarche in girls as well as thyroid problems. Conventional water and wastewater treatment plants are scarcely able to remove completely the present endocrine interferers, and some of the techniques capable of eliminating such compounds as advanced oxidative processes and reverse osmosis, for example, are technologies having high implantation and maintenance costs. Constructed wetlands are natural wastewater and surface water treatment systems that have low implantation and maintenance costs, and have been cited as an efficient method for the removal of endocrine disruptors. In this context, the present work aimed to carry out an extensive bibliographical research on the state of the art of the concentrations of endocrine disruptors found in wastewater, surface and groundwater around the world as well as the efficiency of removal of these compounds by different treatment systems. It was concluded that constructed wetlands are systems that have high efficiency of treatment of endocrine disruptors in wastewater, which can be used alone in rural and isolated communities or as tertiary treatment in conventional wastewater and water treatment plants.

1 Introduction

Endocrine disruptors comprise a broad spectrum of natural and synthetic substances as well as emerging compounds of an exogenous nature (Wee & Aris, 2017). It is difficult to determine exactly, which substances are endocrine disrupters, because although pharmaceuticals and personal hygiene are a well-known and well-defined group, there are several other chemicals and compounds that may interfere with the endocrine functioning of humans and animals, but have not yet been tested, or information available on adverse effects are incomplete or controversial

(Kim et al., 2007). These substances act by binding to estrogen receptors blocking or mimicking the natural hormonal function of organisms (Jugan et al., 2009).

Endocrine disruptors can be transported by water or air, and are commonly found in soils and sediments (Xiong et al., 2018). These compounds accumulate in different types of organisms through biomagnification in the food chain, resulting from their persistent and hydrophobic characteristics (Xiong et al., 2018). In addition, in contaminated waters with estrogens, oocytes of female fish have been found in the gonads of male fish, a sign of feminization (Jugan et al., 2009).

Contamination by endocrine disruptors can be done by point sources, such as the discharge of fresh or treated wastewater, since wastewater treatment plants are not able to completely remove these substances, by diffuse sources as application of pesticides and herbicides in crops, or by the disposal of sludge and wastewater in soil (Kookana et al., 2007). Other sources of pollution by endocrine disruptors may occur during the manufacture, use and application of these products in the industry as well as during incorrect discharge of industrial effluents containing these chemicals (Wee & Aris, 2017).

In this context, the present work aimed to carry out a literature review about the state-of-the-art of the concentrations of endocrine disruptors - mainly of the hormones ethinylestradiol (EE2) and levonorgestrel (LNG), and the chemical compound bisphenol A (BPA) - in wastewater, surface and groundwater around the world as well as the efficiency of removal of these compounds by different treatment systems.

2 Material and Methods

A bibliographic research was conducted in articles and theses (national and international) to find the rates of removal of endocrine disruptors (especially BPA, EE2 and LNG) obtained from conventional water (WTP) and wastewater treatment plants (WWTP), as well as concentrations of these endocrine disruptors in wastewater, groundwater and surface water around the world.

3 Results and Discussion

Removal of endocrine disruptors from wastewater by wetlands

Because slightly hydrophobic pesticides have chemical properties similar to estrogenic hormones, and these pesticides are efficiently removed in wetlands, this provides information for the possible mechanisms of removal of these hormones in these systems (Gray & Sedlak, 2005). Therefore, according to the authors, estrogen hormones could be similarly mitigated in wetlands.

In 2010, Hijosa-Valsero et al. compared wastewater treatment by various wetland configurations with different macrophytes simultaneously to the treatment of the same wastewater in a conventional WWTP. The authors reported that the WWTP was unable to remove diclofenac, carbamazepine, galaxolide and tonalide, while wetlands removed all these substances in greater or lesser amounts. This shows that wetlands were more efficient for the treatment of endocrine disruptors than conventional treatment in WWTP.

He et al. (2018a) used surface flow and subsurface wetlands cultivated with *Phragmites australis* to perform tertiary sewage treatment from WWTP. The authors analyzed ketoprofen, diclofenac, ibuprofen, naproxen, erythromycin, lincomycin, sulfamethoxazole, propranolol, metoprolol, clofibric acid, carbamazepine, caffeine, bisphenol A, estrone, 17β-estradiol, ethinylestradiol, and estriol. The authors did not detect EE2 at the wetlands inlet, and BPA removals ranged from -29.2 ± 116.3% to -88.3 ± 78.2% (accumulation of BPA at the system exit).

Herrera-Melían et al. (2017) studied the presence and removal of 14 types of hormones in wastewater from a university campus by horizontal and vertical flow wetlands, some cultivated with *Cyperus* sp. and others with *Phragmites* sp., containing volcanic residue, palm mulch residue, or gravel as carrier medium, and a capacity ranging from 200 to 265 L. Of the 14 hormones studied, the authors detected 9 in the wastewater: 17β-estradiol, estriol, estrone, boldenone, testosterone, norgestrel, progesterone, norethisterone, and prednisone. Removal rates ranged from 30 to 100%.

Dai et al. (2017) used wetlands with 204 m^2 of vertical flow area coupled to horizontal flow wetlands containing gravel as a support medium and cultivated with *Canna glauca*, *Thalia dealbata*, *Canna indica*, *Typha angustifolia*, *Cyperus alternifolius*, *Arundo donax*, *Acorus tatarinowii*, and *Desmodium styracifolium* to perform the tertiary treatment of sewage from a WWTP. The authors worked with HRT ranging from 6 to 24 hours, and investigated the presence and removal of E1, E2, EE2, BPA, triclosan, 4-tert-octylphenol, and 4-nonylphenol in the sewage by the wetlands. Dai et al. (2017) did not find EE2 in this wastewater, but obtained 45 ± 15% of BPA removal.

Toro-Vélez et al. (2016) performed the secondary treatment of municipal wastewater with horizontal subsurface flow wetlands on a pilot scale, one cultivated with *Heliconia psitacorum*, another with *Phragmites australis,* and another with no plants as control. The authors verified the removal of nonylphenol and bisphenol A ranging from 62.2 to 73.3% of BPA removal. Papaevangelou et al. (2016) studied the removal of bisphenol A, nonylphenol, nonylphenol monoethoxylate, nonylphenol diethoxylate, and triclosan in municipal wastewater from a university campus by wetlands of horizontal subsurface flow and vertical flow, grown or not with *Phragmites australi*s or *Typha latifolia*. The authors reported that the removal of BPA from wetlands ranged from 45.6 to 99.0%.

Ávila et al. (2015) treated municipal sewage through a vertical subsurface flow wetland and a horizontal subsurface flow cultivated with *Phragmites australis*, and a 240 m^2 free-water wetland with several types of plants - all in series. The authors verified the removal of ibuprofen, diclofenac, paracetamol, tonalide, oxybenzone, triclosan, bisphenol A and ethinylestradiol, achieving removals greater than 99% for BPA (if the whole series is taken into account). The concentrations of the hormone EE2 in the samples were below the limit of detection, according to Ávila et al. (2015).

Vymazal et al. (2015) performed secondary treatment of municipal wastewater of about 200 inhabitants by three constructed wetlands of subsurface flow cultivated with *Phragmites australis* and/or *Phalaris arundinacea*, using gravel as support medium. The authors evaluated the removal of estrogens (estrone, estriol, 17β-estradiol, and 17α-ethinylestradiol), testosterone and progesterone. EE2 removals ranged from accumulation at the output of one of the wetlands (higher concentration at the output than at the entrance) to 81.4%.

Carranza-Diaz et al. (2014) evaluated the removal of bisphenol A, caffeine, carbamazepine, diclofenac, galaxolide, ibuprofen, ketoprofen, naproxen, 4-nonylphenol, tonalide, and triclosan, treating municipal sewage by two horizontal subsurface flow wetlands containing gravel as a support medium, one without plant and another cultivated with *Phragmites australis*. The mean BPA removals described by the authors ranged from 2 ± 8% to 5 ± 15%. Li et al. (2014) evaluated the removal of levonorgestrel in tanks containing ultra-pure water fortified with the hormone, one without macrophytes, another with *Eichhornia crassipes,* and the third one containing *Cyperus alternifolius*. The removal obtained by the authors ranged from 78.9% ± 2.5% to 79.8% ± 3.1%.

Ávila et al. (2014a) investigated the retention of EE2 added to municipal wastewater by a hybrid system of wetlands containing two vertical flow (VF), one horizontal flow (FH), and one surface flow (FS) cultivated with *Phragmites australis* on a pilot scale. The authors studied 3 different hydraulic loading rates (HLR), performing continuous injection of EE2 and other endocrine disruptors. The authors observed that the higher the HLR, the lower the retention rates, which were between 20 and 80%.

Chen et al. (2014) evaluated the removal of E1, E2 and E3 in 675 m^2 constructed wetland treating river water contaminated with domestic and rural wastewater (animals). The authors observed that in HRT of 27.5 hours, there was no degradation of estrogens, with HRT of 45.9 hours the degradation rates were 0 - 46.2%, and with HRT of 137.5 hours the degradation rates were of 40-84.3%.

Four vertical flow wetlands with surface area of 6.2 m^2 each were studied for treatment of EE2 and other endocrine disruptors by Ávila et al. (2014b) treating municipal wastewater. Two systems used gravel as support medium, and two others used sand. The collection was done by daily composite samples, but the authors did not identify EE2 in the samples, because it was below the operational detection limit (ODL) of 90 ng/L. Cai et al. (2012) evaluated the capacity of removal of estrogenic and androgenic hormones in wastewater from a dairy farm through wetlands, and their monthly analyses showed a mean removal of 95.2% estrogens and 92.1 % of androgens.

Kumar et al. (2011) studied the natural attenuation of estriol and 17α-ethinylestradiol hormones in three different tanks, one with floating macrophytes (Tank 1), one with integrated emergent and submerged macrophytes (Tank 2) and another one with submerged macrophytes rooted together with microalgae (Tank 3). According to the author, Tank 1 was more efficient in the removal of estrogens (E3 - 61.7%, EE2 - 69.1%) when compared with Tank 2 (E3 - 16.6%, EE2 - 18.5%) and Tank 3, with removals of 15.2% for E3 and 7.7% for EE2.

The efficiency of three wetlands cultivated with *Phragmites australis* of three different depths, vertical flow and sand as a medium to polish a municipal effluent after conventional and tertiary treatment aiming at the removal of estrone (E1), 17-β-estradiol and 17-α -ethinylestradiol was evaluated by Song et al. (2009). Better removals of the hormones mentioned above were found in the extremely superficial wetlands (termed by the authors as ES), which had 7.5 cm depth and HRT of 3.1 hours. The authors reported that the operation of wetland ES under unsaturated conditions, high root density of macrophytes, and maintenance of wetland aerobic conditions were the main conditions for a good estrogen removal - considering that only 12% of the estrogen removal was due to their adsorption on wetland sand (Song et al., 2009).

Shappell et al. (2007) measured the efficacy of a treatment system through anaerobic lagoons along with wetlands cultivated with *Typha Latifolia L*. from an effluent with low hormonal activity. The authors reported a reduction of estrogenic activity by 83-93% after treatment. Gray & Sedlak (2005) investigated the removal of estradiol and ethinylestradiol in upstream treated sewage receiving water from a wetland cultivated with two species of *Typha* and three species of *Scirpus*. The authors reported maximum removal of 41% of EE2.

Conventional treatments for the removal of endocrine disruptors in wastewater and surface waters
He et al. (2018a) reported having found concentrations ranging from 0.9 to 3.7 µg/L of BPA in effluents from sewage treatment plants after secondary treatment in the Netherlands. The authors reported that some of the stations treated only domestic sewage, and others domestic sewage and industrial effluents.

Tran & Gin (2017) investigated the removal of 25 different endocrine disruptors (including BPA) at a municipal WWTP in Southeast Asia, and reported finding 19 of the compounds studied in the raw wastewater with concentrations ranging from 5.3 to 6.9 µg/L. In the activated sludge effluent, the concentrations ranged from 0.6 to 1.0 µg/L, and in the membrane bioreactor the concentrations were between 0.1 and 0.7 µg/L. The BPA removals in the activated sludge system varied from 81.9 to 90.6%, and in the membrane bioreactor from 88.3 to 97.9%.

King et al. (2016) investigated concentrations of ethinylestradiol and levonorgestrel in treated wastewater and surface water samples in Australia. They found EE2 concentrations up to 2 ng/L in the treated effluent and between 0.1 and 0.2 ng/L in surface water, which are higher than the PNEC (predicted no-effect concentration) of EE2 (0.1 ng/L).

Due to the scarcity of levonorgestrel data in the literature, King et al. (2016) calculated a provisional PNEC of 0.1 ng/L for LNG, which was lower than the predicted concentrations of LNG in the effluent (calculated by the consumption of drugs containing levonorgestrel) from 0.2 to 0.6 ng/L. The concentrations of the actual samples obtained by the authors were below the detection limit of the method for LNG.

Pessoa et al. (2014) verified that a conventional WWTP in Brazil (Ceará) was able to remove a mean of 75.8% of ethinylestradiol, and Atkinson et al. (2012) verified in a conventional WWTP removals of -119% (increase of 119% in the output of the system in relation to the entrance) to 100% for ethinylestradiol. Quantifying estrogens in the influent and effluent of a conventional WWTP (activated sludge, anaerobic reactor, and stabilization pond) in Curitiba/PR, Froehner et al. (2011) reported that the removal of ethinylestradiol was between 44.1 and 99.1%, and BPA was 99.9 to 100%.

Grover et al. (2011a) observed a 43% removal for ethinylestradiol in a WWTP designed for removal of endocrine disruptors with granular activated carbon filter (GAC). Grover et al. (2011b) monitored concentrations of ethinylestradiol and other hormones at various points in a river, before and after the water treatment plant located in that river. The authors were not allowed to monitor the WTP influent, but when comparing the concentrations present in the river before and after WTP, they found a reduction of more than 67% for ethinylestradiol. The collections were carried out 3.5 km before WTP and 10 m, 1.7 km and 10 km after WTP, and the authors used an equation to discard the dilution effect of EE2 concentrations in the river.

Zhang & Zhou (2008) studied the removal of 17-β-estradiol and estrone hormones in a WWTP in United Kingdom, from 78 to 92% removal for E1 and from 69 to 90% for E2. The samples were collected before and after sedimentation and biological filtering steps. Since wetlands have both types of processes, this is an indication of a possible estrogen removal efficiency of this type of systems.

In 2010, Gadd et al. investigated the reduction of hormones from milk residue, and observed a 50 to 100% removal after aerobic and anaerobic treatment. The authors reported that because the main mechanisms of removal of these compounds are oxidation and photodegradation, it is possible that the removal in exclusively anaerobic treatment is limited. Therefore, this type of system can be efficient in the removal of these estrogens, because wetlands have aerobic zones and anaerobic zones.

Diniz et al. (2010) observed removals greater than 95% of BPA in a conventional WWTP in Portugal, with mean concentrations of 1.55 μg/L in the raw wastewater, 0.15 μg/L after the sandbox, 0.31 μg/L after the filtration step, and concentrations lower than the detection limit after UV disinfection. Vulliet et al. (2008) found the progestogen levonorgestrel in concentrations ranging from 5.3 to 7.0 ng/L in surface waters receiving domestic treated sewage, and in surface waters close to the rural area.

4 Conclusions

This literature survey allows to conclude that constructed wetlands are systems that have high efficiency of treatment of endocrine disruptors in wastewater, which can be used alone in rural and isolated communities or as tertiary treatment in conventional water and wastewater treatment plants.

5 Acknowledgement

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MICROCONTAMINANTS AND TOXICITY REMOVAL IN SANITARY SEWAGE TREATED BY CONSTRUCTED WETLANDS

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Abstract

The present study analyzed the performance of two different constructed wetlands (CW) systems for sanitary sewage treatment, with the main objective of evaluating the ability of both systems to remove emerging microcontaminants (EMCs) and to reduce the acute toxicity of the sewage. In this way, four categories of MCEs were analyzed: (i) plasticizers and surfactants - Bis(2-ethylhexyl) phthalate, Diethyl phthalate, Bisphenol A and 4-n-nonylphenol; (ii) natural and synthetic hormones - 17α-Ethinylestradiol, Estrone, 17β-Estradiol and Estriol; (iii) drugs - Diclofenac, Acetaminophen, Gemfibrozil, Sulfamethoxazole and Caffeine, and (iv) personal care products - 4-n-nonylphenol and triclosan. The evaluation of CWs to reduce the acute toxicity of the sewage was carried out with the bacteria *Vibrio fischeri* exposure test. Two treatment lines were evaluated, Treatment Line I (TL I) composed of a hybrid vertical-horizontal CW (P5), and Treatment Line II (TL II) with aerated free-flow CW with a settling unit (P3), followed by vertical subsurface flow CW (P4). From the 14 EMCs analyzed, 11 were detected in the raw sewage (P1) and the following average removal efficiencies for TL I were obtained: DEF=67.9%; ACE=85.0%; CAF=92.2%; SUL=80.4% and DIC=68.2. For TL II was obtained: DEF= 89.1%; ACE=89.3%; CAF=98.9%, SUL=62.1% and DIC= 78.4. The mean toxicity reducing efficiency in the *V. fischeri* assays in the assessment of those CW were 71.1% for TL I and 90.5% for TL II.

1 Introduction

The discharge of treated effluents from wastewater treatment plants (WWTPs) is a major pathway for the introduction of pollutants to aquatic ecosystems. Among these substances are emerging microcontaminants (EMCs), whose class of substances is derived from the use of drugs, personal hygiene products, natural and synthetic hormones, industrial by-products and illicit drugs (Richardson & Ternes, 2005). Actually, more than 200 EMCc have been identified in several environmental matrices in concentration ranging from ng/L to μg/L only in the UK (Petrie et al., 2015).

In addition to adverse effects at low concentrations, the occurrence of these substances is of concern because they are present in complex mixtures in the environment, which may lead to synergistic effects on exposed organisms (Bila & Dezotti, 2007). The detection of these compounds in the various environmental matrices and their potentially dangerous effects encourage the need for monitoring studies that cover their occurrence, removal processes and studies of adverse effects on humans and aquatic organisms (WHO, 2012).

In Brazil, several studies have reported the presence of EMCs in effluent of WWTPs, surface water and even tap water (Quadra et al., 2017). However, in decentralized treatment systems that aim at treatment near the source, little has been reported. It is, therefore, important to broaden knowledge in this direction so as to promote access to basic sanitation to that of underserved populations with appropriate and robust technologies, which can minimize sources of chemical and microbiological pollution to the environment (Libralato et al., 2012).

In this sense, constructed wetlands (CWs) have gained space as a viable alternative to decentralized treatment especially in emerging countries such as Brazil. The concept of CWs encompasses designed systems that seek to mimic processes that occur naturally in wetlands, such as the natural wetlands. These systems include the use of vegetation, substrate, microorganisms and water, being permeated by different treatment processes through physical, chemical and microbiological mechanisms that act in the removal of specific contaminants improving the final quality of treated water. Constructed wetlands appear as a cost effective treatment, since they can remove a broad range of contaminants by applying a combination of physical, chemical and biological process, and at the same time presenting low cost.. These systems are particularly interesting to treat wastewater from small and rural communities that are isolated from the main municipality's sewage systems, because they can operate with low energy consumption and do not need highly qualified operators (Machado et al., 2017).

Considering the classification as priority substances for monitoring and the scarcity of studies in developing countries, it is necessary to enhance integrated studies to quantify EMCs and to analyze bioassays as a way of measuring possible ecological impacts (Petrie et al., 2015). In this approach, the chemical characterization of treated effluent as well the use of ecotoxicological essays aiming to evaluate adverse effects of the EMC mixture on organisms associated in aquatic ecosystems are indicated.

Given the above, the present study evaluated the removal of EMCs in sanitary sewage treated by CWs. For this purpose, the following EMCs of different classes were determined and quantified: diethyhexylphthalate, diethylphthalate, bisphenol A as substances present in plastic compounds; 17α-ethynylestradiol, estrone, 17β-estradiol, estriol as natural and synthetic hormones; diclofenac, acetaminophen, genfibrozil and sulfamethoxazole as drugs, 4-n-nonylphenol and triclosan in personal care products, and caffeine. The MCEs chosen for the study were selected considering their occurrence in surface waters and wastewater, and their public consumption according to studies published in Brazil. In order to evaluate the reduction of possible ecotoxicological effects through CWs treatments, an exposure test with the fluorescent bacterium *Vibrio fischeri* was considered. This study aims to contribute to the understanding of the reduction of sources of pollution to aquatic ecosystems and mitigation of ecotoxicological effects of wastewater.

2 Material and Methods

2.1 Constructed wetlands treatment systems (CWs)

Two pilot scale treatment lines were used in this study aiming at the treatment of sanitary sewage. The sanitary sewage treated in this experiment comes from a residential complex and the central restaurant, both located in the Campus of University of São Paulo, Brazil. The preliminary treatment of both treatment lines consists of a railing system followed by a sandbox (Figure 1). After preliminary treatment, the sewage is transported by gravity to a mixing tank and then pumped to the septic tank (primary treatment), where it is then distributed as influent of the two CWs treatment systems, namely:

(1) Treatment Line I (TL I) consisting of a hybrid CW, equipped with a first chamber, classified as a sub-surface vertical flow constructed wetland (CW SSV). The second chamber is fed by gravity with effluent from the first one and is classified as sub-surface horizontal flow constructed wetland (WC SSH);

(2) Treatment Line II (TL II) consisting of three treatment units: (2.1) surface free-flow constructed wetland with forced aeration (CW SF-A); (2.2) settling unit (SU), which receives the effluent from unit 2.1; (2.3) sub-surface saturated vertical flow constructed wetland (CW SSV-S), which receives the effluent from unit 2.2.

Figure 1: Treatment lines composed of hybrid constructed wetlands. Railing system (arrow left), followed by a sand box (arrow right). (1) Treatment Line I, composed of a hybrid vertical-horizontal CW; (2) surface free-flow CW with forced aeration; (3) settling unit; (4) sub-surface saturated vertical flow constructed wetland

The TL I received flow rate of 0.8 m^3/day, equivalent to the volume of sewage per capita generated by high-standard housing with 5 inhabitants, where the contribution of wastewater is 160 L/person x day. The flow rate of TL II was 1.5 m^3/day. This flow was applied in order to evaluate the removal efficiency of the system considering an application of overload. In this work, the emergent macrophyte selected for cultivation was *Vetiveria zizanioides*, popularly known as Vetiver grass, for TL I. For TL II, the emergent macrophyte *Cyperus spp*. was grown in the free-flow unit, and *Canna x generalis* cultured in the sub-surface flow module.

2.2 Sampling

Considering the variability in the composition and concentration of the evaluated EMCs reported in the literature, the sampling considered in this study aimed at a continuous monitoring during a nine months period between March and November of 2016. In order to assess the removal efficiency of the different units applied for the treatment of EMCs, thereby considering the multiple mechanisms of substance removal of in CWs, reported by Ávila et al. (2014), the following sample collection points were selected: sewage mixture tank (P1); septic tank (P2); effluent of free-flow CW unit (P3); effluent of sub-surface saturated vertical flow CW (P4); and effluent of vertical-horizontal hybrid CW (P5) (Figure 2).

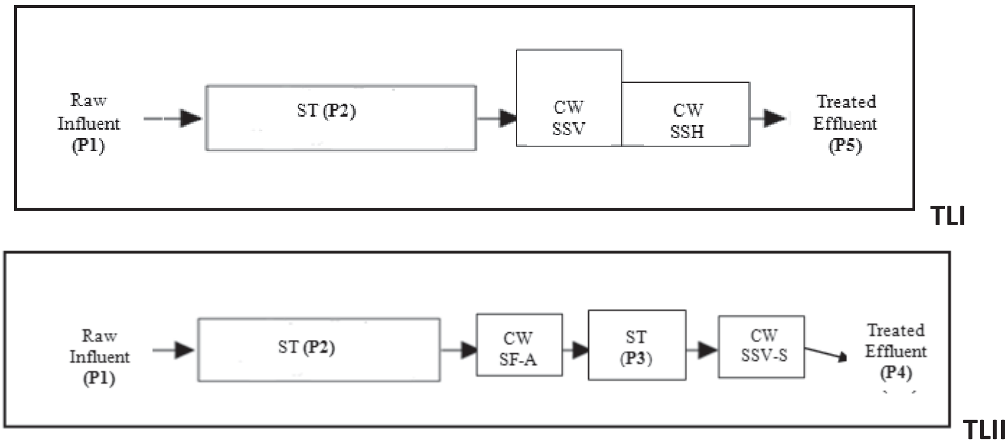


Figure 2: Treatment lines and sampling stations

2.3 Sample preparation and solid phase extraction (SPE)

Samples collected in 1 L glass bottles were submitted to two vacuum filtration processes: (1) 6.5 µm cellulose-fiber filter (Nalgon, BR) and then 0.7 µm glass-fiber filter (Whatman, UK) to remove suspended solids prior to SPE (solid phase extraction). SPE was adapted from the method No. 1.694 (US EPA, 2007). Cartridges Strata X were used for compounds' concentration (6 mL, 500 mg, modified divinylbenzenepyrrolidone), from Phenomenex, USA. Techniques of SPE extraction and elution were carried out manually on a vacuum manifold from Phenomenex at a liquid constant flow rate of 10 mL/min.

2.4 Chromatographic techniques

All target compounds were analyzed by ultra-performance liquid chromatograph/mass spectrometry (UPLC-MS/MS). The liquid chromatograph used was from Shimadzu, consisting of the modules automatic sampler (Sil-20A XR), binary pressurization pumps (LC-20AD XR), oven (CTO20A), and UV-Vis detector with diode array (SPD-M20A). The mass spectrometer used was the Shimadzu model 8030, consisting of a triple-quadrupole electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI).

2.5 Ecotoxicological Essay

Analyses were carried out with the luminescent bacterium *Vibrio fischeri*. The criteria for the selection of this aquatic organism took into account its sensitivity to various chemical agents, possibility of cultivation and maintenance in the laboratory, and wide geographical distribution. As a consolidated and standardized test for ecotoxicological analyses in wastewater in many countries, it was possible to compare the studies with literature outcomes.

2.5.1 Acute toxicity test with Vibrio fischeri

All samples collected at points P1, P4 and P5 were analyzed according to ABNT Standard NBR 15411-3 / 12 for acute toxicity with *V. fischeri* in lyophilized form (Silva et al., 2016). The bacterial assay was performed with the system known commercially as Microtox® (Microbics mod. 500). The test response is expressed by EC50, calculated from the reduction of the amount of light emitted by the test microorganism after exposure to the dilutions over a period of 15 min under standard conditions. The EC50 can be transformed into toxic unit TU from the equation

$$TU = \frac{100}{EC50} \tag{1}$$

3 Results and Discussion

3.1 Occurrence and quantification of EMCs in raw and treated wastewater samples

Between March and November 2016, 11 campaigns were carried out, in total 44 samples collected from raw sewage and effluent of the two CWs treatment systems were considered in this study. The number of samples collected in each unit of treatment is following: P1 (n = 11); P2 (n = 6); P3 (n = 6); P4 (n = 11) and P5 (n = 10).

The evaluation of the occurrence of microcontaminants was conducted for the 44 samples analyzed in this study. Figure 3 shows the frequency of EMCs detected in this study. Considering the 44 analyzed samples, the antipyretic acetaminophen and the plasticizer diethyl phthalate were the most frequent substances, being detected in all samples analyzed. The stimulant drug caffeine, the antibiotic sulfamethoxazole and the anti-inflammatory diclofenac showed a high frequency of detection (95.4%, 97.7%, 93.2%, respectively). The high frequency of EMCs detection in the samples might be related to the high production and consumption rates of these compounds in Brazil with emphasis on the southeast region. Brazil is the ninth largest producer of medicines in the world, with an estimated per capita consumption of 16 boxes per year. In addition, high excretion rates are reported for drugs, about 70% by the urinary tract and only 30% by feces (Moffat et al., 2004).

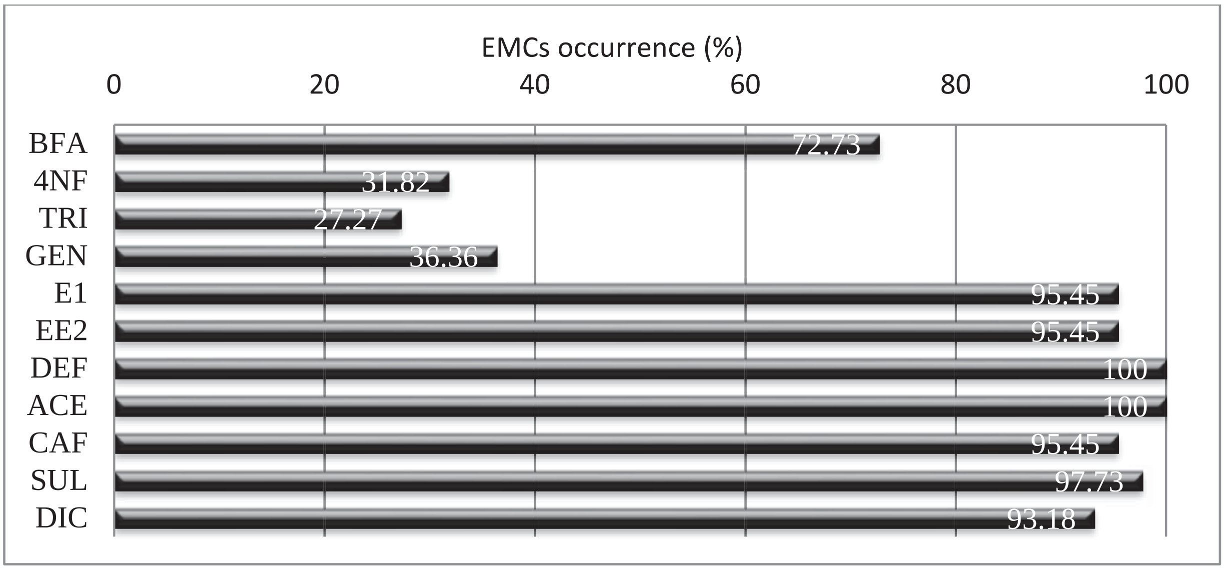


Figure 3: Occurrence of microcontaminantes in samples analyzed (n = 44)

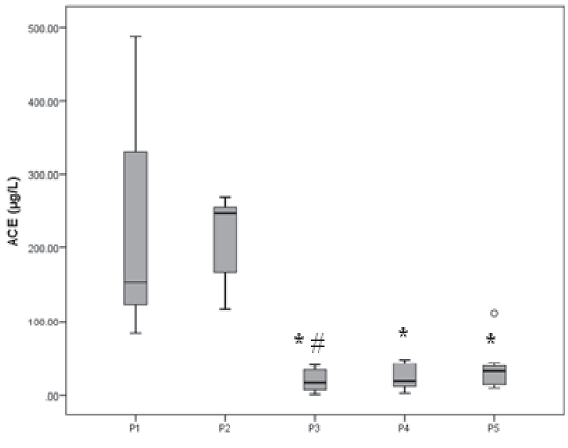
The hormones estrone (E1) and 17α-Ethinylestradiol (EE2) presented a high frequency in the analyzed samples, being detected in 42 of 44 analyzed samples. Natural estrogens, such as estrone, 17β-Estradiol and estriol, are daily produced and excreted by women (Aquino et al., 2013). It is estimated that 650 µg per capita E1 is excreted daily by pregnant women, and 35 µg EE2 by women using this synthetic hormone (Bila & Dezotti, 2007). The substance bisphenol A, used as monomer in the production of polymers and as additive in plastic compounds, showed a moderate frequent detection (n = 32). The lipid regulator gemfibrozil (n = 16), the surfactant 4-n-nonylphenol and the microbiocide triclosan(n = 12) showed a low frequent detection. In general, the EMCs quantified in this study were also detected in wastewater in European countries (Deblonde et al., 2011; Luo et al., 2014). In a study for drug occurrence in European rivers, carbamazepine (95%), diclofenac (83%), ibuprofen (62%) and genfibrozil (35%) were detected in the collected samples.

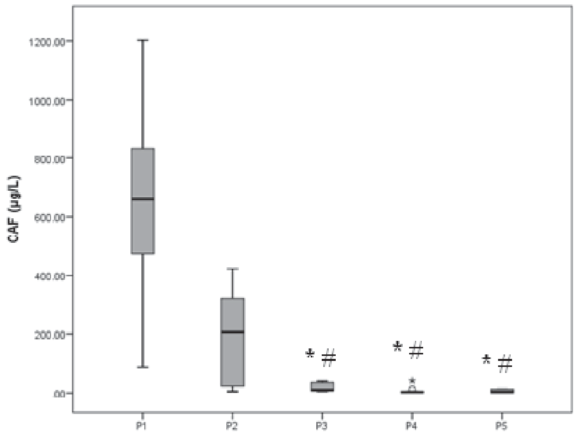
3.2 Removal of ECMs in wastewater treated by hybrid constructed wetlands

In order to analyze the removal efficiency in Treatment Lines I and II, the mean concentrations of ECMs in the effluents of Treatment Lines I (P5) and Treatment Line II (P4) in relation to the raw sewage (P1) were compared. The Wilcoxon-Mann-Whitney test (W-M-W) was used for comparisons between groups to evaluate differences in EMCs concentrations.

For **acetaminophen**, a statistically significant difference was found in the effluent of the two treatment lines P4 and P5, when compared to the influent - P1 (Figure 4). There was a statistically significant difference between the P5 samples in relation to the ST (P2) samples. TL I showed a mean removal efficiency of 85.7% while TL II 89.3%. Avila et al. (2014) obtained 99% removal efficiency for acetaminophen by evaluating the effluent of a CW SSV with a flow rate of 500 L/d.

The authors reported a high efficiency of removal due the oxygen dissolved instauration conditions in the CW SSV that can enhance microbial aerobic degradation processes.

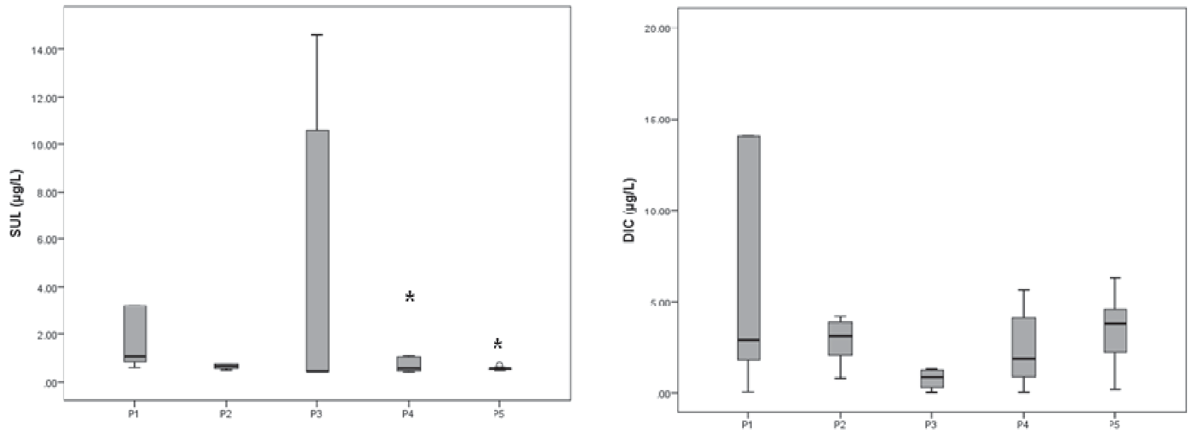




Figures 4 and 5: Boxplots for acetaminophen and caffeine concentrations (µg/L) in the different experimental units;*statistically significant differences in relation to P1; # statistically significant difference in relation to P2

For **caffeine**, the W-M-W test demonstrated a statistically significant difference in the medians between the effluents of the two treatment lines (P4 and P5) and the raw sewage (P1) and the septic tank (P2). The test also showed a statistically significant difference between WC FLA effluent (P3) and septic tank (P2) (Figure 5). A high efficiency of caffeine removal was observed in both treatment lines, 92.2% for LT I and 98.9% for LT II. A high removal efficiency of 91.2% was also detected in the CW SF-A (P3) effluent in relation to P2, evidencing the importance of this treatment unit in the removal of this substance. The results evidenced in this study were higher than those reported by Hijosa-Valsero et al. (2010), evaluating the caffeine removal in a system consisting of anaerobic lagoons, succeeded by a facultative lagoon and a maturation lagoon. The authors detected a removal efficiency of 82.6% for the system (n = 4), considering an influent concentration to the systems of 12.62 µg/L

For the **sulfamethoxazole**, it was observed a mean removal efficiency of 80.4% for TL I and 62.1% for TL II. Statistical analysis of W-M-W showed a statistically significant difference for TLI and TL II in relation to untreated wastewater (Figure 6). The removal efficiencies of this study were more expressive than those reported for the SUL by Ávila et al., (2014) considering the evaluation in hybrid CW cultured with Phragmites australis. The mean removal efficiencies reported in this study for sulfamethoxazole might be associated with the biological degradation process. An experiment evaluating the removal of these compounds in WWTPs showed high biological degradation coefficients (K_{Biol} = 5.9 to 6.7 L/g SS.d) for sulfamethoxazole in a conventional activated sludge unit (Joss et al., 2006)



Figures 6 and 7: Boxplots for acetaminophen and caffeine concentrations (µg/L) in the different experimental units; *statistically significant difference in relation to P1; # statistically significant difference in relation to P2

For **diclofenac,** a mean removal efficiency of 68.2% was observed for TL I and 78.3% for TL II compared with the wastewater influent (Figure 7). The mean values reported for effluent from the treatment systems considered in this study were 3.57 ± 1.94 µg/L for TL I and 2.43 ± 1.92 µg/L for TL II. Similar results were reported by Zhang et al., (2012) evaluating vertical subsurface flow CW systems applying different hydraulic conditions. Diclofenac is often classified as recalcitrant compound to biological treatments. This substance has a low biodegradation constant, K_{Biol} <0.1 L/g SS.d (Joss et al., 2006). Substances with K_{Biol} < 0.1 L/g SS.d do not show satisfactory removal by the biodegradation mechanism. The maximum removal efficiency in WWTPs reported in literature for substances with these low biodegradation constant is less than 20% for compounds with a high tendency for sorption (Joss et al., 2006).

3.3 Acute toxicity test with Vibrio fischeri

For the *V. fischeri* bacterial assay, nine campaigns were carried out between March and July 2016, namely S1, S2, ... S9, totaling 26 samples. Of these were 9 in P1, 9 in P4 and 8 in P5. All samples *were* collected in effluent*s* of both treatment lines (P4 and P5) and showed a significant reduction of toxicity, expressed in toxicity units (Figure 8).

In the evaluation of toxicity reduction of the effluents treated in the analyzed CWs, the exposition tests with *V. fischeri* showed a reduction efficiency of 71.1% for TLI and 90.5% for TL II, respectively. The ANOVA showed a significant difference between the raw sewage - P1 and the effluent of LT I - P4 and TL II - P5. There was a significant difference in the reduction of V. fisheri toxicity expression between the effluents from Treatment Lines I and II. The differences might be due to the removal of organic matter (COD and TOC), and nitrogen compounds (N-total and NH4) being higher in TL II compared with TL I.

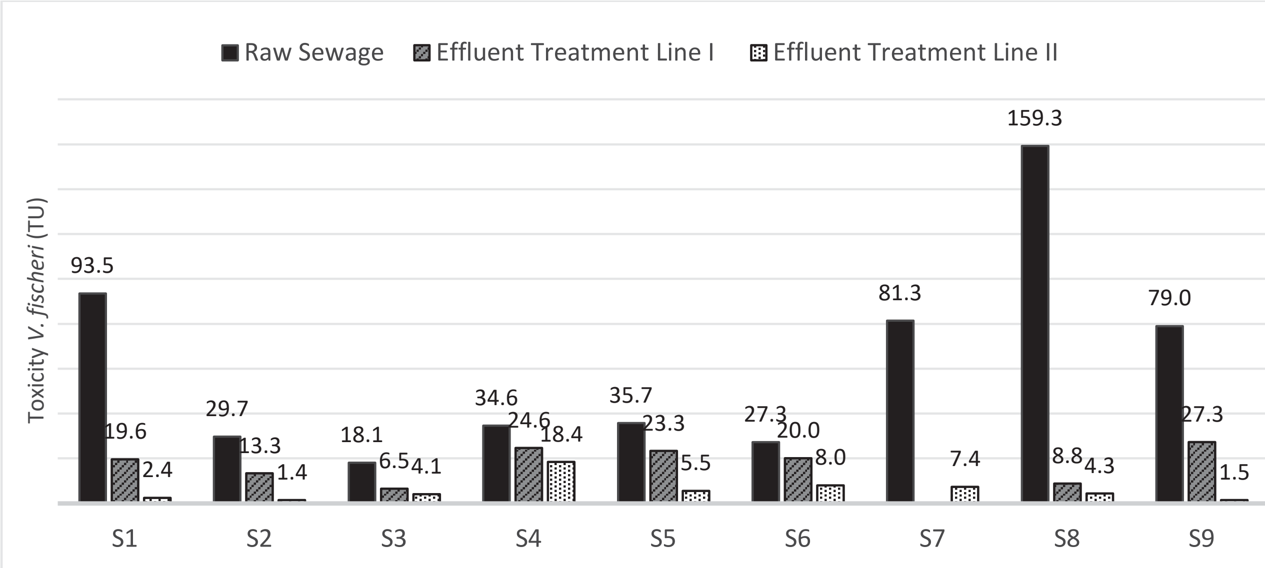


Figure 8: Results of acute toxicity test for *V. fischeri* expressed in toxicity units (TU)

4 Conclusions

Treatment Line I presented high removal efficiencies (E > 75%) for acetaminophen (85.0%), caffeine (92.2%) and sulfamethoxazole (80.4%). For diclofenac, the TL I showed a moderate removal efficiency (68.3%). Treatment Line II showed high removal efficiencies for acetaminophen (82.3%), caffeine (98.9%), and diclofenac (78.4%). A moderate removal efficiency (50% <E <75%) was found for sulfamethoxazole (62.1%). Significant removal efficiencies reported for acetaminophen, caffeine, diclofenac and sulfamethoxazole might be associated with biological degradation processes and high biodegradation constants of these substances. Thus, the role of the microorganisms present in the root zone of the plant species and the support medium can be considered as fundamental in the biodegradation of these substances.

The hybrid CWs systems considered in this study were efficient in the reduction of acute toxicity considering the organisms *V. fischeri.* There was a significant difference in the reduction of *V. fisheri* toxicity expression between the effluent from Treatment Lines I and II. The systems showed toxicity reduction of 71.1% and 90.5%, respectively. The differences might be due to removal of organic matter (COD and TOC) and nitrogen compounds (N-total and NH_4) being higher in TL II compared with TL I.

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MICROPOLLUTANTS IN THE AQUATIC ENVIRONMENT AND THEIR REMOVAL IN MEMBRANE BIOREACTORS

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Keywords: Micropollutants; endocrine disrupting compounds; membrane bioreactors

Abstract

In recent years, the endocrine disrupting chemicals (EDCs) including pharmaceuticals, personal care products, some industrial and household chemicals, and pesticides are increasing in the environment due to the results of growing population rates, urbanization and personal preferences (Caliman and Gavrilescu, 2009). Many EDCs can reach aquatic media from a variety of sources from wastewater treatment plant effluents to leakages of septic tanks, or from landfill sites to terrestrial run-offs. It is important to increase the removal rates of micropollutants before their discharge into aquatic media. Membrane bioreactor (MBR) systems offer satisfactory removal rates for conventional water quality parameters. Recently, some studies showed that micropollutants might be removed by MBRs. In this study, a variety of different micropollutants in domestic wastewater were treated by MBR and the results obtained were found to be promising.

1 Introduction

After the industrial revolution, rapid economic development and increasing population jeopardize the world's precious water resources. The main objective of the European Union Water Framework Directive is to prevent and to reverse the adverse situation of all surface water and groundwater resources starting from the year 2015. The directive explained the precautions to improve the current status of river basins to "clean and secure" in a step by step approach. However, most of the developing countries could not reach that goal yet.

In last decades, researchers tried to improve wastewater treatment technologies. It was shown that membrane bioreactor (MBR) systems have some advantages over conventional biological treatment systems for the removal of specific pollutants (Zhang et al., 2012). Membrane bioreactor technology (MBR), a combination of the activated sludge process with microfiltration and ultrafiltration is a novel and rapid growing technology for the treatment of domestic and industrial wastewater (Hoinkis et al., 2012; Oh et al., 2012; Sari-Erkan et al., 2018). The activated sludge in the biological unit is responsible for the biodegradation of the pollutants in wastewater, and the physical separation of the treated wastewater from the mixed liquor suspended solids (MLSS) is ensured by the membrane module (Lesjean et al., 2008; Hoinkis et al., 2012). The membrane pore diameter is generally between 0.01–0.1 µm, therefore, bacteria and particles in MLSS can be kept out of permeate (Deowan et al., 2015). Hence, MBR offers the advantage of a high quality of treated water and a low plant footprint. Because of its advantages, MBR technology has been also used with the aim of reusable water production and process water recycling using through osmosis membranes (Farias et al., 2014).

Compared with conventional activated sludge (CAS) processes, the quality of treated wastewater from MBRs is higher than from CAS. MBRs have also more advantageous sides than CAS, because the MBRs can be operated with high MLSS concentrations, and this flexibility provides to reduce waste sludge production (Wang et al., 2009; Kimura et al., 2009). Another important property that make MBR more advantageous than CAS process is the longer sludge retention times (SRT), consequently higher effluent quality. Typical SRT values in MBRs are above 20 days, whereas CAS process can be operated at 5-15 days. The membrane materials, module configurations (hollow fiber, flat sheet), biological operation conditions (SRT, temperature), membrane operating conditions (back washing), and properties of activated sludge can influence the capabilities of MBRs. It should, however, be noted that MBR technology has some disadvantages as well, such as high operation cost and common membrane fouling problems. The most important disadvantages in MBR is membrane fouling, as it increases the operation cost and reduces the treated water quality and quantity (Liao et al., 2004; Mahendran et al., 2011). Considering this, it should be noted that several small and large-scale applications indicated the technical feasibility of the MBR process (Deowan et al., 2015; Sari-Erkan et al., 2018).

Endocrine disrupting compounds are becoming of primary concern, given their increased use and, in turn, their increased presence in our aquatic systems (Tijani, et al., 2013; Palacios-Rosas and Castro-Pastrana, 2017). These human-made micropollutants such as EDCs (e.g., phenolic compounds, phthalates and hormones), pharmaceuticals and pesticides can be found in aquatic environment, and consequently were found in the effluent of conventional activated sludge processes at various concentrations from few nanograms per liter (ng/L) up to several micrograms per liter (µg/L) due to their limited capability to remove these contaminants (Verlicchi et al., 2012; Neguyen et al., 2013). The biodegradation of micropollutants is influenced by SRT, which is considered as the most significant parameter for pharmaceuticals (Nasirabadi et al., 2016).

The physicochemical features of contaminants such as octanol-water partition coefficient (P_{ow}) (hydrophilicity or hydrophobicity), and aqueous solubility are other influential parameters that control biodegradation and/or sorption to sludge particles. Hydrophobic trace organic compounds are reported to be removed by sludge adsorption during the MBR treatment (Tadkaew et al., 2011). The properties of the biomass present in the MBR can also play an important role for the removal capacity of organic contaminants. It was shown that biomass containing a mix culture of bacteria and fungi could have better removal rates than a system including fungus or bacteria alone (Nguyen et al., 2013). Additionally, the combining treatment process with MBRs physical; NF/RO membranes, adsorptive materials (granular or powdered activated carbon GAC-PAC), and chemical processes (ozonation, UV oxidation) could be used to eliminate micropollutants (Taheran et al., 2016).

This paper presents possible treatment of some EDCs by submerged membrane bioreactor equipped with ceramic membranes. The preliminary studies having sludge retention time of 15 days proved the ability of submerged MBR for the treatment of EDCs.

2 Materials and Methods

The lab scale MBR system (Figure 1) includes a plexi-glass reactor of 5 L effective volume and a submerged ceramic flat sheet MF membrane module with a nominal pore size of 0.1 µm and a total surface area of 0.057 m^2 (Cembrane, Denmark). The systems have two reactors, one for the test and the other as control. Oxygen was supplied with a stainless steel diffuser located at the bottom of the reactor and installed on an air pump. The temperature of mixed liquor was kept constant 22.0 ± 1 °C by recirculating water in the heat jacket of the reactors, and pH was remained stable between 7.4-7.8. Initial seed sludge was obtained from a municipal wastewater treatment plant in Istanbul. The MBR systems were operated at a constant flux value of 7.3 L/m^2xh at a hydraulic retention time (HRT) of 12 hours, which was controlled by an automation unit having half hour suction and half hour relaxation time. The ceramic membrane modules were cleaned manually with tap water and then back-blown with pressured air (1 bar) once in five days and chemically cleaned once a month. The system was fed with synthetic municipal wastewater having concentrations of 400 mg/L COD, 20 mg/L NH_4^+-N, 5 mg/L PO_4^{3-}-P (prepared with tap water according to Bakaraki et al., 2016) and operated at 15 day sludge retention time (SRT).

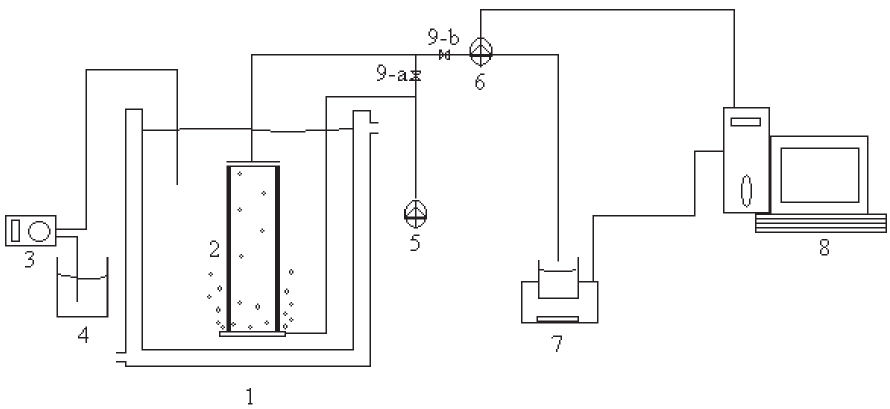

Figure 1: The membrane bioreactor system used in the study

Nine organic micropollutants, namely, 4-*tert*-octylphenol (endocrine disruptor), estrone (hormone), fluoxetine (pharmaceutical), and atrazine, malathion, chlorpyrifos ethyl, cypermethrin, penconazole (pesticides) were selected for this study. All organic compounds were purchased from Sigma-Aldrich (Germany). A stock mix solution was prepared with pure methanol and kept in a freezer. When the MBR system reached the steady state conditions, known amounts of micropollutants were added to the synthetic wastewater from the stock mix solution. The system was operated for a duration of 45 days and samples were taken three times a week to monitor removal efficiencies for conventional parameters as well as for micropollutants. The concentration of each analyte in the synthetic wastewater, diluted from stock solution thousand-fold, were determined and found to be between 7-605 µg/L according to the detection limits in the GC/MS protocol.

The analyses of micropollutants in the liquid samples were conducted with dispersive liquid-liquid micro-extraction (DLLME) method by a GC/MS system (Agilent 6890) equipped with HP-5MS capillary column (30 m x 250 µm; 0.25 µm) and a mass selective detector. Helium was used as carrier gas at a constant flow rate of 1.8 mL/min, and all the injections were carried out in splitless mode with a sample volume of 1.0 µL. The temperature program was as follows: an initial oven temperature of 70 °C ramped at 40 °C/min to 150 °C, 20 °C/min to 200 °C and 50 °C to 300 °C, where it was held for 3.5 min. The DLLME procedure was carried out by injecting a mixture of 200 µL chloroform and 3.0 mL methanol into a 15 mL centrifuge tube containing 8.0 mL liquid sample/standard solution with a polypropylene syringe, and vortexing for 30 s and centrifuging for 2.0 min at 6000 rpm (Chormey et al., 2017). About 50 µL settled chloroform phase was taken by discarding the upper aqueous phase, and it was put into 100 µL insert vials for injection in the GC-MS.

The measurements of COD (APHA [240] SM 5520C Closed Reflux Titrimetric), ammonia nitrogen (NH_4^+-N) (APHA 4500-NH_3-B), and orthophosphate (PO_4^{+3}) (APHA 4500-P D (Stannous Chloride Method)) in the feed wastewater and permeate, and the MLSS analysis (APHA 2540 D (Dried at 103-105 °C)) in the sMBR were carried out according to the Standard Methods (2005).

3 Results and Discussion

After the addition of micropollutants mix solution to the MBR system at steady state conditions, treated effluent samples were taken from the reactor three times a week to monitor the MBR performance. The MLSS concentration was about 2,800 ± 1,000 mg/L throughout the study at an SRT value of 15 days and at an HRT value of 12 hour. The average removal efficiencies for COD, NH_4^+-N and PO_4^{+3}-P were found to be 96.7, 86.1 and 56.1%, respectively.

The removal efficiencies for micropollutants were also monitored and the average values are presented in Table 1. As can be seen, the lowest removal rate was obtained for atrazine, as the biodegradability of this compound is very low. Tadkaew et al. (2011) had reported poor removal rates for atrazine (less than 5%). The second lowest removal rate obtained was obtained for penconazole (fungicide), with a removal rate of 57%. The rest of the removal efficiencies were between 82.6-91.7%, which were higher than reported in the literature (Serrano et al., 2011).

Table 1: Average removal rates of micropollutants in the test reactors (SRT 15 d, HRT 12h)

Micropollutants	Removal Rate (%)
4-tert-octylphenol	87.2
Atrazine	14.9
Fluoxetine	82.6
Malathion	91.7
Chlorpyrifos Ethyl	91.7
Penconazole	57.0
Estrone	91.6
Di-n-Octyl phthalate	91.7
Cypermethrin	91.7

4 Conclusions

The preliminary results obtained for the simultaneous removal of micropollutants in a submerged MBR indicated that high removal rates can be obtained. For atrazine, which is known as a persistent organic pollutant widely used in agriculture, few studies were carried out, especially in membrane bioreactors. Higher SRT values might have a positive effect for the removal of micropollutants including atrazine. In addition, the fate of all micropollutants in the MBR should be further studied in order to determine the possible pathways of the removal mechanisms.

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GEOCHEMISTRY OF HIGH CONCENTRATIONS OF FLUORIDE AND MAJOR IONS OF SMINJA AQUIFER IN ZAGHOUAN (NORTH-EAST OF TUNISIA) AND RISKS TO HUMAN HEALTH FROM EXPOSURE THROUGH DRINKING WATER

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Keywords: Geochemistry; Fluoride; Hydrochemical facies; Human health; Sminja aquifer; Tunisia

Abstract
Sminja aquifer, located in Zaghouan district in Northeastern Tunisia, has been used to meet the needs of Zaghouan agglomerations for drinking purposes and irrigation uses. On the other hand, the region has suffered from inefficient usage and mismanagement of water resource as result of inappropriate legal, political, and economic frameworks taking into consideration the regional vulnerability to climate change and population growth. Tunisia is like most North African countries, which are characterized by a harsh arid and semi-arid climate with scarce water resources and poor water quality on most of its territory. The main objective of the study was to evaluate the chemical quality, to identify the sources of dissolved ions of Sminja aquifer, and to verify its suitability for various uses. 23 wells and boreholes were sampled during the winter and summer of 2013. Chemical analyses have involved the main physicochemical variables (temperature, pH, Total Dissolved Solids, Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-} , K^+, HCO_3^- and F^-). Two types of facies predominate the water of Sminja aquifer. The first hydrochemical facies is Na–Ca–Cl–SO4, located in the recharge zone of the aquifer. The second facies is Na–Cl, corresponding to the downstream part of the Sminja aquifer (discharge area). The results showed that the fluoride concentrations in Sminja aquifer have been constantly increased in the last decades as a result of the point source inputs related to mining discharges, and diffuse inputs linked to the agricultural activity in the district. The soils, the unsaturated zone, and the aquifers have gradually become charged with fluorine over time. The results also confirmed that fluoride contents in Sminja aquifer range from 5 to 25 mg/L in 2013. These concentrations are very high and exceed allowable standards of World Health Organization (1.5 mg/L) and Tunisian National Standards NT.09.14 (1.2 mg/L). Many medical studies have proved the enormous danger of high doses of fluoride in water on human health, among others dental and bone fluorosis.

1 Introduction
With only 1% of the world's renewable water resources, the Middle East and North Africa (MENA) region is the most water scarce region in the world. The factors driving the regional water scarcity are mainly linked to the climate conditions of the region, which is characterized by arid and semi-arid climate with low annual rainfall and high evaporation.

Water is an essential factor for the development of the agricultural, industrial and tourism sector, and is vital for the supply of drinking water. MENA region is the poorest one regarding water in the world, and this situation affects more and more the economic and social development of most of its countries. By contradiction, MENA has more than 5% of the world's population with less than 1% of the world's freshwater resources. Despite these characteristics, many countries such as Tunisia continue to inappropriately use considerable quantities of these scarce water resources, which have led to the deterioration of its quality for priority uses for irrigation and drinking water. Tunisia remains arid to a semi-arid country on three-quarters of its territory. It is characterized by the scarcity of its water resources and an accentuated variability of the climate in space and time. Tunisia receives on average a volume of water of 36 BCM of annual precipitation. This volume varies from a dry year to another rainy year. It is in the order of 11 BCM/year in a drought year and can reach 90 BCM during a rainy year while the water potential is 4.8 BCM/year, of which 2.7 BCM/year represents surface water, being just 8% of the country's rainfall, and 2.1 BCM/year, supplying the underground aquifers.

The Zaghouan governorate has five groundwater reservoirs in the plains of Nadhour, El Fahs, Sminja, Oued Rmel and Boucha, and seven deep aquifers housed in the Jurassic limestone formations of Djebels Zaghouan, Bent Sâadane, Zrass and in the Oligocene and Miocene of the Nadhour-Saouaf syncline (Khanfir, 1984). The volume of water stored in these aquifers is estimated at 23 Mm^3, or 20% of the total resources of the governorate. The aquifer of the study area is formed by the Sminja aquifer, which is in hydraulic connectionwith the Oued Rmel aquifer (Rekaya, 1981). The main objective of the study was to evaluate the chemical quality, to identify the sources of dissolved ions of Sminja aquifer, and to verify its suitability for various uses.

2 Study Area

The Sminja aquifer is one of the important aquifers of Zaghouan district, 60 km away from Tunis. It belongs to the watersheds of Meliane and Rmel (Figure 1). The climate of the region belongs to the upper semi-arid stage with torrential precipitation causing accelerated runoff. The relief is very rugged with Djebels and hills that dominate the landscape. The hydrographic network is very hierarchical with two main watercourses: Wadi Meliane and Wadi Rmel. Agriculture has undergone a transition from agro-pastoralism, dominated by sheep breeding on the rangelands, and episodic cereal farming to an intensive farming system based on arboriculture.

The geology of the study area shows the existence of formations, which constitute of aquifer systems of variable importance by their lithology and structure. The stratigraphic series that appear in this zone is of age ranging from the Triassic to the Quaternary. The flow of the Sminja aquifer is mainly from the south to the center and the northeast of the groundwater. In the center and north, the flow converges towards the Wadi Meliane, showing that the latter drains the aquifer (Hechemi, 1989). The losses of the groundwater are mainly through evapotranspiration and drainage. Evapotranspiration becomes important, where the aquifer is sub-flush, especially near the village of Sminja. The piezometry of the Sminja aquifer is monitored twice a year since 1982. The first measurement is made in March, a period of high waters, and the second one is done in August, a period of low waters. Beginning in the 1990s, the aquifer showed a decrease in the piezometric level. Piezometric monitoring during 1996 showed a decrease varying from 0.06 m to 1.46 m, respectively, in periods of high and low waters. This decline can be explained by excessive exploitation at certain locations, such as Sminja and Mograne. In 2010, the piezometric level of Sminja groundwater also decreased from 0.1 m to 2.64 m, in average by 0.48 m.

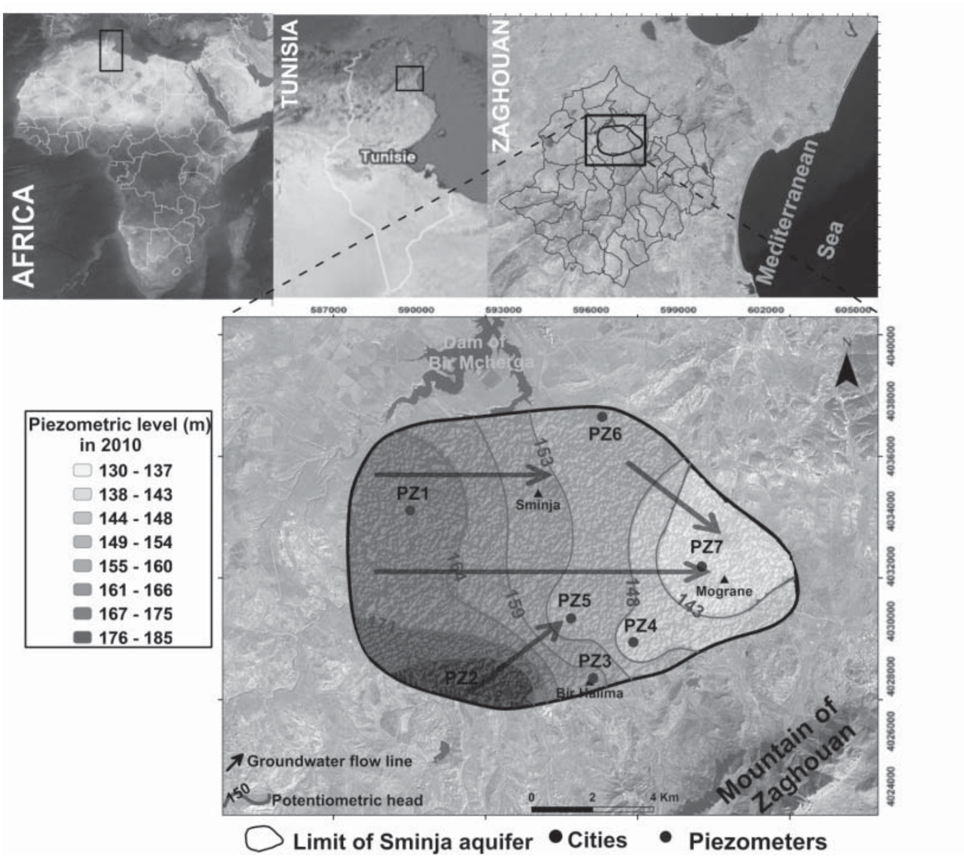

Figure 1: Geographic location and piezometric head (m) of Sminja aquifer

3 Materials and Methods

3.1 Sample collection, analytical techniques, and validation of chemical analyses

The present work focuses on the physicochemical characteristics of groundwater of Sminja aquifer, in order to validate and to understand, how the mineralization of these waters has occurred. The selection of water samples was made to ensure that boreholes capturing the aquifer are accessible to the collection and cover the maximum of the study area. The water sampled during the year 2013 comes from two sampling campaigns in winter and summer. The number of samples was 46 during the two seasons. The groundwater sampling protocol in the field was conducted in several stages: in situ measurement of some physicochemical parameters, sample collection from groundwater, the user's survey of groundwater using a standard form, and the transfer of samples to the laboratory (Thierrin et al., 2003). Water pumped out of its initial environment can undergo in contact with the atmosphere many Irreversible transformations. Non-conserved physico-chemical parameters must be measured *in situ* at the time of sampling (Bermes et al., 1963).

Water sampling was done from water points equipped with an electric pump to guarantee the renewal of water. A sample was taken after at least 30 min of pumping until stability of the temperature and pH values. The water samples were collected in sterile 1 L polyethylene bottles, rinsed with water to be analyzed at least three times. Water samples were cooled at 4 °C (Hounslow, 1995). Coolers were used for storage of samples that have been sent to the laboratory. The water samples were filtered through a 0.45 µm Millipore membrane using a filtration assembly to retain suspended solids, which are capable of absorbing light when analyzed by colorimetry and can cause false analysis. The analyses of the collected water samples were carried out in the laboratory of Geochemistry and Geology of the Environment at the Faculty of Sciences of Tunis. The electrical conductivity EC (accuracy ± 0.5% of the measured value), temperature (accuracy ± 0.1 °C) and pH (accuracy ± 0.01) were measured *in situ* with a conductivity meter, a thermometer and a pH meter, respectively.

The analyses of major elements concerned chlorides, sulphates, alkalinity, alkaline elements (Na^+ and K^+) and alkaline earth elements (Ca^{2+} and Mg^{2+}). The chlorides were assayed by the Mohr titration method (Rodier, 2009). Titration was carried out with 0.1 N silver nitrate in the presence of potassium dichromate ($K_2Cr_2O_4$). Sulphate analysis was conducted by means of gravimetry. It consists of precipitating these ions in an acid medium by barium chloride ($BaCl_2$) of known titer (10%) in the presence of potassium dichromate. The alkalinity was determined by the volumetric method, which is based on the neutralization of a volume of water to be analyzed with HCl of known normality (0.02 N) in the presence of a colour indicator. The cations were determined by atomic absorption spectrometry. The spectrometer used was *Perkin-Elmer AAnalyst 800 FAAS*, with a double beam and background correction. The content of nutrients was determined upon arrival at the laboratory within 24 hours of collection, and was carried out by a colorimetric method (Ameur et al., 2016). The results of analyses of major elements were validated by the calculation of ionic balance (or electroneutrality). The accuracy of the quality of chemical analyses was checked by calculating charge percentage balance errors (% CBE) from Ca^{2+}, Mg^{2+}, Na^+ and K^+ cations as well as anions Cl^-, SO_4^{2-} and HCO_3^-. This calculation was done for each sample. The result of electroneutrality is given in percent. The formula of Freeze and Cherry (1979) is used to calculate error percentages (Appelo & Postma, 2005):

$$\%CBE = \frac{\sum[\text{cations }]Zc - \sum[\text{anions}]Za}{\sum[\text{cations }]Zc + \sum[\text{anions }]Za} \times 100$$

∑ [cations] Zc = ∑ [anions] Za; with Z is the absolute value of ion charge.

An analysis is reliable, when the ionic balance is less than 5%, which is the case for all water samples from the Sminja aquifer.

3.2 Methods and approaches adopted

The results of the chemical analyses were integrated into a georeferenced database. Then, all results were validated before being used for statistical analyses.

3.3 Geographic Information System

In order to make the data accessible and easy, a structured database has been created. It attempts to group together all information (piezometric, hydrogeology, and geochemistry) inside tables linked together and referenced under a geographic information system, which is here ArcGis 10.2 (Ameur et al., 2015).

3.4 Multivariate Statistical Analysis

3.4.1 Correlation matrix

The linear correlations between relevant chemical elements make it possible to investigate the origin of the mineralization by evaluating the degrees of dependence between the various parameters concerned. The evaluation is carried out using the determined correlation coefficients by statistical calculations. The correlation between two parameters will be more significant as the correlation coefficient R will be close to 1. Thus the correlations were established between all major elements taken in pairs that allowed obtaining binary correlation diagrams for interpretation.

3.4.2 Principal Component Analysis (PCA)

In order to define the relationships that link the different parameters on the one hand, and to identify groups of waters with the same characteristics on the other hand, a Principal Component Analysis (PCA) for all the waters of the aquifer was carried out (Qian et al., 1994; Hamzaoui et al., 2009).

3.4.3 Geochemical Modelling

It is necessary to discuss the different processes contributing to the mineralization of water through the thermodynamic approach and the equilibrium diagrams constructed from the contents of major chemical elements. The thermodynamic approach makes it possible to study the chemical evolution of water according to its state of equilibrium with respect to the primary and new minerals of the reservoir rock during the sampling. If one considers a chemical reaction between water and a mineral, the thermodynamic equilibrium constant of this reaction, K(T) is defined as follows:

$$\mathbf{K\ (T) = PIA}.$$

PIA is called a product of ionic activity. The equilibrium gap is defined by the saturation index SI, which is expressed by the equation:

$$\mathbf{SI = \log\ (PIA) - \log\ (T)}$$

When SI = 0, the water is in equilibrium with the mineral

When SI < 0, the water is under-saturated and capable of dissolving the mineral

When SI > 0, the water is super-saturated and capable of precipitating the mineral

The calculation of the saturation indices was carried out using the Phreeq C software of the WATEQ Debye thermodynamic program.

4 Results and Discussion

4.1 Hydrochemistry

Several approaches have been used to perform groundwater geochemical classifications. In order to identify the origin of the mineralization of the waters of the Sminja aquifer and to analyze the geochemical behavior of the solutes, a spatial and temporal monitoring (summer and winter of 2013) of physicochemical parameters, contents of major elements and nitrates was carried out, and presented in Table 1. The chemical analyses of the major elements concerned the cations Na^+, K^+, Ca^{2+}, and Mg^{2+}, and the anions Cl^-, SO_4^{2-} and HCO_3^-.

Table 1: Summary of the hydrochemical parameters in groundwater samples from Sminja aquifer

	Summer					Winter				
Parameter (mg/L)	Mean	Median	Min	Max	SD	Mean	Median	Min	Max	SD
T°C	18.3	18.7	11.8	23.0	2.99	25.7	25.7	22.1	31.0	2.20
pH	7.25	7.21	6.70	7.83	0.24	7.08	7.09	6.52	7.75	0.30
TDS	2,860	2,030	1,170	9,570	1,814	2,916	2,319	1,114	9,308	1,874
SO_4^{2-}	181	123	82.0	617	123	453	370	123	1152	246
HCO_3^-	393	390	271	537	71.6	275	272	198	374	40.6
Cl^-	907	613	319	4,341,	842	897	550	284	4,153	853
Mg^{2+}	86.4	87.0	31.9	156	35.0	93.6	77.8	35.0	205	47.5
K^+	8.63	5.54	0.20	43.4	10.1	9.57	5.00	2.23	60.0	13.8
Na^+	449	294	169	2,825	537	496	307	142	2,854	570
Ca^{2+}	201	168	56.6	458	101	190	172	31.0	405	87.5
NO_3^-	81.4	87.1	8.26	137	37.1	84.3	96,9	14.3	107	29.00

4.1.1 Total Dissolved Salinity

The salinity of waters varies from 1,170 to 9,570 mg/L in the winter season, and from 1,110 to 9,310 mg/L in the summer season. The maximum salinity was found in the downstream part of the aquifer, which is the most mineralized one, with a saline load greater than 3,000 mg/L (Figure 2a).

4.1.2 Chlorides and Sodium

Concentrations of chlorides in the water of Sminja range from 319 to 4,341 mg/L for the winter season and from 284 to 4,153 mg/L for the summer season. Cl^- concentrations do not show great temporal variability from one season to another for the same year. The spatial distribution of the chloride contents (Figure 2b) shows the same evolutionary trend as that of salinity. In fact, the waters with the lowest chloride concentration are those with the lowest total salt load. On the other hand, the Cl^- content increases or decreases in the same direction as the salinity. Since chlorides are the dominant anions, the salinity of the waters of the Sminja aquifer is, therefore, mainly controlled by the concentration of Cl^- for the anions. The sodium content in water of Sminja varies between 169 and 2,825 mg/L for the campaign of January, and between 142 and 2,854 mg/L for the August campaign. The spatial distribution of Na^+ concentrations (Figure 2c) is, on the whole, similar to that of chlorides, and therefore, to that of salinity. The lowest values are identified in the waters of the southern part of the aquifer, while the highest values characterized the waters taken in the north-western part of the Sminja aquifer. It should be noted that for the same sampling points, the concentration gap is very low between January and August. Sodium is the dominant cation, its content, therefore, controls, together with that of the chloride, the total saline load of the waters of the Sminja aquifer.

4.1.3 Nitrates

Nitrate levels in the waters of the Sminja aquifer are highly variable. They are between 8.26 and 137 mg /L in January and 14.3 and 107 mg/L in August. The distribution maps of these contents (Figure 3a) show that the highest values concern water taken from irrigated areas, over-fertilized by nitrogen fertilizers, in particular, calcium nitrate (Moussa, 2012). The waters taken from these places are oxygenated, which shows the prevalence and stability of nitrates compared with other forms of dissolved inorganic nitrogen.

4.1.4 Fluoride

The fluoride content of the waters of the Sminja aquifer ranged from 5 to 25 mg/L in 2013 (Figure 3b). Thermal water is among the sources of fluoride in groundwater. In the governorate of Zaghouan, there are two thermal springs, Dj Oust and Hammam Zriba, which are partly responsible for the high concentrations of fluoride in the two slicks of Sminja and Oued Rmel. The thermal waters of these springs rise along the abnormal contact limiting the Dj Oust dome after having washed the Triassic terrains giving rise to chloride-sodium water. The thermal water is captured in a natural cave at the bottom of a mining gallery and transported by a gravity pipeline to the pumping station located at the exit of the gallery; then part of the water is forced back to the spa, the other part is dripping towards the Oued Meliane (Hezzi, 2008).

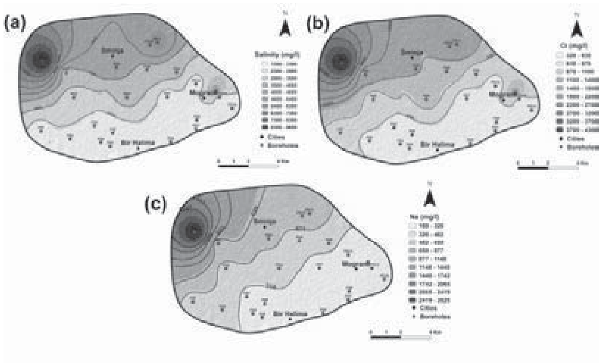

Figure 2: Spatial distribution of (a) salinity, (b) chlorine ions, and (c) sodium ions in Sminja aquifer

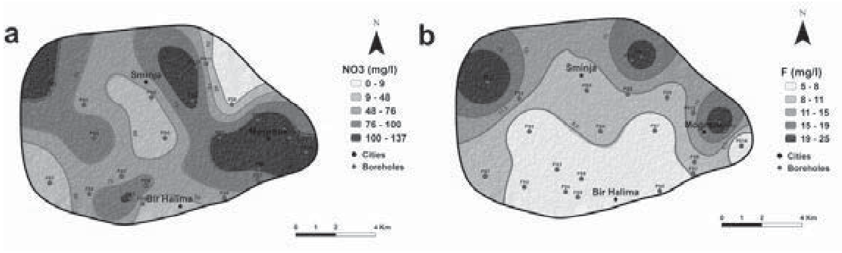

Figure 3: Spatial distribution of (a) nitrate and (b) fluoride in Sminja aquifer

4.2 Hydrochemical Facies

To characterize the geochemical facies of the waters of the Sminja aquifer, the representative points of these waters are plotted on the Piper diagram (Figure 4a), which shows two groups of water with different facies:

- Na-Cl facies, which characterizes the water taken from the discharge zone of the aquifer (PS1, PS2, PS3, PS5, PS6, PS10, PS11, and FS1);
- Na-Ca-Cl-SO_4 (or HCO_3) facies type, characterizing the boreholes situated in the north part of the aquifer as well as in the recharge zone. The spatial distribution of these facies (Figure 4b) shows an enrichment according to the direction of flow of the aquifer, of Na with respect to Ca and Cl towards SO_4 or HCO_3.

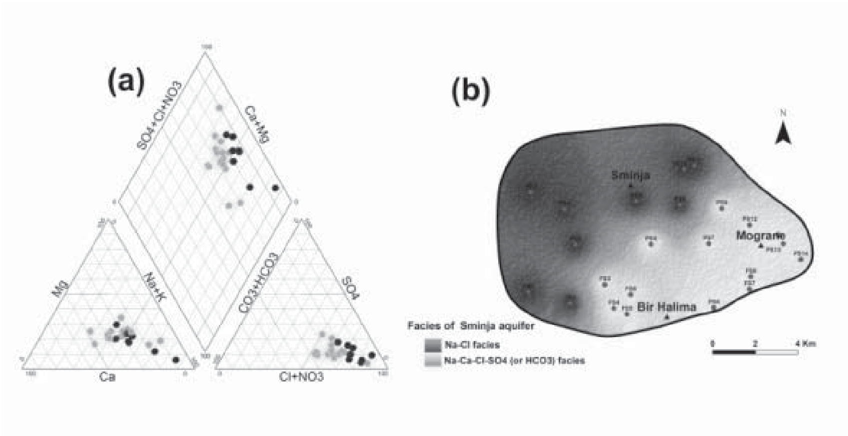

Figure 4: (a) Piper diagram; (b) hydrochemical facies of Sminja aquifer

4.3 Groundwater mineralization processes

4.3.1 Rock-water interaction

The rock-water interaction and chemical processes reflect the chemical composition of groundwater. A lot of dispersion diagram like the Gibbs diagram and correlations between chemical elements can inform and identify the rock-water interaction (Figure 5) (Elango & Kannan, 2005). The sodium contents, expressed in meq/L, are very well correlated with those of chlorides (Figure 5a). The correlation coefficient is very close to 1 (R^2 = 0.96) and indicates that these two elements have similar geochemical behavior. Their principal origin is the dissolution of the halite in the superficial horizons of soil. Evolution of the calcium content as a function of sulphates (Figure 5 b) shows a positive correlation with a coefficient around 0.7. This shows that calcium in parts and sulphates are involved in the same geochemical processes. There is, however, a tendency to increase the sulphate content as calcium increases, but with a relatively variable ratio.

This indicates that sulphates originate from the dissolution of gypsum, and that calcium would also originate from the alteration of the alkaline-earth carbonate minerals. The variation of the bicarbonates concentration as a function of calcium (Figure 5 c) shows a negative correlation for the most concentrated Ca^{2+} waters. This evolutionary trend is related to the complexation of Ca^{2+} and HCO_3^- in the saltiest waters, which are saturated or supersaturated with respect to calcite. This confirms that calcium cannot originate from calcite. Figure 5d shows that the majority of water samples from the Sminja aquifer are located along the 1:1 line in Ca^{2+} +Mg^{2+} vs HCO_3^- + SO_4^{2-} scatter diagram, what means that these ions come from gypsum or anhydrite, therefore, from the alteration of carbonates and sulphated minerals. The samples, which are very close to the Ca^{2+}+ Mg^{2+} axis, indicate that the origin of this excess of calcium and magnesium contents lead to reverse ion exchange phenomenon (Belkhiri et al., 2012). The water points on the left axis of the 1:1 line show an excess of sulphates and bicarbonates concentrations, indicating the dominance of ion exchange process (Datta & Tyagi, 1996; Subramani et al., 2010).

In order to identify the significance of cation exchange in controlling the groundwater composition, a cross plot of (Ca^{2+} + Mg^{2+}) - (HCO_3^- - SO_4^{2-}) versus (Na^+ + K^+) - Cl^- was represented. Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^- represents the pole of amount of Ca^{2+} and Mg^{2+} that can be lost or gained with regard to that provided by the dissolution of gypsum, calcite and dolomite, while Na^+ + K^+ - Cl^- represents the axis of quantity of Na^+ + K^+ that can be lost or gained with regard to that given by the dissolution of halite (Jalali, 2007). In the case, where these reactions are absent, all data will be very close to the origin (McLean et al., 2000). If these two parameters are linear and slope is -1, then these processes control the chemical composition of the water. Figure 5e shows an increase of Na^+ + K^+ associated with a decrease of Ca^{2+} + Mg^{2+} or increase of HCO_3^- + SO_4^{2-}. The correlation between major elements (Figure 5e) indicates that the data are close to a straight line ($r = 0.95$) with a negative slope of -0.935, so the dominance of the cation exchange is the dominant phenomenon. Thereafter, the increase of Na^+ in both water classes is generated by the ion exchange process (Garcia et al., 2001).

4.3.2 Calculation of the saturation indices (SI) with respect to the mineral phase

Using the Phreeq C software, it was possible to calculate the water saturation indices of Sminja aquifer with respect to certain minerals, such as calcite, dolomite, and gypsum. The results obtained show that all the waters of the Sminja aquifer are under-saturated with respect to gypsum, indicating the possibility of acquisition of Ca^{2+} and SO_4^{2-} by dissolution of the mineral present in the aquifer. However, the majority of these waters are saturated to super-saturated with calcite and dolomite, indicating that the saline charge is not influenced by the water-mineral carbonate interaction (Figure 6).

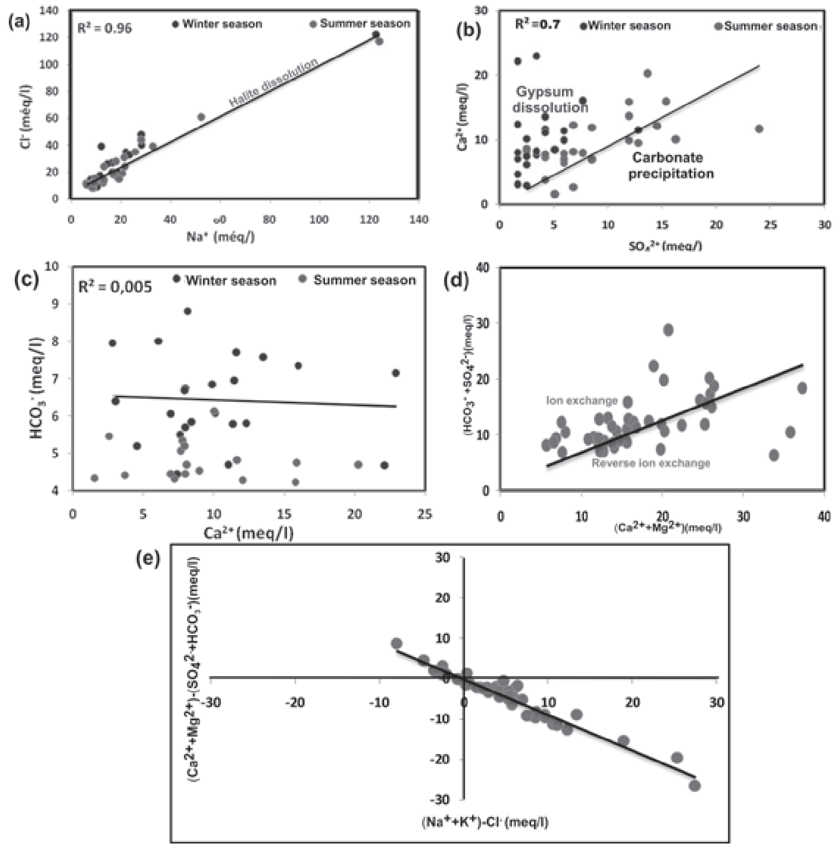

Figure 5: Plots of (a) Na vs Cl; (b) SO_4 vs Ca; (c) HCO_3 vs Ca; (d) (Ca^{2+} + Mg^{2+}) vs (HCO_3^- + SO_4^{2-}); and (e) [(Na^+ + K^+)–Cl^-] vs [(Ca^{2+}+Mg^{2+})–(SO_4^{2-}+HCO_3^-)]; *all in meq/L*

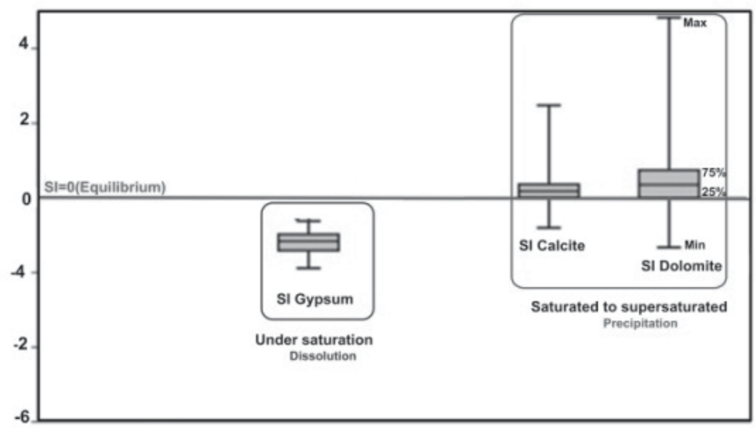

Figure 6: Saturation indices for several minerals

4.4 Statistical Analyses

4.4.1 The correlation matrix

The correlation matrix is composed of 11 variables, which are the physicochemical parameters (temperature, pH and salinity) and the major elements (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-) of 46 water samples, taken during the two winter and summer seasons in 2013. It shows that the concentrations of Na^+, Cl^-, Ca^{2+}, SO_4^{2-} and Mg^{2+} are well correlated with the salinity, with correlation coefficients higher than 0.55 (Table 2), indicating that the mineralization of the waters of the Sminja aquifer is controlled mainly by the contents of these elements. HCO_3^- levels were not correlated with salinity, with a correlation coefficient of 0.09. This shows that the variation in salinity is not influenced by the contents of the bicarbonate ions.

Table 2: Matrix of the correlations between the different variables for the year 2013

Variables	T °C	pH	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	Salinity
T °C	**1**									
pH	-0.22	**1**								
HCO_3^-	-0.46	0.30	**1**							
SO_4^{2-}	0.41	-0.17	-0.35	**1**						
Cl^-	0.04	0.11	0.07	**0.63**	**1**					
Ca^{2+}	-0.01	0.25	0.03	0.41	0.44	**1**				
Mg^{2+}	0.12	0.07	0.07	**0.54**	0.50	**0.69**	**1**			
K^+	0.16	-0.04	0.10	0.48	**0.63**	0.27	0.21	**1**		
Na^+	0.06	0.06	0.06	**0.63**	**0.97**	0.26	0.35	**0.64**	**1**	
Salinity	0.06	0.13	0.09	**0.68**	**0.98**	**0.55**	**0.63**	**0.61**	**0.93**	**1**

*Values in **bold** indicate a correlation coefficient r^2 greater than 0.5*

4.4.2 Principal Component Analysis

The PCA classifies as variables major elements, nitrates and physicochemical parameters, and as individuals the analytical results of the waters of Sminja for the year 2013. The percentages of variability are established unequally in several axes: F1, F2, and F3 (Table 3). The study of the eigenvalue spectrum shows three main axes, of which F1 represents 42% of the variance. The axis F1 corresponds to the mineralization factor, also called the main plane, which includes the maximum information. The F2 and F3 axes contain 18% and 12% of the total variance, respectively, a total of 72%, which is significant. For the variables, the F1 axis shows a good correlation between the salinity and the Na^+, Cl^-, SO_4^{2-}, K^+ and Mg^{2+} contents, with correlation coefficients greater than 0.7 (Table 4). These elements reflect the rock-water interactions and constitute mostly of the mineralization of the waters of the Sminja aquifer (Figure 7). The axis F2, which accounts to about 18% of the variance, is characterized in its positive pole by bicarbonates and pH. This shows that the variation of salinity is not influenced by the contents of the bicarbonate ions (Figure 8). Nitrates and calcium are represented by the axis 3 with a percentage of 12% of the variance. This correlation is mainly related to anthropogenic processes that are closely related to nitrogen pollution through excessive use of chemical fertilizers.

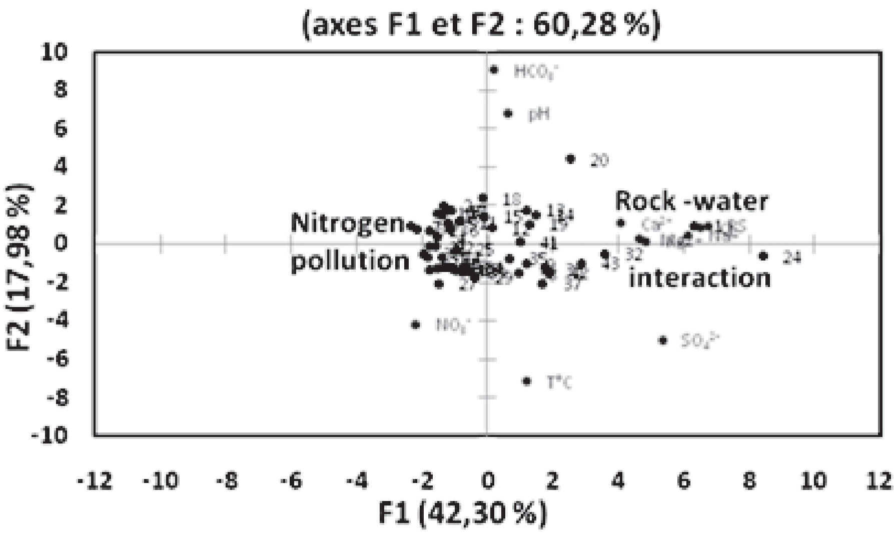

Figure 7: Analysis of Principal Components of Sminja aquifer

Table 3: Eigenvalues of the correlation matrix

	F1	F2	F3	F4	F5	F6	F7
Eigenvalue	4.653	1.978	1.325	1.035	0.742	0.511	0.351
Variability (%)	42.299	17.983	12.041	9.411	6.742	4.647	3.192
% Accumulated	42.299	60.282	72.323	81.734	88.476	93.123	96.314

Table 4: Factor coordinates of variables of waters of Sminja aquifer

	F1	F2	F3	F4	F5	F6	F7
T°C	0.177	**-0.676**	-0.183	-0.570	0.108	0.055	0.367
pH	0.096	**0.634**	0.233	-0.289	0.656	0.038	0.022
HCO_3^-	0.035	**0.846**	-0.133	0.002	-0.349	0.033	0.339
SO_4^{2-}	**0.772**	-0.473	0.053	-0.044	0.001	-0.070	-0.100
Cl^-	**0.941**	0.075	-0.106	0.227	0.115	-0.111	0.060
Ca^{2+}	**0.591**	0.097	**0.685**	-0.116	-0.064	0.305	-0.033
Mg^{2+}	**0.675**	0.022	**0.509**	-0.274	-0.337	-0.182	-0.006
K^+	**0.699**	0.010	-0.412	0.042	-0.067	0.552	-0.080
Na^+	**0.888**	0.041	-0.276	0.273	0.153	-0.160	0.070
NO_3^-	-0.315	-0.394	**0.480**	0.626	0.131	0.137	0.271
Salinity	**0.973**	0.087	0.009	0.130	0.039	-0.117	0.047

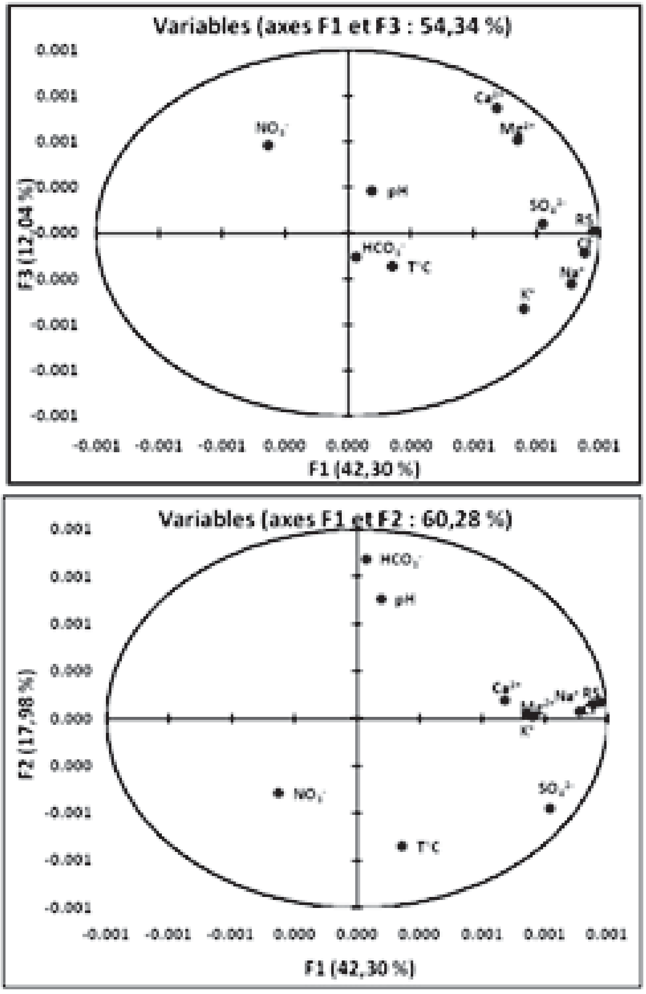

Figure 8: Variables correlation circle on the rF1-F2 and F3 factorial plane

5 Conclusions

For understanding the hydrodynamic functioning of the Sminja aquifer, its rock-water interaction and its control of chemical mineralization was identified by a multiple geochemical and statistical approach of the major elements, fluoride, and nitrate. This paper has clearly shown that the salinity of the waters of Sminja aquifer Increases from upstream to downstream. The upstream zone, captured at shallow depths, benefits from a large recharge from the beds of the Wadis and at the level of the foothills that drain the Djebel massif of Zaghouan. In the downstream zone, the aquifer becomes deeper and deeper. This increase of salinity according to the direction of flow of the aquifer is influenced mainly by the origin of the water, the water-rock interactions, the residence time, and by the thickness, the lithology and the grain size of the unsaturated zone.

The majority of waters of this aquifer exceed the drinking standards set by the WHO and by the Tunisian standard NT.09.14 with respect to the physicochemical parameters, nitrate and fluoride levels. A preliminary treatment of these waters is necessary before being consumed as drinking water.

From the research that has been done, it is possible to conclude that two chemical facies characterize the waters of the Sminja aquifer:

- Na-Cl facies concerning water collected in the discharge zone of the aquifer (PS1, PS2, PS3, PS4, PS5, PS10, and FS1);
- Facies of Na-Ca-Cl-SO4 (or HCO_3) type for the waters, taken from the recharge zone of the aquifer. The scatter diagram formed by Ca^{2+}+ Mg^{2+} vs HCO_3^- + SO_4^{2-} shows that these ions come from gypsum or anhydrite, therefore, from the alteration of carbonates and sulphated minerals.

Many phenomena control the chemical composition of the waters of Sminja aquifer, among others reversed ion exchange, ion exchange process, and cation exchange. Statistical analysis by the correlation matrix and PCA of the contents of major elements shows that mineralization of the water is mainly controlled by the concentrations of Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-} and K^+.

The calculation of the water saturation indices with respect to the calcite and dolomite shows that the saline charge is not influenced by the carbonate water-mineral interaction, but is done at the expense of gypsum with respect to which they are under-saturated.

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ARSENIC POLLUTION THROUGH DRINKING GROUNDWATER IN BURKINA FASO: RESEARCH OF A CHEAP REMOVAL TECHNOLOGY

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Keywords: arsenic pollution, groundwater, granular ferric hydroxide, ferrihydrite, laterite rock.

Abstract

In several parts of Burkina Faso, there is an urgent need of purifying arsenic contaminated water. The medical effect of the arsenic exposure has also been evaluated among the inhabitants of affected villages, indicating that the problem is critical. Results of previous investigations using a commercial Granular Ferric Hydroxide (GFH) as adsorbent material showed a capacity of 370 µg/mL of arsenic removal from water with arsenic concentrations varying between 90 and 196 µg/L. Being GFH very expensive, other adsorbent materials have been tested instead. In this study, natural laterite rock has been used as adsorbent in column experiments and the results indicated a low adsorption capacity (5.2 µg/mL). Then, the same lateritic sand has been coated in ferrihydrite by drying the two materials together in an oven. Results showed an adsorption capacity ranged between 31.2 and 48.1 µg/mL indicating an increase of the adsorption capacity. Although results showed an improvement after ferrihydrite-coating, the adsorption capacity is still significantly lower than the one of GFH. It is concluded that ferrihydrite-coated sand is still a possible low-cost adsorbent material for treating arsenic contaminated water in developing countries, although factors like sand material, grain size and coating method should be evaluated further.

1 Introduction

Drinking water supply is one of the most important challenges of African countries, mainly in Sub-Saharan Africa. There still is lack of properly sanitation, with some lack of appropriated systems for groundwater treatment, groundwater from tube wells being used in rural area for the consumption and cooking without any prior treatment. Nowadays, water resources are facing to severe problems such as increasing demand, pollution, scarcity, etc. Some trace elements in water including arsenic are toxic and impact the human health, if occur above the guidelines of World Health Organization for drinking water. Arsenic is released to the environment mostly through combustion of fossil fuels, mining activities, the use of arsenical minerals and pesticides (Jain & Ali, 2000; Smedley & Kinniburgh, 2002). It is well known that the ingestion of inorganic arsenic can result in both cancers (skin, lung, liver and urinary bladder) and non-cancer effects (melanosis, hyperkeratosis, prostate diseases) (National Research Council, Arsenic in Drinking Water, 1999). Out of the occurring trace elements in the ground water of northern Burkina Faso, arsenic has the greatest impact on human health. Medical problems such as skin lesions and cancer are widely known to occur as a consequence of chronic arsenic intake. The presence of high concentrations of arsenic in drinking water is a major problem in northern part of Burkina Faso. Out of the occurring trace elements in the ground water of northern Burkina Faso, arsenic has the greatest impact on human health. The shallow dug out wells, traditionally used in the rural areas, provide small inconsistent yields and are vulnerable to microbes. Medical problems such as skin lesions and cancer are widely known to occur as a consequence of chronic arsenic intake. Skin lesions such as melanosis and keratosis on hands and feet are among the first seen effects, usually occurring after 5-15 years of arsenic exposure (Agusa et al., 2009).

Previous studies in Yatenga Province showed the presence of skin lesions such as melanosis and keratosis on hands and feet, which are among the first seen effects due to arsenopyrite species in the bedrock, coinciding with high arsenic concentrations in the drinking water being pumped up from deep boreholes, while tube-well water is used by approximately 87% of the villagers in this province (Somé et al., 2012)**.** Among the first recognized consequences from chronic exposure to arsenic is melanosis, skin disorders of hyperpigmentation or keratosis, where the skin goes rough and dry with skin papules. The arsenic effects on human health depend on dose and duration of exposure, but arsenic related diseases also include internal types of cancer (Somé et al., 2012). The concentration of arsenic in wells' groundwater of Yatenga Province is varying and range from 0.5 to 1,630 µg/L (Smedley et al., 2007). That has caused the closing of some wells, where arsenic concentration has been higher in Lilgomde and Tanili villages (Knudsen et al., 2005).

According to Bretzler et al. (2017), 15.5% of tube-wells water in Ganzourgou Province, 42% of ground waters in Yatenga Province, 13% of wells water in Soum Province, 16% of ground waters in Bale Province, and 14% of tube-wells water in Bam Province have an arsenic concentration above the WHO Guideline of 10 µg/L. Consequentially, many of them have now been replaced with drilled tube-wells, intercepting water from fractures in the bedrock and providing reliable water sources. However, as arsenic is naturally present in the bedrock in many parts of the country, previous studies have shown that water from a lot of these wells is not safe to drink (Knudsen et al., 2005). In some cases, the wells had to be closed due to high arsenic concentrations. Ground waters are particularly vulnerable to accumulation of high arsenic concentrations because of water-rock reactions and the high ratios of solid to solution in aquifers compared with surface waters. Almost all various technologies developed for the treatment of arsenic in water are limited by the high costs of process and materials.

To mitigate this water pollution problem, column adsorption experiments are undertaken to remove arsenic from tube-well waters as the only source of drinking water available at these rural areas of Burkina Faso. In this study, physical-chemical composition of groundwater was determined. Through filtering method on laterite and/or ferrihydrite-coated laterite, this work aims to find a purification method suited for developing countries and to contribute to the safe drinking water supply in rural areas of Burkina Faso.

2 Materials and Methods

2.1 Sampling

Water was collected from two wells near central Ouagadougou on April 15th and May 6th, 2017. The first well was located in the village of Ziniare at 25 km from Ouagadougou, and was handled by hand. The flow from this well was low, and the well was, therefore, thought to be quite shallow. The second well was located in the suburbs of north-east Ouagadougou, and was driven by solar power pump and thought to be deeper. For the first occasion, two 20 L containers were used for sampling at each well, while for the second time 40 L were collected only from the first well. After collection, the water was brought to the laboratory for analyses of the ingredients.

2.2 Preparation of laterite

The laterite was collected at the village of Balkouin, 10 km from Ouagadougou (Figure 1). It was then crushed with a hammer into small particles and sieved by hand both dry and under running tap water as for removing the finest particles. The crushed laterite was then thoroughly washed in tap water until the red color had gone, and finally washed in distilled water before left to air dry at room temperature (30-35 °C) for three days. Three different samples were prepared from different sites and ground levels in the sampling area of Balkouin. The samples were collected within a radius of 100 m from each other.

Figure 1: Image of laterite in Balkouin area

According to Giorgis et al. (2014), Balkouin laterite properties of geochemistry, minerology and genesis were determined. In this study, it is clear that the top most layer in the form of rock contains a significantly higher concentration of Fe_2O_3 (54.9%) than all the other samples. The amount of Al_2O_3 is also high (16.2%), although not the maximum, and the quantity of SiO_2 (19.0%) is considerably lower than all other samples.

2.3 Preparation of ferrihydrite coated laterite

Ferrihydrite used in this experiment was prepared using 40 g of $Fe(NO_3)_3 \times 9H_2O$ dissolved in 500 mL distilled water. Approximately 300-330 mL of 1 M NaOH was then added to the solution at slow rate using a magnetic stirrer, until pH 7.4 ± 0.1 was reached. Laterite sand was coated with ferrihydrite by drying the materials together in an oven for one day.

2.4 *Arsenic removal and analysis*

Continuous fixed bed experiments were carried out according the Table 1 and Figure 2. In order to remove the red color of the material, the system was filled and washed with distilled water 5 times. The arsenic concentration in the influent and effluent water was analyzed by using a Wagtech Arsenator at a wavelength of 193.7 nm.

Adsorption Capacity (Q) in µg/mL was calculated as follows:

$$Q = (C_0 - C_e)\frac{V_{water}}{V_{ad}}$$

With V_{water}, volume of treated water (L), and V_{ad}, volume of adsorbent packed in column (mL), C_0 and C_e, As concentrations at the beginning and the end of the experiments.

Table 1: Parameters in the setting up of column for the large column experiments

Parameter	**Quantitative values**
Height of glass wool and glass beads (cm)	7.5
Weight of glass beads (g)	52.6
Column height (cm)	20
Column diameter (cm)	6.5
Adsorbent volume (cm^3)	664
Weight of dried adsorbent (g)	720
Flow (L/h)	10
Empty bed contact time (h)	0.066

Figure 2: Experimental device of column experiments

3 Results and Discussion

3.1 Arsenic removal using GFH

The pH of the effluent was very low at the beginning of the experiment, but after several hours it increased and did not fluctuate much. When we let the effluent sample take a rest for an hour after it had been sampled, the pH increased slightly. The temperature of the effluent followed the temperature in the laboratory and varied a bit between the measurements. The flow was stable at 10 L per hour during the whole experiment.

The pH of the influent was higher than that of the effluent and did not fluctuate as much during the experiment. This indicates that protons (H^+) are released into the solution, when arsenic is adsorbed. The temperature of the influent also varied less than the one of the effluent. The concentration of arsenic varied with the time and method of measurement. Indeed, some differences were noted with arsenic concentrations at the date of sampling, the date of lab analysis, and experiments had been done (Table 2 for details). Maximum values were obtained at the date of sampling and minimum values at the end of column experiments using GFH as adsorbent of arsenic. Average values were calculated using maximum and minimum values including the intermediary analyses (Table 2).

Table 2: Max, min and average values of pH, temperature and arsenic concentration in the influent using a large column test

Parameter	**Qualitative value**
pH max	8.1
pH average	7.8
pH min	7.6
T max (°C)	28.5
T average (°C)	26
T min (°C)	24
As max	196
As average (µg/L)	162
As min	90

Figure 3 shows an increase of adsorbed arsenic per milliliter of GFH, when the volume of treated water increases (green line). GFH material was very efficient with arsenic concentrations closed to 0 µg/L when 1,500 L of water was treated. The low arsenic concentration below of 10 µg/L beyond 1,500 L of water were due to the self-regeneration of worn out GFH causing a desorption of arsenic on the active sites of GFH.The maximum capacity of GFH (430 µg As removed /mL of adsorbent) was obtained after the treatment of 1,800 L of water.

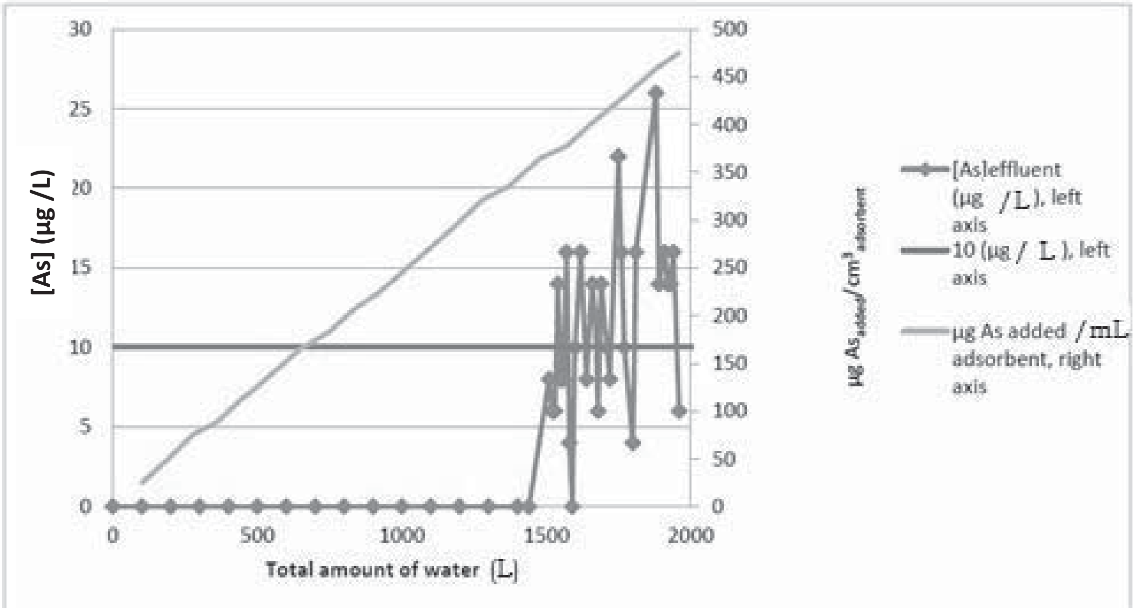

Figure 3: The blue line corresponds to the total amount of water versus arsenic concentration in the effluent water. The green line shows the accumulated amount of added arsenic per milliliter of adsorbent. The red line is the WHO limit value of 10 µg As/L.

In Figure 4, the breakthrough corresponds to the limit value of 10 µg As/L, where the blue and the red line cross. Even though the concentration of arsenic in the effluent fluctuated, a steady increase could be noted. Sometimes, the regeneration of worn out GFH could be noted, when the adsorbed arsenic starts to desorb from the surface of material causing an increase of arsenic concentrations in the effluent. It was noted a low time for the self-regeneration of worn out GFH.

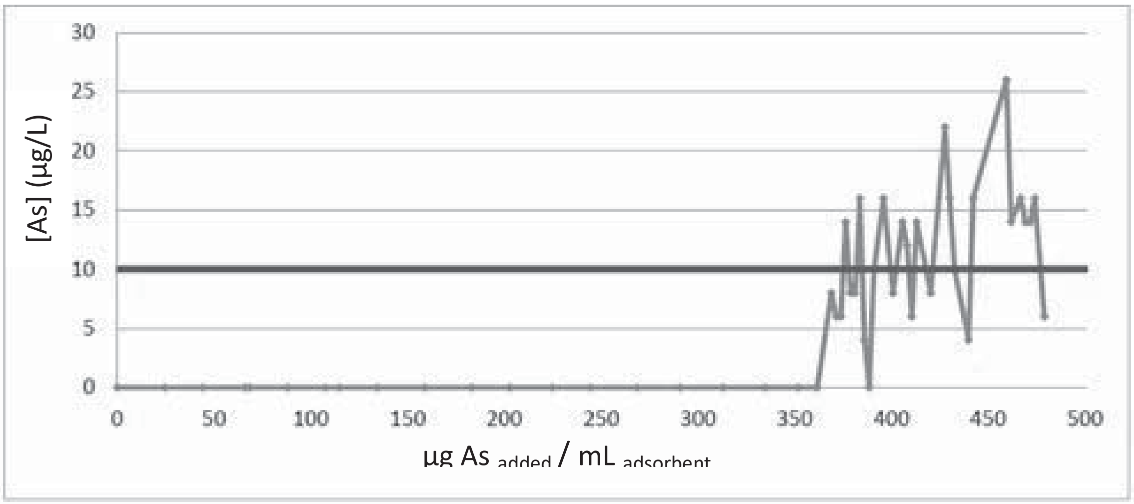

Figure 4: The blue line corresponds to the amount of added arsenic per milliliter of adsorbent vs arsenic concentration in the effluent water. The red line is the WHO limit value of 10 µg As/L.

Data from the analysis of water are given in Table 3, where one noticed a low iron content, and the concentrations of other constituents were within regular limits of WHO (Table 3). It was noted the presence of some species such chloride, sulfate, nitrate, phosphate and bicarbonate, which can compete with arsenic ions in the adsorption process (Mahler and Persson, 2013; Maiti et al., 2010). When one compares the influent water with the effluent, it is clearly shown that phosphate, calcium, and magnesium are removed in the column. That could be due to their negative charges, similar to arsenic ions (arsenates and arsenites) causing a competition for the occupation of active sites on the surface of GFH with the contribution of surface charge density (Sanou, 2017). Moreover, the total hardness as well as pH decreased. The removal of calcium and magnesium could be due to the negative active sites from repulsion arsenates-GFH surface beyond the pH of zero point charge of GFH with the contribution of the charge density on the surface.

Table 3: General water parameters for influent and effluent after 1,440 L had passed.

Parameter	**Influent**	**Effluent**
pH	8.1	7.6
Electrical Conductivity (µS/cm)	345	343
Phosphate (mg/L)	0.35	0.17
Nitrate (mg/L)	7.1	7.9
Sulfate (mg/L)	2	2
Iron (mg/L)	0.01	0.01
Bicarbonate (mg/L)	66	102
Chloride (mg/L)	10	8
Calcium (mg/L)	32	23
Magnesium (mg/L)	35	26
Total hardness (mg $CaCO_3$/L)	226	168
Total Alkalinity (mg $CaCO_3$/L)	54	83

During the experimental course, no significant problems were encountered. Even though the recommendation of having a column length of five times the diameter was not followed, no problems with clogging were observed. Since an upward flow was used, no problems with air bubbles in the system were encountered.

The results from the large column test with GFH show that it works well as adsorbent material for arsenic removal. Furthermore, GFH does not affect other parameters of the water to a large extent. As observed by Sanou et al. (2016), a drastic decrease of pH occurred at the beginning of the experiment. After a while, the pH of the effluent got more stable; and even though the pH of the effluent was lower than that of the influent, it remained within the an acceptable range of pH for drinking water. Another observation, when analyzing the water, was that phosphate, calcium, and magnesium were adsorbed in the column as well. It is well known from earlier studies that phosphate compete with arsenic, but calcium and magnesium might thus also affect the arsenic adsorption capacity.

As stated in earlier studies, GFH has a large ability to self-regeneration. When evaluating the results from the large column test with GFH, this has to be considered. The pump was turned off during the weekends, nights, breaks for lunch, and blackouts. During these times, the system was able to self-regenerate. However, the concentration of arsenic in the effluent fluctuated, even though the pump had not been turned off. Most likely, the decrease of arsenic concentration after a longer pause was due to regeneration. Due to uncertainties in the arsenic analysis, it is hard to state, how large the regeneration effect is. Because of regeneration the calculated arsenic removal capacity in this experiment might be higher than it would have been, if the pump had been running nonstop. The time for breakthrough was near the expected time for breakthrough, based on the results from Sanou et al. (2016). The capacity of arsenic removal was slightly lower than their best result but better than their mean value. In this experiment, the empty bed contact time was also higher than in earlier experiments. This probably increased the adsorption capacity. In summary, the column can be up-scaled without notably affecting the adsorption capacity.

Calculations revealed that the arsenic removal capacity was between 106 and 463 µg/mL of adsorbent. The average value of arsenic removal capacity was calculated to approximately 370 µg/mL of adsorbent. The breakthrough occurred, when 1,510 L of contaminated water had passed the column. The maximum capacity of GFH was 463 µg/mL of adsorbent.

In a real case scenario, the pump will probably be used every day but not during nights. People tend to get water approximately at the same time of the day, thus the pump will be more utilized during these times and less during others. Since the pump will not be constantly used, the flow will not be regular. Before a full scale arsenic removal set up will be available for villages, further research has to be done. Practical problems such as how to construct the setup, how to change the adsorbent material, what to do with the used adsorbent material, and how often to change it, have to be solved. Problems with the set up could be such as how to control the flow and to keep it stable, how to avoid growth of microorganisms, how to prevent the adsorbent material to dry out, and how to guarantee directly the quality of water when started to pump. Another problem could be, how to control that the right water is used as drinking water. Some suggestions for further research is thus to investigate maximum possible flow in order to see if there is any growth of microorganisms in the used GFH. From the above results, it is deduced that GFH is a good and efficient adsorbent for arsenic removal, but the technology using GFH material is not economically feasible because of its high cost. Consequently, low-cost material is looking for and laterite rock is available and renewable in Burkina Faso for this purpose. In the following experiments, laterite soil is tested as an adsorbent to remove arsenic from groundwater.

3.2 *Arsenic removal using laterite rock*

During the first hour, some adsorption of arsenic may have occurred, but since no tests were done during this time, there is no evidence of that. During the second test, adsorption was notable, but after an hour, when the first sample was taken, the arsenic level was already high above breakthrough. During the first hour, at least 92 µg of arsenic was adsorbed, which corresponds to an arsenic removal capacity of approximately 5.2 µg/mL of adsorbent. Since no measurements were done, before one hour had passed, the uncertainty of this value is quite large.

Comparison between the pH of the influent and the effluent showed that the pH of the latter is slightly higher (Table 4). The pH of the effluent after an hour is also slightly higher than the pH of the effluent, when measuring directly after water had passed the column. However, since the pH variation is not very notable, it will not be discussed further.

Table 4: pH, temperature, and arsenic concentration in the influent and effluent with lateritic soil

Parameter	**Influent**	**Effluent**
pH	7.73	8.02
Temperature (°C)	25.1	25.2
As (µg/L)	172	118

The results from the small column test showed that the lateritic soil did not work well as column adsorbent material. The breakthrough occurred very fast. After the first test had been running an hour, the first sample for analysis was taken. This sample from the effluent showed no difference of arsenic concentration when compared with the arsenic concentration of the influent. For the second test, some arsenic was adsorbed and the lateritic soil had not been saturated during the first hour. However, breakthrough had occurred and the arsenic concentration was well above the accepted value. In the same column dimensions and flow rate as in optimum conditions using GFH, the maximum capacity of the lateritic soil was 7 µg/mL. Comparison between the capacities of both materials showed the removal capacity of GFH is approximately 66 times better under optimal conditions.

The difference between the first and the second test was that the column in the first test was a bit bent. This made the water flow faster on one side of the column, and more small particles were probably washed away from there than from the rest of the column. In the second test, the column was totally straight and, therefore, the flow through the column was more evenly distributed. Less small particles were washed away than in the first test, but in order to have sufficient flow some small particles still had to be washed away. The lateritic soil has shown some tendency to adsorb arsenic. However, it is not suitable for this column technique. The small particles are most likely necessary for adsorption to occur in a larger scale, but with this column technique the flow gets too low, if all small particles remain in the material. Nevertheless, lateritic soil might still be useful for arsenic removal. If the lateritic soil would be processed in some way before the column is packed, for example by adding some kind of binder, the column technique might better work.

Experiments carried out in this study indicate that the laterite sampled in Balkouin area, close to Ouagadougou, has a low arsenic removal capacity. Breakthrough (10 µg/L) was reached after only 1-2 L with an initial concentration of ~100 µg As/L. However, a smaller grain size seems to have a great impact of the adsorption capacity, as the experiment with 125-2000 µm grains adsorbed approximatively the double amount of arsenic as the sample with ~400-1000 µm. It is, therefore, thought that the adsorption capacity could be improved by using a small and even grain size that is still large enough to avoid clogging. Another possible solution to the problem of clogging would be using an upward flow instead. Further research is needed in this area, desirably with sieve fractions at specific sizes, ranging from 150-700 µm, to find an optimal particle size distribution.

Self-generation was observed at several occasions, and is thought to have a significant impact on the adsorption capacity at a full scale system. Samples were generally collected up to few minutes before the break and then approximatively 50-60 minutes after the break depending on the flow rate. A lot of water had, therefore, passed the column after the break, and the observed difference in the effluent concentration was still not a source of error.

Although the samples of laterite rock were collected from the same area in Burkina Faso, where Giorgis et al. (2014) did their studies, it is possible that there are some changes in the geological composition of laterite rock due to the climate change and natural phenomena like rain and soil pollution. The iron content varies to a large extent throughout the soil profile according to Giorgis et al. (2014), and consequentially, it is possible that the laterite used in this study is not of the optimal sort. For further analysis on laterite as arsenic adsorbent, sampling from different regions, elevations and climate zones within the country would be needed. If possible, characterization of laterite and especially the elemental composition prior to experiments would simplify the research.

3.3 Arsenic removal using ferrihydrite coated laterite

Preliminary experiments showed the efficiency of ferrihydrite as adsorbent in arsenic removal using batch adsorption. By testing as fixed bed in the column, it was noted a high solubility and the clogging of ferrihydrite, but this material was efficient when using a low volume of water. In order to increase its efficiency and to avoid the clogging problem, a mixture of ferrihydrite with laterite soil was chosen. Both experiments with a high volume of water improved the adsorption capacity of ferrihydrite coated laterite. When the improvement was measurable, the capacity seemed to be three to five times higher throughout the experiment that was carried out during a longer period of time, and self-generation might have had a great impact on the results.

In this experiment, the removal capacity of ferrihydrite-coated sand was ranged between 31.2 and 48.1 µg/mL of adsorbent; this capacity is 10-15 times less than the one of GFH. The capacity of the coated sand might be even lower using water from Yatenga Province. When the smaller grain size is adjusted to an even one, the adsorption capacity of the sand itself could be improved. That is the result of the use of laterite like the solid stand of the ferrihydrite increasing its adsorption capacity. The result seemed to be similar for both coating the sand by drying the materials at high temperatures in the oven and through the centrifugation method with some alterations following the procedure used by Mahler and Persson (2013). By judging the colour of water, the washing of the coated sand caused a washing off of a lot of ferrihydrite, and it is thought that the coating methods used in this study could be further improved. In addition, the effect of laterite grain size on the adsorption capacity and the coating report (laterite / ferrihydrite) will be further evaluated in future studies.

4 Conclusions

In conclusion, the method works in larger scale, and its capacity/efficiency is not notably affected by the up-scaling. Because of this, no major barriers for the development of a full-scale method to remove arsenic from natural water using GFH has been encountered. However, when lateritic soil was packed as fixed bed in the column instead of GFH, this possibility will not be a realistic option. But, there might be other ways to use it as arsenic removal material. The results from this study indicate that GFH column method can be used to remove arsenic in drilled tube wells in Burkina Faso. There are still some problems to overcome, before a final system can be applied in the villages. But no greater hindrances to solve these problems can be seen. Balkouin laterite itself has a low arsenic adsorption capacity. However, sampling was only done from one geographic area, and it is possible that laterite from another region or even another part of the soil profile might have a higher adsorption capacity. When coating the laterite with ferrihydrite, the adsorption capacity was improved approximately six to ten times.

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NATURAL PRODUCTS AS ADSORBENT FOR WASTEWATER VALORISATION

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Abstract

Various countries in arid areas have oriented their efforts to use wastewater WWs as an alternative source to cope with water deficiency. Usage of recycled WWs depends on successful infrastructure, reliable treatment process, financial and economic analyses, and public acceptance (overcoming health and environmental concerns). Wastewater might contain excreted pathogens (bacteria, viruses, protozoa and helminths (worms)) that cause gastro intestinal diseases, highly poisonous chemical toxins, and hazardous materials from hospital waste, heavy metals, hormones and antibiotics. The magnitude of pollution of WWs was evaluated according to the importance for the population. Various reports attest to the failure of the different treatment processes used to clean WWs, raising concerns about the remaining pollutants in WWs released into the rivers or reused in agriculture. Usage of local material for treatment could improve the quality of WW. Adsorbents have been prepared from some vegetable waste. Individual tests of adsorption have been performed with pollutants and different adsorbents. Isotherms of adsorption have been derived in batch experiments. Different equilibrium concentrations of the pollutants will enable to draw the isotherm and to compare different common models such as Freundlich or Langmuir. The parameters of adsorption have been deduced from the more fitting model to the data and reported in this study.

1 Introduction

Morocco is experiencing a disturbing level of water stress, as it is the case in the Middle East and North African Countries (MENA Region) in general. This is why Morocco has deployed its national water plan, in which reuse of purified wastewater is taken into account even if it remains limited actually. Wastewater depollution can offer the possibility of their reuse in agriculture and industry, and therefore, can respond to the problem of drinking water, which becomes increasingly scarce and expensive. In this context, this work was carried out aiming at decontaminating liquid effluents of textile industries. An adsorption technique was adopted to remove the targeted dye using natural adsorbents. Many agricultural wastes were subject of several WWs treatments like buriti shells (*Mauritia flexuosa* L.), waste tea (Gokce & Aktas, 2014), hazelnut husk (coconut shell), *Diplotaxisharra*, macadamia nut endocarp (*Macadamia integrifolia*), olive stones, chlorella-based algal residues, rice husk residues, coconut shells and corncobs (Farnane et al., 2018).

In this study, corncob and date seeds were the subject of investigation. Corncob is used in different activities such as the daily meals like salads, production of cooking oil and as material to feed for livestock (Chutrtong, 2015). Also date seeds had become a raw material for different commercial activities, which make the waste resulting from this product very abundant.

Individual adsorption tests have been performed with pollutants and different adsorbents. Isotherms and kinetics of adsorption have been derived in batch experiments. Different equilibrium concentrations of the pollutants will enable to draw the isotherm and to compare different common models such as Freundlich or Langmuir. Pseudo first order and pseudo second order models were used to determine and to study the kinetic order and parameters of the adsorption systems.

2 Material and Methods

Sorbent

The dye considered in this study is methylene blue (MB) with a very high degree of purity (98%). Figure 1 shows its molecular structure. It was used as it was supplied without any prior purification. A stock solution of 50 mg/L was prepared by dissolving 50 mg of MB in distilled water. The colored solutions of different concentrations used in this study were prepared by further dilution with distilled water (Belaid and Kacha, 2011).

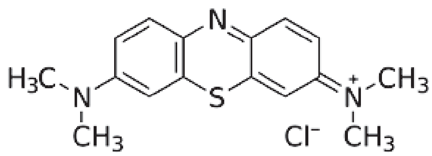

Figure 1: Molecular structure of methylene blue

Biosorbents

The biosorbents used in this work are date seeds (Elmajhoul variety) and corncob, two wastes resulting from Moroccan agriculture. Both products were washed with distilled water and then dried in an oven at 50 °C for 12 hours, then ground in their natural state. Finally, they were sieved to retain only the fraction between 1 and 2 mm.

Characterization

Infrared (FTIR): Fourier Transform Infrared Spectrophotometer, Shimazdu 2000, is used to analyze the surface functional groups of corncob and date seeds before adsorption. Potassium bromide disks were prepared by mixing 1 mg of the samples with 200 mg KBr, and the spectra were recorded from 4000 cm^{-1} to 400 cm^{-1}.

pH of zero charge (pHpzc): The zero charge point (PZC) is determined by treating 0.5 g of the biosorbents in 10 mL KOH solution. The mixture is stirred for 48 hours. The pH of the solution is measured (Elbariji et al., 2006).

Kinetic and isotherm studies: The adsorption kinetics were carried out by introducing 30 mL of an adsorbate solution at a concentration of 50 mg/L and 1.5 g of adsorbent in several stirred beakers at 25 °C ± 0.2 °C and pH 8.5. At each minute, the adsorbent is separated from the solution by filtration (0.45 µm). The adsorption isotherms are carried out according to the same protocol after an equilibrium time determined during the study of the adsorption kinetics. The determination of the new concentration is followed by UV-Visible spectrophotometer.

The adsorption capacities at the time t (q_a (mg/g)) are calculated by the following relation:

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

Where C_0 and C_e represent the concentration of MB in the initial solution and at time t (mg/L), m is the mass of date seed and corncob (g), and V is the volume of the solution in the beaker (mL).

3 Results and Discussion

Characterization

Infrared (FTIR): Figure 2 presents the characteristic absorption bands of the biosorbents. For the corncob, the absorption bands at 3310 cm^{-1}, 2795 cm^{-1}, 1650 cm^{-1}, 1252 cm^{-1} and 1011 cm^{-1} indicate the cellulosic nature of the studied material. The band at 3310 cm^{-1} corresponds to the deformation of O-H on the molecular chain of cellulose. Bands at 2895 cm^{-1} and 1011 cm^{-1} are attributed to the stretching vibration of C-H and C-O-C on the cellular structure of cellulose (Hai et al., 2017). Concerning date seeds, the large and intense band located around 3275 cm^{-1} on the FTIR spectrum is attributed to the valence vibration νOH of the OH groups of phenols, and primary and secondary alcohols of lignin and polysaccharides (cellulose and hemicellulose). The band observed at 1330 cm^{-1} is related to the deformation vibration in the δOH plane of the phenolic hydroxyl groups of lignin and the OH groups of hemicelluloses and cellulose. The band observed at around 2950 cm^{-1} corresponds to the asymmetric vibration, $\nu_{as}CH_3$ of aromatic methoxy groups ($-O-CH_3$) of lignin. The absorption, which appears as wide bands around 1740 cm^{-1} is characteristic to the valence vibration of C = O group of ketones, carboxylic acids and/or xylan esters present in lignins and hemicelluloses (Alqaragully, 2014 ; Danish et al., 2014).

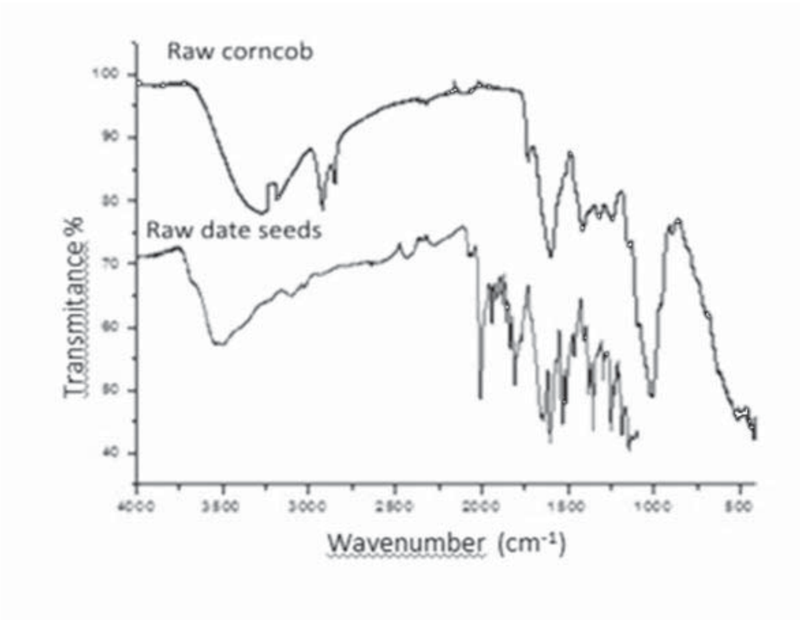

Figure 2: FTIR spectra of corncob and date seeds

pHpzc: Figure 3 shows that pHpzc is 6 for corncob and 4 for date seeds. The surface charge is positive for pH solutions below these values and is negative, when pH values are above pHpzc. As the dye used is basic, its dissolution in water causes the release of colored ions of positive charge (cations).

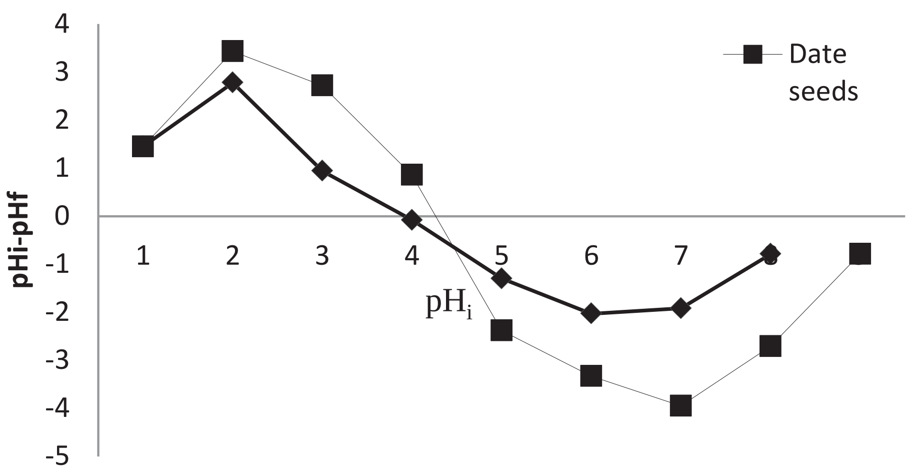

Figure 3: The point of zero charge (pHpzc) of corncob and date seeds

The used biosorbents contain polar functional groups such as hydroxyl and carboxyl. In addition, the electrical charge of the biosorbents depends on the pH of the medium because of the ionization of these functional groups on the surface. Hameed (2010) noted that the discoloration of MB on the used biosorbents is favored because the pH of the solution (8.5) is higher than the pHpzc (4 and 4.3, respectively, for corncob and date seeds). This is explained by the presence of the OH^- ions in the solution causing the deprotonation of the surface functional groups that increased electrostatic forces between the negative charge of the adsorbent and the positive charge of dye.

Kinetic study

Figure 4 shows the evolution of the adsorption capacity of each adsorbent for MB as a function of time at 25 °C.

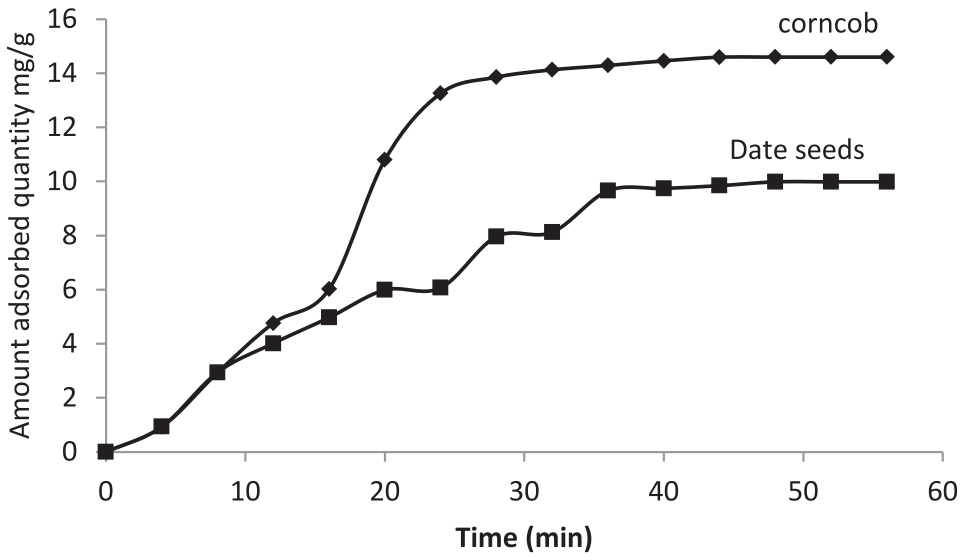

Figure 4: Adsorption kinetics of MB onto corncob and date seeds

The results show that the time required to reach the equilibrium state is 44 min for corncob and 48 min for date seeds. This equilibrium state can be explained by the saturation of the active sites of corncob and date seeds (Consolin Filho, 2007). The kinetic models are represented in Figure 5 and Figure 6. The corresponding kinetic parameters are grouped in Table 1.

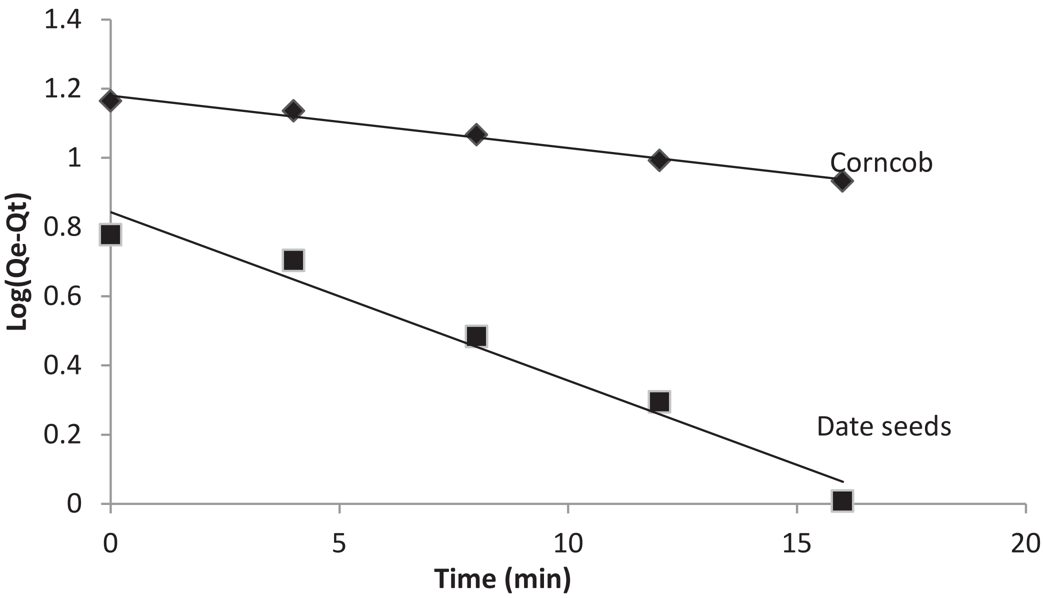

Figure 5: Pseudo-first-order kinetic model of MB adsorption onto corncob and date seeds

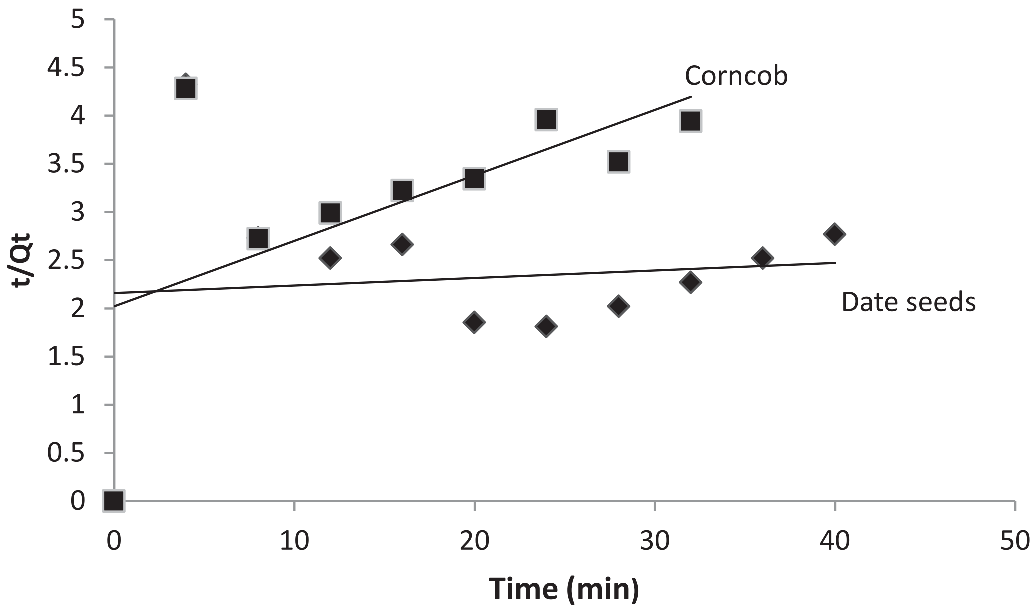

Figure 6: pseudo-second-order kinetic model of MB adsorption onto corncob and date seeds

Table 1: Characteristic parameters for kinetic models

Kinetic model	Parameter	Corncob	Date seeds
Pseudo-first-order (Lagergren, 1898)	Qe (mg/g) exp	14.95	9.98
	Qe (mg/g) cal	15.11	7.97
	K_1 (min^{-1})	0.03	0.12
	R^2	0.98	0.96
Pseudo-second order (Ho and Kay, 2000).	Qe (mg/g) exp	14.95	9.98
	Qe (mg/g) cal	1.3	14.72
	K_2 (mg/g.min)	0.27	0.29
	R^2	0.11	0.34

From these results, it can be seen that in the case of first-order kinetics, the equilibrium-adsorbed quantity determined experimentally is equal to the calculated one, and the determination coefficient is close to 1 for both corncob and date seeds. In contrast, for the second-order kinetics model, the equilibrium adsorbed amount determined experimentally is different from the calculated value, and also the coefficient of determination is lower than 1, which indicates that first-order is well applied for the study of the systems MB/corncob and MB/date seeds.

Isotherm studies

Adsorption isotherms are often used to determine the maximum adsorption quantity of the pollutants and to identify the type of adsorption. Figures 7 and 8 represent the plots of Langmuir and Freundlich models for the studied adsorption system.

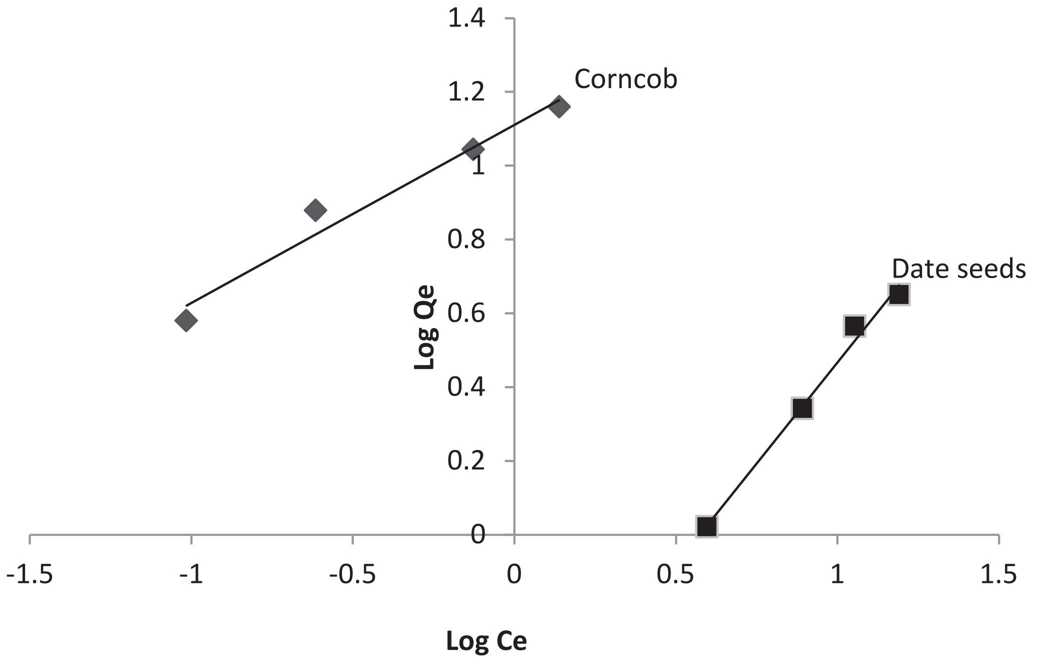

Figure 7: Freundlich isotherm models plots of MB adsorption onto corncob and date seeds

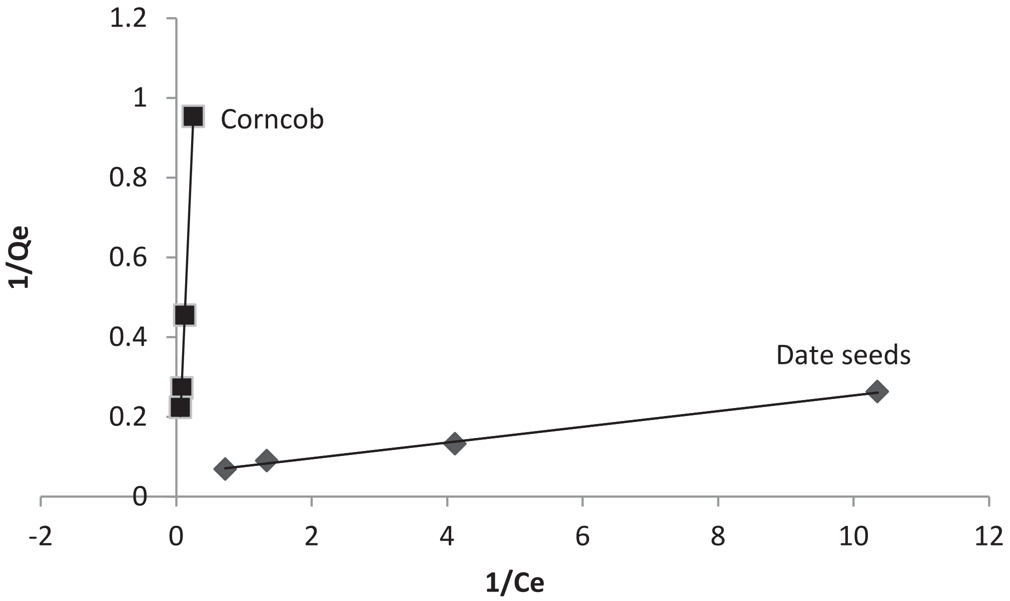

Figure 8: Langmuir isotherm models plots of MB adsorption onto corncob and date seeds

The results, reported in Table 2 and processed according to the Langmuir and Freundlich mathematical models, enabled to calculate the maximum adsorption capacity as well as the adsorption parameters (Table 2).

Table 2: Parameters of the isotherms

Isotherms	Parameters	Corncob	Date seeds
		BM	
	Qmax (mg/g)	16.863	3.508
Langmuir	**k (L/mg)**	3.0886	0.807
(Langmuir, 1919).	R^2	0.998	0.9776
Freundlich	K_f	1.625	13.69
(Freundlich, 1928).	**n**	0.899	2.439
	R^2	0.9833	0.9788

The results show that the Langmuir model describes well the adsorption process of MB on corncob because its correlation coefficient (R^2 = 0.998) is close to 1, while the MB/date seeds data are more fitted to Freundlich isotherm (R^2= 0.9788).

The results of the kinetic and isotherm study indicate that the adsorption of these systems is a first order reaction, which indicates physisorption. The Langmuir model indicates that the distribution of the MB molecules on corncob is done as monolayer, while the Freundlich isotherm with the presence of pseudo-first order model does not confirm this theory for MB adsorption on date seeds, which could be mono or multilayers distribution (Feng et al., 2014; Abou-Gamra and Medien, 2013).

4 Conclusions

The study of methylene blue adsorption mechanisms on corncob and date seeds was subject of this work. The study of adsorption kinetics has shown that the pseudo-first order model is the most suitable one for describing the kinetics of dye adsorption, thus implying a physisorption mechanism. The study of adsorption isotherms has shown that the Langmuir model is suitable for experimental isotherms for corncob, and the Freundlich model for date seeds.

5 Acknowledgements

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HYDROPHOBIC CARBON OF YAM PEELS AS SUSTAINABLE ADSORBENT TO TREAT WATER-OIL SPILLAGE

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Keywords: Crude oil, Yam peels, Activated carbon, Adsorption, Isotherms

Abstract

The potential use of carbonized white yam peels (*Dioscorea rotundata)*, a common food crop in West Africa and Nigeria, was examined as an adsorbent to remove crude oil from contaminated water. The efficiency on the adsorption was investigated through batch studies using direct reading from UV-Visible spectrophotometer. The recovered crude oil was characterized and properties such as viscosity (kinematic and dynamic), pH, density, specific gravity, and API gravity were determined. The thermal properties such as heat of combustion, thermal conductivity, specific heat capacity and latent heat of vaporization were also determined. Proximate analysis was carried out on the raw yam peels, and the physicochemical properties were examined after carbonization. Some of the carbonized yam peels were activated with $ZnCl_2$ and comparatively studied with the raw carbon. The activated carbon was found to be more effective than the inactivated one at removing the oil from water at varying pH (3-13), oil concentrations in water (2.0-5.0 g/L), absorbent dosage (0.2-1.4 g), and contact time (0-80 min). The conditions for maximum adsorption capacity for inactivated carbon (285 mg/g) and activated carbon (316 mg/g) were pH 7, contact time 40 min, adsorbent dosage for activated carbon 0.4 g, and for inactivated carbon 1.4 g. The equilibrium adsorption data were better fit by the Langmuir isotherm for the adsorption of the crude oil on the activated carbon and by the Freundlich isotherm for the inactivated one, as was indicated by their high R^2 of 0.6698 and 0.7569, respectively. On the other hand, the kinetic studies showed that the pseudo second order model had a better fit for the adsorption experiment with R^2 of 0.994 and 0.9693 for the activated and inactivated carbon, respectively. The intra-particle diffusion experiments revealed the influence of film diffusion and external mass transfer.

1 Introduction

Over the last six decades, an estimated 11-15 million tons of oil has been spilled into the Niger Delta ecosystem of Nigeria. Between 1976 and 1996, a total of 4647 incidents resulted in the spilling of approximately 2,369,470 barrels of oil into the environment. Of this quantity, an estimated 1,820,410 barrels (77%) were not recovered (Oviasuyi and Uwadiae, 2010). The inability to effectively manage wastes from oil extraction has numerous socio-economic, health, and environmental implications. The Niger Delta area of Nigeria is home to oil explorations and spills in Nigeria. The Niger Delta is a wetland of about 76,000 km^2 and has the largest mangrove forest in Africa (11,134 km^2) and the fourth largest in the world (Spalding et al., 1997). It is rich in fishery resources providing breeding grounds for numerous species of finfish, prawns and habitats for crabs and mollusks (IPIECA, 1993). The extensive mangrove forest also provides nesting sites for sea and shore birds, stabilizes and protect the coastline, filters and traps water borne pollutants, and provides logs, charcoal, paper pulp, medicinal products (Simeon et al., 2016). The main sources of oil spill on the Niger Delta are vandalism and aging of oil pipelines, oil blow outs from the flow stations, and cleaning of oil tankers on the high sea. Higher concentration of the hydrocarbon molecules, which are the main constituents of crude oil and petroleum products, are highly toxic to living beings, including humans. Petroleum products also comprise trace amounts of sulfur and nitrogen compounds, which are hazardous and can react in the environment to produce secondary poisonous chemicals (Alexander, 1999; van Hamme et al., 2003).

Oil in water constitutes a major contaminant, and researches are ongoing to develop techniques for removing these contaminants especially through low cost agricultural waste. Many authors try to use an efficient and economic way of remediation with available local materials. There are many techniques available for oil-in-water (o/w) separation regardless of being physical, biological or chemical such as gravity separation, chemical treatment methods, flotation system, coagulation, filtration, hydrocyclone, electrical process, reverse osmosis and membrane reactor, which offer advantages and drawbacks over others (Fakhru'l-Razi et al., 2009). Some existing methods are expensive, and sometimes some supplementary treatments are needed in order to achieve the stipulated environmental standards. Among these methods, sorption process has emerged as a highly efficient treatment method due to its simplicity of the design, ease in operation and inert to toxic substances in removing dissolved organic components from water.

Among the various sorbents that have been employed for oil spill remediation, synthetic materials, such as polypropylene and polyurethanes, are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties (Teas et al., 2001). However, these materials are not biodegradable, which is a major disadvantage. Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products. Attempts have been made to use local materials such as wheat straw, sawdust, rice residues, corncob, coconut husk, kenaf, kapok fibers, cotton, wool, and wood (Sun et al., 2003; Vlaev et al., 2011; Ibrahim et al., 2009). The advantages of these materials include being low cost, biodegradable and non-toxic (Tembhurkar and Deshpande, 2011).

White yam, *Dioscorea rotundata,* is a crop commonly grown in Nigeria and West Africa, and consequently yam peels are an agricultural waste that are easily accessible. Due to its abundance, this material can be used as a raw cheap adsorbent for crude oil sorption in aqueous medium. The present study aimed to investigate the adsorption parameters, efficiency and adsorption isotherms for activated carbon made of yam peels and to compare with raw carbon in order to remove crude oil from water. The objectives of this study were (i) to work on a selected biomass that would give a high adsorption capacity of crude oil from oil spills; (ii) to optimize the influence of operational variables such as moisture content, ash content, crude fibre, carbohydrate content etc. on the selected biomass; (iii) to evaluate the adsorption behavior of the selected biomass, kinetically and thermodynamically; (iv) to investigate the effect of various parameters, such as contact time, pH, initial concentration and adsorbent dosage on the biomass adsorption capacity; and (v) to ascertain the optimum adsorption capacity of the selected biomass at the various optimum conditions.

2 Materials and Methods

The crude oil used for this research was obtained from the Warri Refinery and Petrochemical Company (WRPC) in Warri, Delta State of Nigeria. Distilled water was used for solution preparation throughout the experiments. The yam peels were collected from cafeterias within the University of Ibadan, Ibadan North Local Government, Oyo State. The waste yam peels were washed and dried in sunlight for one week. The sundried peels were further dried in an oven at 110 ^{0}C for 1 h and carbonized in a muffle furnace at 400 ^{0}C for another 1 h in the absence of air. The charcoal obtained was allowed to cool, ground, and sieved through a 12 x 40 US Mesh (0.42 to 1.70 mm) to obtain a uniform particle size. Part of the carbon obtained was activated with $ZnCl_2$ according to Awoyale et al. (2012). This resulting activated carbon was then stored in a plastic container until further analysis.

2.1 Physicochemical analysis

Proximate analysis was carried out on the yam peels to ascertain its content for crude protein, fat, ash, moisture content, and crude fibre using methods reported by Azubuike and Okhamafe (2012).

Crude fat was determined by Soxhlet extraction using 2 g of sample. The boiling flasks were weighed correspondingly, labelled and filled with about 300 mL of petroleum ether (boiling point 40 to 60 ^{0}C). The Soxhlet apparatus was assembled and allowed to reflux for about 6 h. After extraction, the petroleum ether was collected in the top container of the set-up and the container was drained. When the flask was almost free of petroleum ether, it was removed and dried at 105 ^{0}C for 1 h in an oven. The flask was taken into a desiccator and allowed to cool. The content of the flask was then weighed.

$$\% \text{ Fat} = \frac{\text{Weight of Fat}}{Weight\ of\ sample} \times 100 \qquad (1)$$

Ash content was determined using the drying ash procedures. Water and other volatile materials were vaporized and organic substances were burned in the presence of the oxygen in air to CO_2, H_2O and N_2 in a high temperature muffle furnace capable of maintaining temperatures between 500 to 600 ^{0}C. The sample was weighed before and after ashing to determine the concentration of ash present. 1 g of the sample was weighed and placed in a furnace at 550 ^{0}C. The process was carried out for 1 h, after which the sample was allowed to cool in a desiccator and then weighed.

$$\%\text{ASH (dry mass)} = \frac{\text{Mash}}{\text{Mdry}} \times 100 \qquad (2)$$

Where Mash refers to the mass of the ashed sample and Mdry refer to the original mass of the dried sample.

Moisture content was determined by weighing 1 g of the sample and drying at 110 ^{0}C for 5 h in an oven, cooling in a desiccator and weighing. The procedure was repeated thrice for the sample and the average was determined.

$$\%\text{ Moisture content} = \frac{\text{weight of the moisture evaporated}}{\text{weight of sample}} \times 100 \qquad (3)$$

Crude fibre

1 g of sample was weighed into a 500 mL conical flask and 100 mL of the digestion reagent (trichloroacetic acid) was added. This was boiled and refluxed for 40 min. The resultant was filtered through a 15 cm of No. 4 Whatman paper and washed 6 times with hot water and once with methylated spirit. The paper was then opened, the residue removed with a spatula and the fibre transferred to a silica dish. The residue was dried overnight at 105 ^{0}C, then transferred to a desiccator and weighed when cooled. It was ashed at 600 ^{0}C overnight in a muffle furnace, cooled in a desiccator and weighed.

$$\%\text{ Fibre} = \frac{\text{Difference in weighing}}{Weight\ of\ sample} \times 100 \qquad (4)$$

2.2 Batch adsorption experiments

The sorption isotherm and kinetics experiments were performed by batch adsorption techniques, which were carried out by agitation of specific amounts of the sample (activated and inactivated carbon of the yam peels, respectively) in 50 mL of the oil/water mixture at room temperature (26 ^{o}C) in an orbital shaker. Several parameters influence the uptake on the adsorbent, so studies were undertaken to choose the best conditions. The adsorptions were carried out at various pH. The pH of the working mixtures was adjusted to the desired value with 0.1 M HCl or 0.1 M NaOH. Contact time and different initial crude oil-in-water concentrations and adsorbent dosage were varied. At the end of a preliminary determined period of time, samples were withdrawn by vacuum filtration and analyzed using UV adsorption spectrophotometer (UV-1800 UV-Vis Spectrophotometer-SHIMADZU) at the Department of Chemistry, University of Ibadan to obtain the final concentrations of the oil in the sample. The amount of crude oil adsorbed per unit mass of adsorbent at equilibrium (q_e mg/g) and at time t (q_t) was calculated according to the following relations:

$$q_e = (C_o - C_e)\,\frac{v}{m} \quad (1) \qquad \text{and} \qquad q_t = (C_o - C_e)\,\frac{v}{m} \quad (5)$$

Where C_o and C_e are the initial and final concentrations of the sample in g/L, v is the volume of the crude oil-water mixture in L, and m is the amount of adsorbent used in g.

The percentage of oil removed was determined using the equation (6):

$$\%\ \text{Removal} = (C_o - C_e)\,\frac{100}{Co} \qquad (6)$$

Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of adsorption isotherm and adsorption kinetics, respectively.

3 Results and Discussion

3.1 Characterization of yam peels and carbonized yam peels

The result of proximate content (w/w %) shown in Table 1 presents a relatively low amount of 5.81 % of moisture, and an ash content of 4.99 %, crude fibre of 11.40 %, crude protein of 10.58 %, and crude fat of 0.61 %. The low crude fibre value of the yam peel obtained indicates that it could make a good activated carbon, as confirmed by others (Ekpete, 2011). Crude protein (10.6%) is an organic compound, and low organic material is necessary to produce activated carbon with low ash content (Nurul'ain, 2007). The percentage of carbohydrate was obtained from the sum of all compounds present in the sample subtracted from 100.

Table 1: Proximate analysis of yam peels

Parameter	Value (w/w %)
Moisture content	5.81
Ash content	4.99
Crude Fibre	11.4
Crude Protein	10.6
Crude Fat	0.61
Carbohydrate (CHO) Content	78.0

The parameters for the characterization of the activated yam peel are summarized in Table 2, which shows that the bulk density is 0.21. Generally speaking, the lower the bulk density, the higher are the porosity and the surface area. This means that it is a good quality carbon to be activated.

Table 2: Characterization of the carbonized yam peels

Parameter	Value
Moisture content	0.50%
Ash content	14%
Bulk Density	0.210 g/cm^3
Carbon yield	69%
Particle size	1.00 mm

3.2 Batch adsorption

3.2.1 Effect of contact time on adsorption

Adsorption is a time dependent process. In order to design and to evaluate the sorbent performance of oil removal, it is important to know the rate of sorption. An initial concentration of 8.0 g/L of crude oil was prepared. 0.3 g of the adsorbent was used, varying the time from 0 min to 80 min at 5 min intervals, and 20 min intervals after 40 min. The adsorption was carried out in 15 mL (0.015 L) of crude oil-water mixture.

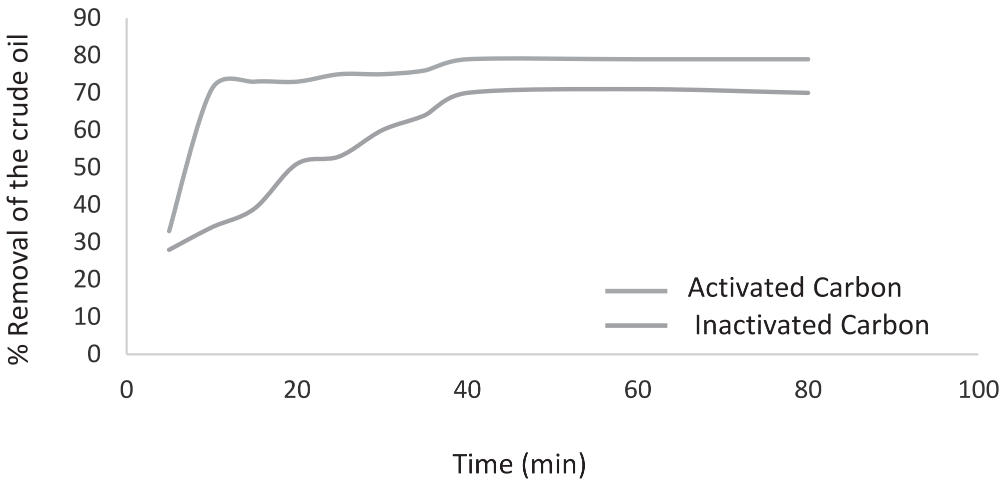

Figure 1: Percentage removal of crude oil versus contact time (min)

For both sorbents, it was found that there was an increase in the percentage removal until 40 min where the maximum removal was attained. The highest sorption capacity obtained were 285 mg/g and 316 mg/g for the inactivated and activated carbon. respectively. During the adsorption process, the particles of the crude oil attach to the surface of the adsorbent by forces of attraction and occupy/clog the available sites. The longer the time of contact, the more the available sites would be occupied until all the adsorbent sites are filled up. This is when the breakthrough time is achieved and no more adsorbate can be adsorbed. The plot percentage of removal against time becomes constant.

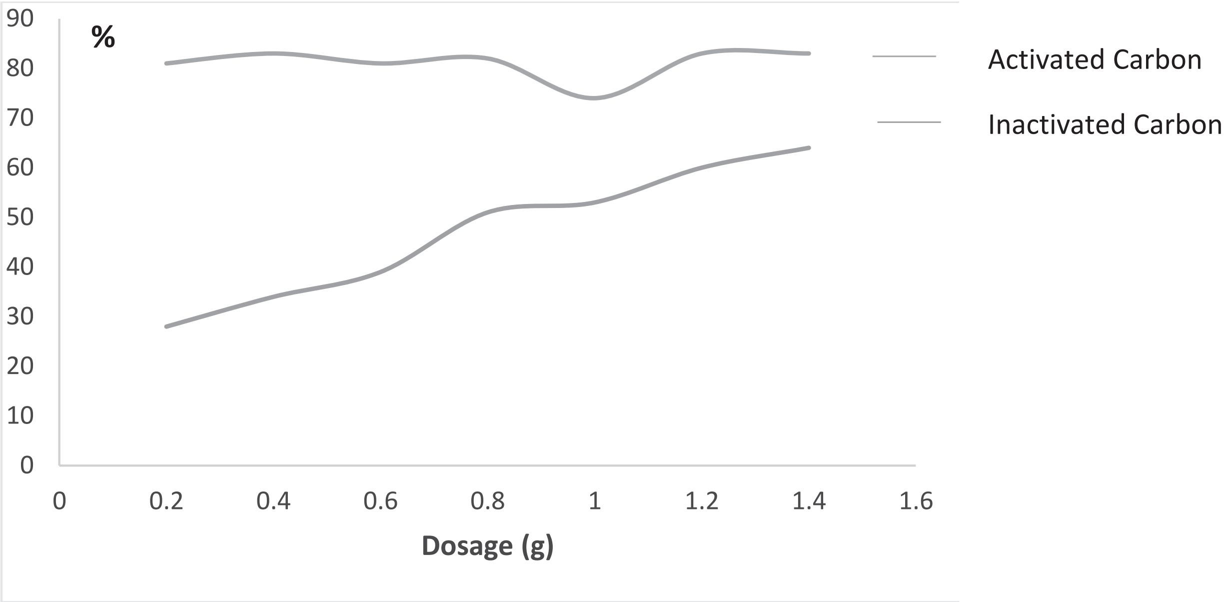

Figure 2: Percentage removal of crude oil versus adsorbent dosage (g)

3.2.2 Effect of dosage on adsorption

The effect of the adsorbent dose on the oil sorption capacity is shown in Figure 2. As the mass of the sorbents increased from 0.2 g to 1.4 g, a corresponding increase in the oil sorption capacity was observed which was primarily due to an increase in the surface area as well as the availability of more active binding sites (Nwadiogbu et al., 2014). The maximum adsorption capacity was obtained at 0.4 g and 1.4 g for the activated and inactivated carbon, respectively.

3.2.3. Effect of concentration on adsorption

The study on the effect of initial concentration on oil sorption onto activated and inactivated carbon of yam peels sorbents was carried out by varying the initial oil concentration from 2.0 g/L to 5.0 g/L at 0.5 g/L intervals, while other parameters like sorbent dosage (20 mg/mL), contact time (10 min) and pH (6.5) were kept constant. The results show that an increase in the initial concentration of the crude oil-water solution resulted in an increase in the percentage removal of crude oil for both adsorbents. The maximum sorption capacity was obtained at 4.5 g/L, after which there was a decrease in the percentage removal (Figure 3). This is because all sorption sites on the sorbent surfaces were completely occupied by oil, and this hindered more oil to be adsorbed. Increasing the initial concentration would increase the mass transfer driving force, and, therefore, the rate, at which molecules pass from the bulk solution to the particle surface. This would result in a higher adsorption capacity. When the sites at the sorbent are occupied, there would be opposition to the mass transfer driving force, which would lead to desorption (Kermani et al., 2008).

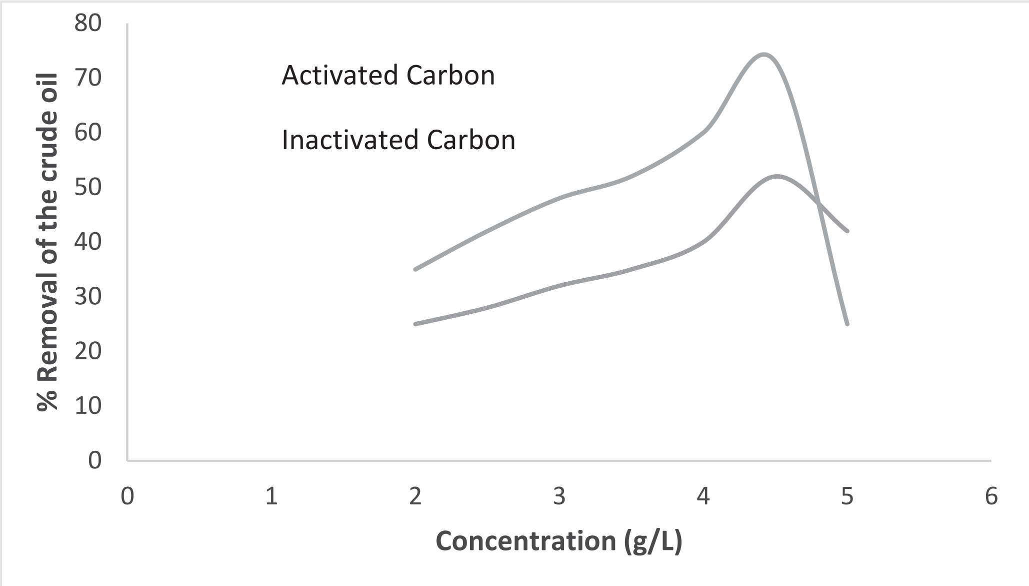

Figure 3: Percentage removal of crude oil versus concentration (g/L)

3.2.4 Effect of pH on adsorption

The pH of the solution is a crucial parameter to study the sorption process, as it influences the solute chemistry and surface binding sites of the sorbents (Ibrahm et al., 2010). The pH was varied from 3 to 13 at an interval of 2, while sorbent dosage, concentration and contact time were kept constant. An increase of the pH of the crude oil-water system resulted in an increase in the percentage removal of crude oil by the adsorbents at pH 3 to 7 and a decline in removal efficiency from pH 7 and above (Figure 4). As noticed by Low et al. (1995), the functional groups on the surface of the adsorbent is repulsively associated with hydroxonium ions (H_3O^+) at low pH, which invariably reduce the removal efficiency of organics during adsorption.

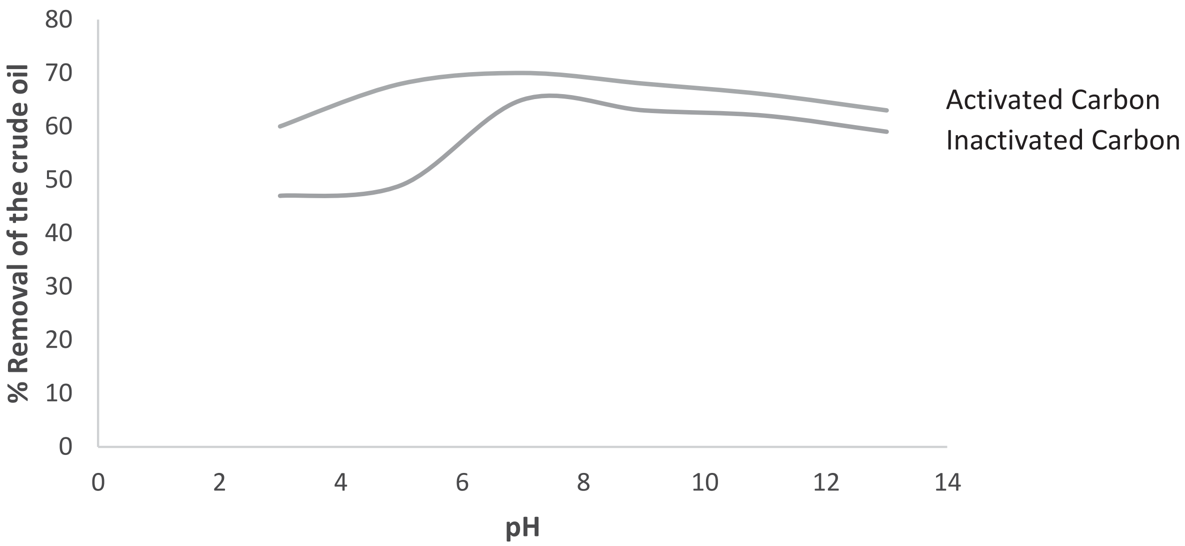

Figure 4: Percentage removal of crude oil versus pH

3.3 Sorption isotherms

In order to study the distribution of the adsorbed molecules between the liquid system and solid phases in the equilibrium state, sorption data were analyzed with the use of isotherm models. The sorption isotherm represents the relationship between the amount of adsorbate removed from the liquid phase and the unit mass of the adsorbent at constant temperature. This is crucial for a better understanding of the fundamental aspects of the sorption process and for optimizing the use of sorbents in the oil removal process (Sokker et al., 2011). The Langmuir and Freundlich isotherm models were used to test the adsorption efficiency of the carbonized samples in treating oil spill.

The model equations are the following:

Langmuir: $$\frac{Ce}{qe} = \frac{1}{bQ} + \frac{Ce}{Q} \qquad (7)$$

Freundlich: $$\text{Log } q_e = \log K + \frac{1}{n}\log C_e \qquad (8)$$

Where, q_e is the amount of oil adsorbed per gram of sorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), Q and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively, K and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Table 3).

The equilibrium parameters can provide useful information on the sorption mechanism, surface properties and affinity of the adsorbent. Therefore, the most suitable correlation of the equilibrium curves needs to be determined to optimize the conditions for designing adsorption systems (Vaghetti et al., 2008).

Table 3: Adsorption isotherms

Isotherms	**Parameters**	**Values**	
		Activated Carbon	**Inactivated Carbon**
Langmuir	Q	0.0605	-0.0393
	B	-5.3184	-0.2728
	R^2	0.6698	0.6076
Freundlich	K_F	0.057	0.01
	N	-12.94	0.4202
	R^2	0.0012	0.7569

3.4 Kinetic models

The surface chemical interactions between solute and sorbent surface active sites can be either physical (physisorption), chemical (chemisorption) or a combination of both depending on the interaction forces involved. Several chemical reaction kinetic models have been reported to describe these interactions, and the most widely used are the pseudo-first and pseudo-second order models. Whilst the pseudo-second model predicts the behavior over the entire range of the adsorption process, the pseudo-first order model is applicable over the initial stage. Both models assume that the sorption process is a pseudo-chemical reaction, but while pseudo-first order model assumes that the rate of occupation of binding sites is proportional to the number of the unoccupied sites of the adsorbent, pseudo-second order assumes that the rate of occupation of binding sites is proportional to the square of the number of unoccupied sites on the adsorbent surface. The pseudo-first and pseudo-second order models can be expressed in a linear form as shown below:

Pseudo-first order: $$\text{Log}\,(q_e - q_t) = \log q_e - \left(\frac{k1}{2.303}\right) t \qquad (9)$$

Pseudo-second order: $$\frac{1}{qt} = \frac{1}{\text{k2 qe2}} + \frac{t}{\text{qe}} \qquad (10)$$

Where q_t and q_e, respectively, are the initial (t = 0 min) and time t (min), and equilibrium sorption capacities (mg/g), k_1 (g/mg.min) and k_2 (g/mg.min), respectively, as well as the rate constants of the pseudo-first order and pseudo-second order.

It is generally known that the sorption process is a rate-controlled process, in which the slowest step determines the process rate limiting step. The kinetic data were further analyzed assuming that the mechanism of oil sorption can generally be described by four consecutive rate controlling steps, which are external mass transfer (transport from the bulk solution to the sorbent surface), film diffusion (diffusion across the liquid film from the sorbent surface), intraparticle diffusion (pore diffusion, surface diffusion or combination of both mechanisms), and surface interactions at active sites (Ho et al., 2000; Ocampo-Pérez et al., 2012). Most of the time, only film and intraparticle diffusion are considered as the rate limiting steps, since the process of external mass transfer and chemical surface interaction are generally rapid. The rate limiting step of the sorption can be qualitatively determined by analyzing kinetic data using the Weber-Morris model (Ofomaja, 2010):

$$q_e = K_i t^{0.5} + C \qquad (11)$$

Where, k_i is the diffusion coefficient (mg/g.min$^{0.5}$) and C is a constant that gives an indication of the thickness of boundary layer. The sorption process is said to be intraparticle diffusion controlled, if the straight line plot passes through the origin, while the boundary layer diffusion (external mass transfer or film diffusion) may take place, if it does not pass through the origin (Ho et al., 2000). The plot for both the activated and inactivated carbon did not pass through the origin indicating external mass transfer or film diffusion. The high R^2 values indicate applicability.

Table 4: Kinetic models

Models	Parameters	Values	
		Activated Carbon	Inactivated Carbon
Pseudo-first order	K_1	0.0131	-0.0269
	Q_1	0.0378	0.0798
	R^2	0.0220	0.2460
Pseudo-second order	K_1	0.3391	1.1654
	Q_1	0.3166	0.3282
	R^2	0.9693	0.9940
Intraparticle diffusion	K_{ipd}	0.0327	0.0338
	R^2	0.6653	0.9126
	C_1	0.1010	0.0327

The relationship between log $(q_e - q_t)$ and time in the pseudo-first order kinetics was not linear over the entire range for the adsorption of oil onto both the activated and inactivated carbon compared to the pseudo second order kinetics. In addition, the best fitting of the equilibrium data, which was the pseudo-second order kinetics is indicated by the high R^2 values obtained.

4 Conclusion and Recommendations

This study has shown that yam peels, which is an agricultural waste product, can be used to develop a carbonized adsorbent material with good surface characteristics for the removal of crude oil from water. Yam peels based carbon performs best, when activated after carbonization. While the activated carbon required a much lesser dosage (0.4 g) for optimum adsorption, the inactivated carbon required substantially more (1.4 g). Adsorption with the activated carbon was a clean process without any color impact from the carbon unlike that of the inactivated carbon. The optimum conditions for adsorption for both the activated and inactivated carbon from the yam peels were: pH 7.0, contact time 40 min, and an optimum oil concentration of 4.5 g/L. The experimental evidence indicates that oil removal from suspended oil-in-water system was controlled by a physical phenomenon with film diffusion as the rate-limiting step, which is similar to those results previously reported for dispersed oil-in-water sorption studies.

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QUALITY AND POTENTIAL USE OF WATER FROM GREEN ROOFS MADE WITH TETRA PAK® CARTON BOXES

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Keywords: Low impact development, Storm water runoff, Urban drainage, Water quality

Abstract

In urban areas, where building coverings make up a large fraction of the landscape, the application of green roofs may be a way of partially offsetting the environmental and hydrological damages. Conventional roofs, which do not allow water retention and accelerate rainwater flow, once vegetated, can store part or all of rainwater, reducing runoff volume. This study aims to evaluate the quality of drained water from two experimental green roofs targeting the potential use of this water for non-potable purposes. For this, two small experimental green roofs made with Tetra Pak® boxes were built. After precipitation, water samples were collected from water reservoirs and sent for laboratory analysis. There was always a sample of each green roof and a third sample (reference) corresponding to rainwater collected from the atmosphere. Physical, chemical and microbiological parameters were evaluated and the quality of the green roof water was compared with the reference sample. After nine months of study, it was verified that the green roofs did not offer improvement in rainwater quality. However, comparing the results over time, an improvement in the general water quality was noticed, proving that the age of green roofs interfere with the drained water. It was also possible to conclude that green roofs made with carton boxes can be efficient and durable, allowing to install them in homes or small buildings. Moreover, when assembled from recycled material, they can become an affordable, inexpensive and an environment-friendly alternative.

1 Introduction

In the world, the number of urban areas increased from 600 million in 1920 to 2 billion in 1986, and it is estimated that the urban population will occupy 80% of the world's territory by the year 2100 (Santamouris et al., 2001). In Brazil, researches indicate that more than 84% of the population is already concentrated in urban areas, mainly in the Southeastern, Midwestern and Southern regions (Instituto Brasileiro de Geografia e Estatistica, 2010). It is common urbanization processes resulting in adverse effects on the environment, such as quality impairment of water bodies and changes in the urban hydrological cycle, mainly due to the reduction of green areas and waterproofing of the soil, resulting in an increase in surface runoff and aggravation of floods (Tucci, 2005). With no prior planning, urban drainage problems grow concomitantly with the development of urban areas in Brazil.

Particularly floods are considered as natural disasters characterized by high frequency and low severity in terms of deaths. They account for a large proportion of damage to local infrastructure, housing, and the living conditions of communities and low-income societies (Freitas & Ximenes, 2012). In the search for a solution to these and other social, environmental and economic problems, unconventional measures are being sought, highlighting improvement in the process of infiltration, retention of flows in reservoirs and/or delay of flow in river and river gutters, among others (Canholi, 2014).

Several techniques have been adopted, mainly in the scenario outside Brazil, in order to mitigate the negative environmental impacts resulting from urbanization (Souza et al., 2012), among them the American Low Impact Development (LID) approach. The LID strategy seeks the qualitative and quantitative conservation of hydrological processes, mitigating the effects of urbanization, by directing surplus flows to vegetated areas, taking advantage of natural control and treatment. In this way, alternative means of controlling the pluvial flow next to its source can be adopted, aiming at minimizing (or even eliminating) the volumes and peak flows to values close to those that occurred in the stage before the urbanization process. This type of technique should preferably be inserted in the natural landscape with low visual impact and using the nature to promote the management of rainwater (USEPA, 2003). To this end, small bioretention, landscaping with rainwater, rainwater harvesting, infiltration trenches, permeable pavements and green roofs have been used (Tassi et al., 2014).

Regarding green roofs, their benefits include the mitigation of heat islands in urban areas, improvements in thermal comfort benefits of ecosystem services and aesthetic value as well as rainwater retention and detention (Jarret & Berghage, 2017). Green roofs are usually constructed by placing a drainage system, a planting medium and vegetation on a waterproof surface on a roof (EPA, 2014). The vegetation, the planting medium and the drainage system act controlling the superficial rainfall through interception processes, water storage and evapotranspiration (Yang et al., 2008). For these reasons, the adoption of green roofs becomes an ecological and efficient option for regions with surface urban drainage problems. Additionally, if the extra runoff is diverted to a reservoir, this water can be used for non-potable purposes, contributing to drinking water sources conservation.

The United States Environmental Protection Agency (EPA, 2010) recalls that although many studies have focused on the efficiency of green roofs in reducing the amount of surface runoff, few studies have focused on their impact on the quality of drained water, and there is much controversy about the results. Some studies indicate that green roofs have the capacity to improve rainwater quality, sequestering pollutants and reducing their concentrations in the storm water (Berndtsson, 2009; Carpenter & Kaluvakolanu, 2011; Gregoire & Clausen, 2011). Other studies, however, point to opposing results, in which green roofs would serve mainly as a source of pollutants (Moran, 2005; Pessoa, 2016), or even that the slope (Moruzzi, 2014) and the previous soil moisture (Pessoa, 2016 & Moruzzi, 2014) influence the transport of material from the roof to the storm water drainage system, directly influencing the quality of water bodies.

Furthermore, to achieve higher efficiency and sustainability, there might be also the possibility of employing green roof water for internal and external domestic uses, such as household washing, toilet flushing, irrigation and potentially human consumption (Ngan, 2004). Around 20% of domestic water consumption is used in toilet flushing, while 34% in gardening activities (EPA VICTORIA, 2006). In addition, water collected from green roofs can be used to irrigate the plants of the green roof itself in times of scarcity.

This research consisted of a qualitative monitoring of two experimental modular green roofs, assembled with reused Tetra Pak carton boxes. Tetra Pak® carton boxes are a common part of consumption habits of Brazilians, making them a constant item in their waste baskets. Due to their physical characteristics, green roofs made with Tetra Pak® cartons can present good results in terms of thermal and acoustic control. Besides, this proposal is a way to reuse products that do not have adequate destination guaranteed in Brazil, so this initiative can minimize problems related to the environment and be adopted in environmental educational projects.

The objective of this research was to verify the quality improvement or impairment of the water drained from the green roofs in comparison with the water collected directly from the atmosphere during precipitation events, and to evaluate its potential use for non-potable domestic purposes such as toilet flushing, irrigation of lawns and ornamental plants, washing vehicles, and cleaning sidewalks and streets, etc.

2 Materials and Methods

Assembly of the green roofs

In March 2016, two experimental green roof units were installed in an experimental area of the Federal University of Santa Maria (UFSM), in the city of Santa Maria in southern Brazil in order to simulate the behavior of small green roofs. They were settled over two benches with surface area of 1.6 m² and positioned 1.2 m from the ground. The slope was one degree from the center, so each bench simulated a two flap roof. The support system adopted for the green roofs was extensive and modular. A green roof is called extensive, when it has a small layer of planting medium, making it light and, therefore, easily implanted in building covering. The system is called modular, when built in "pieces", which means in detachable parts that allow an easy upkeep of the green roof. If problems occur, one can simply replace the damaged part with a new module, and there is no need to dismantle any structure.

Regarding the aspects of the support system, it is important to note that Tetra Pak® carton boxes are suitable for use in both modular and extensible forms. Therefore, these boxes were used as basis for the assembly of modules to constitute a small experimental green roof. In the development of this project, 176 Tetra Pak® carton boxes measuring 20 x 7 x 7 cm and removable lid were made use of. The carton boxes are usually found in Brazilian commerce as one liter containers for milk or juice.

In order to have one side of the box to be fully opened and to allow vegetation to be planted in, the largest face (20 x 7 cm) opposite the lid was extracted that allows the packaging to drain. This pattern was determinant to employ the opening to release the water from the bottom of the green roof, allowing the drainage of excess water that had not been trapped in the soil. Without this prediction, the soil could be permanently saturated, leading to the decay of the vegetation.

After removing one of the faces of each box, the sides would be opened, and Tetra Pak® multilayers would be exposed. Thus, in an attempt to prevent damage to the carton boxes and to reinforce the roof structure, the open edges were protected with a geotextile blanket followed by the pieces that were cut out before. Then, the cartons were folded, cut in the longer half and positioned them on the geotextile blanket already accommodated, making the union between the sides of two boxes. With the aid of a paper punch, two holes on this set were made and the boxes were joined with plastic clamps. To build modules, boxes were grouped five by five, directing the lids to the same side. In Figure 1, it is possible to see the cutout on the faces of the carton boxes (A) and the modules after their assembly (B).

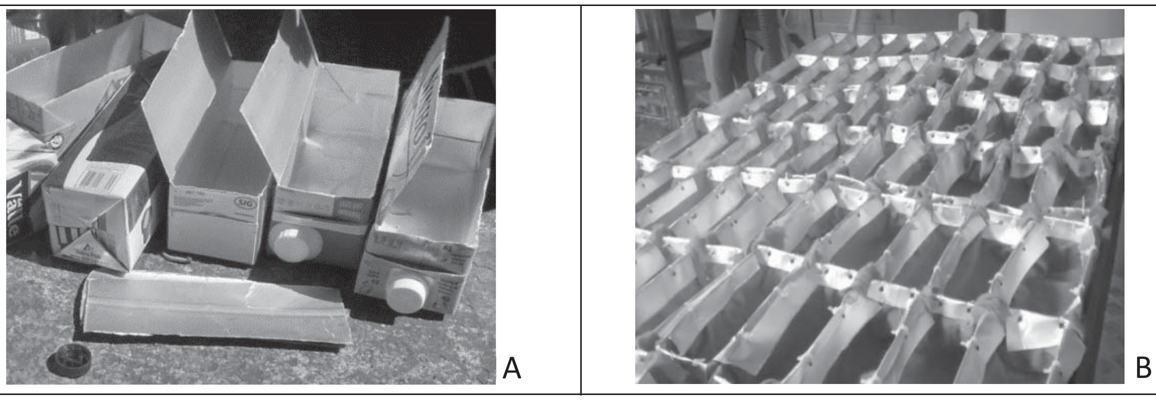

Figure 1: (A) Process of cutting Tetra Pak® boxes to assemble the modules. (B) Tetra Pak modules after assembly

On the surface of each bench, a waterproofing and drainage system was installed, on which the support system of the green roof was put, formed by Tetra Pak carton boxes. Inside the boxes, a geotextile blanket was fit to prevent the loss of planting medium material by leaching. Under the benches, four drains were installed two in each side of the roof in order to guide the excess flow to the reservoirs.

On the geotextile blanket, in each box, the planting medium was placed approximately 6 cm deep. It was composed of local soil, vermiculite and soil conditioner, mixed in a ratio of 3: 1: 1, respectively. After mixing the components, a sample was sent for physicochemical analysis. Thus, the soil used at the beginning of the experiment was rich in Calcium, Magnesium, Potassium and organic matter, presenting 28% of clay.

The plant species used were *Sedum rupestre* (SR) and *Callisia repens* (CR), popularly known as Sedum and Turtle Vine (or Bolivian Inchplant) (Figure 2). The benches were assembled with a central partition, so each species was planted separately, one on each side of the benches. The general structure of the experimental green roofs and the distribution of the plants on the benches can be seen in Figure 3.

A B

Figure 2: (A) Plant species *Sedum rupestre* (SR). (B) Plant species *Callisia repens* (CR)

A B

Figure 3: (A) General structure of the benches with green roof at the top and reservoirs below. (B) Distribution of plant species, *Sedum rupestre* on the left and *Callisia repens* on the right

Qualitative water monitoring
During rainfall, the excess flow, i.e., water that was not retained on the green roof was drained by hoses connected to the base of the top to four reservoirs of 25 L each, installed below the bench system. The drainage systems were independent from each other in order to avoid mixing the drained water on each side of the bench. After rainfall events, water contained in the reservoirs were homogenized, and proceeded with the water sampling of each reservoir, identification and referral for laboratory analysis.

The quality of the green roof waters was compared with the qualitative situation of the rainfall collected directly from the atmosphere (reference sample) by means of an open bottle, installed in support for this purpose. The comparison between the samples allowed evaluation of the compromise or improvement of the quality of rainwater after passing through the green roofs. Thus, after each rain event, two samples of green roof water were collected, one characterized by the plant species *Sedum rupestre* and the other by the species *Callisia repens*, and a third sample collected directly from the water precipitated from the atmosphere (reference).

The laboratory analyses were performed at intervals of two weeks during the first months of evaluation, however, the exact period between collections varied according to the occurrence of rainfall. For each rainfall event, physical and chemical analyses were performed for three samples (Figure 4). Only the samples drained from green roofs were sent for microbiological analyses, since the reference sample did not cover any physical surface before being collected.

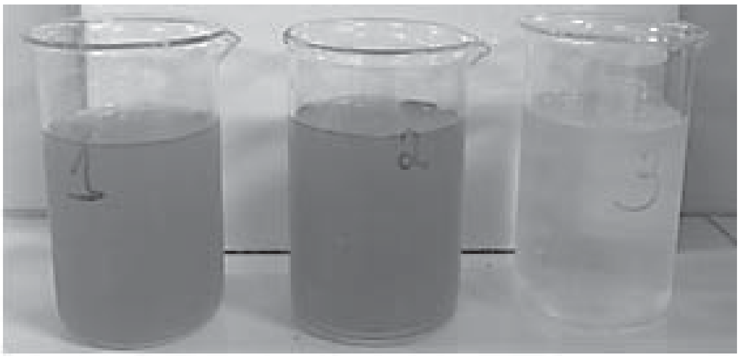

Figure 4: Beakers with the following samples (left to right): water drained from the modules with CR (1), water representative of the modules with SR (2), and reference sample (3).

The parameters of analysis were chosen based on the review of similar works (EPA, 2014; Pessoa, 2016; Glass, 2007), financial resources available to purchase material and payment of analyses as well as instruments provided by the Laboratory of Engineering and Environment (LEE), UFSM. Analyses of the physical parameters (Turbidity, Apparent and True Color, Total Solids, Total Dissolved Solids and Suspended Solids) were performed in the LEE as well as microbiological parameters (Total Coliforms and Thermotolerant Coliforms – E. coli) and pH. The other chemical parameters (Phosphate, Nitrate, Nitrite, Chlorine and Sulphate) were determined by the Laboratory of Forest Ecology (LABEFLO), Department of Forestry Sciences, UFSM.

The analytical results were compared, verifying the difference between the quality of the water passing through the substrates and the water collected directly from the atmosphere. The comparison also made it possible to verify the difference in the action of each plant species on water quality and their ability to adapt to green roof conditions and local climate.

3 Results and Discussion

Water Quality

The results from qualitative analyses showed that, in relation to the physical, chemical and biological aspects, the green roofs did not contribute to an improvement of the quality of precipitated water compared with the water samples collected directly from the atmosphere during the precipitations. However, the content of the chemical parameters (Chlorine, Nitrate, Nitrite, Sulphate and Phosphate) in some rain events was reduced by the action of the green roof. In addition, the results indicate changes in green roof water quality compared with the reference samples and also between green roofs with plant species *Sedum rupestre* and *Callisia repens*.

The physical parameters apparent color, true color, turbidity, total solids (TS), total dissolved solids (TDS), total suspended solids (TSS) and pH were analyzed in all nine samples (Table 1). The other chemical and microbiological parameters were analyzed in events considered more typical, that is with higher rainfall volumes.

Table 1: Physical analyses results separated by date of collection, rainfall volume and concentration of TS, TDS and TSS leached in each rain event

Event	Date of collection	Rainfall Volume (mm)	TS (mg/L)		TSS (mg/L)		TDS (mg/L)	
			CR	SR	CR	SR	CR	SR
1	03/21/2016	50.5	848	991	126	360	722	630
2	04/07/2016	10.6	180	201	31.5	39	148	162
3	04/25/2016	26.5	422	427	47	59	375	368
4	05/09/2016	18.5	224	212	53	46	171	166
5	05/30/2016	7.3	242	280	44	130	198	150
6	07/06/2016	24.2	207	227	1	1	206	226
7	08/08/2016	18.3	197	67	90.5	17.5	106	49.5
8	10/06/2016	48	221	204	32	29.5	189	174
9	12/19/2016	14.5	274	274	113	66	161	208

TS (total solids), TDS (total dissolved solids), TSS (total suspended solids), CR (Callisia repens) and SR (Sedum rupestre)

One can see that in the first rain event the amount of solids carried by the water is much higher than in the following events. This is due to the fact that in the first event the particles of soil were still very loose, since the assembly of the experiment had occurred only two days before, and there was no time for the planting medium to form soil aggregates.

The plant species *Callisia repens* did not withstand the winter frosts, and in July, they were already dead in practically every part of the green roof. For this reason, it is believed that in the seventh event, the large volume of leached solids of these modules, outside the pattern of behavior previously observed, and not compatible with the behavior of the species *Sedum*, is due to the organic matter of the Turtle Vine (in decomposition process) being carried along with the planting medium by the water. In addition, with the dead plant, the effect of the roots also extinguishes, releasing particles and nutrients until then retained.

The turbidity in the water of green roofs is caused by suspended solids, such as clay, silt and organic matter. Dissolved solids, on the other hand, are directly related to true color levels (Pessoa, 2016). One can make these comparisons by observing the data in Table 2 and the data set in Table 1.

Table 2: Turbidity and true color values observed in the analyzed samples

Event	**Turbidity (NTU)**			**True Color (Mc)**		
	CR	**SR**	**Reference**	**CR**	**SR**	**Reference**
1	82.6	99.3	0.53	86.6	52.8	0
2	18.7	26.6	0.69	104	139	0
3	134	138	2.25	500	500	0
4	92	79.7	0.02	500	500	0
5	86.2	90.6	0	500	472	0
6	42	36.5	1.14	314	364	20.3
7	45.8	16.2	2.74	209	167	40.3
8	61	48	3	435	391	0
9	29.8	9.7	2.5	295	312	17.9

CR (Callisia repens) and SR (Sedum rupestre)

It is possible to note that the turbidity measured in the collected water samples decreased gradually over time, but not linearly and not related to the registered rainfall volume. However, the same does not occur with color parameters, which has its growth evidenced in the third rain event with slight slope after the sixth one. The presence of color and turbidity in the reference samples is due to the accumulated dust in the atmosphere and the wind action. It was common to find leaves of trees or small insects in the collecting container.

The green roof with the species *Callisia repens* was more efficient in the retention of suspended particles until Event 6 in July (winter time in Brazil), when the plants do not resist the constant occurrence of morning frosts, a phenomenon common in the southern region of Brazil. The condition of the plants during the monitoring period can be seen in Figure 5, and the chemical parameters are given in Table 3.

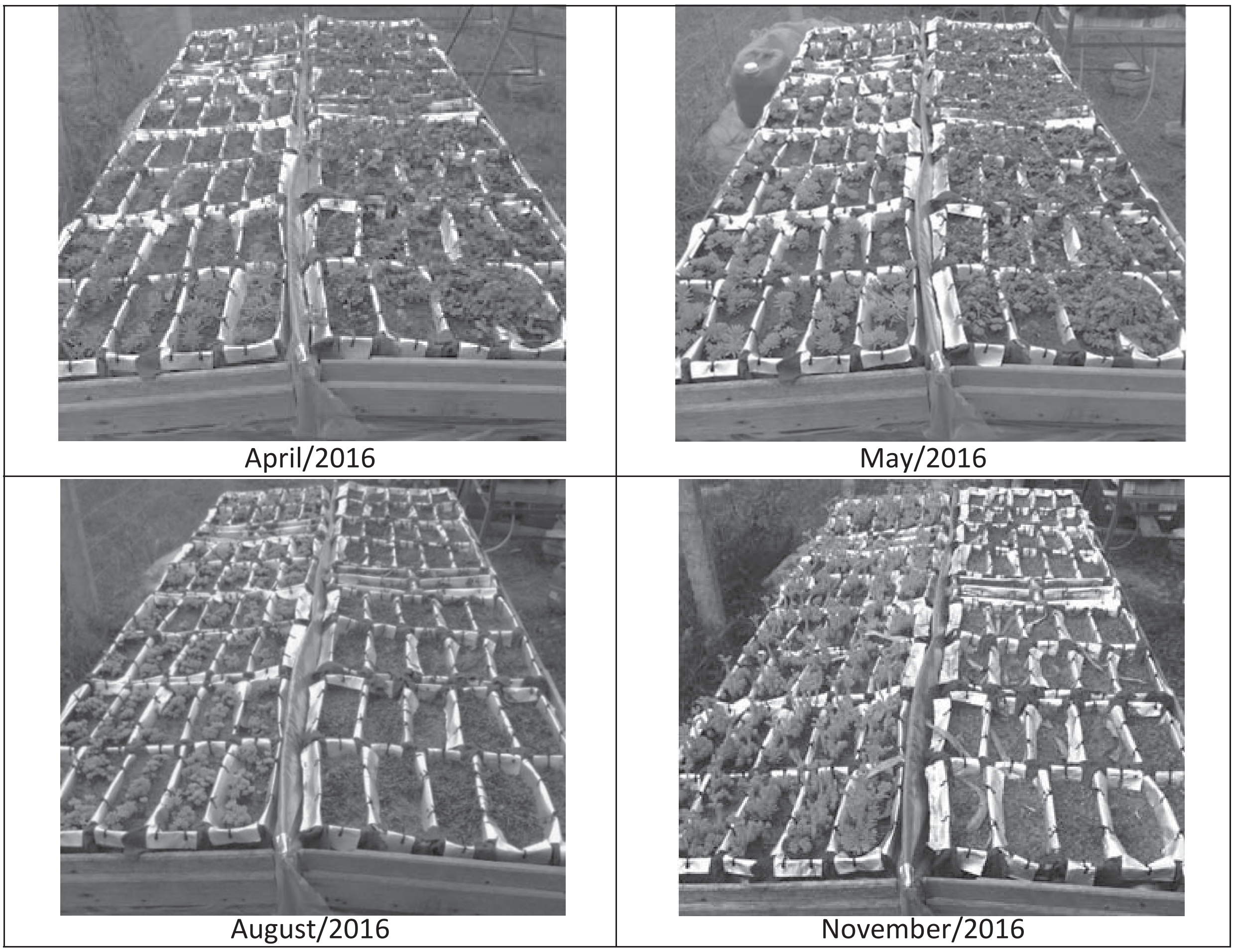

Figure 5: Plants' phytosanitary conditions over time. *Sedum* (left) and Turtle Vine (right side)

Table 3: Chlorine, Nitrite, Nitrate, Phosphate and Sulphate contents present in the samples

Parameter	**Chlorine (mg/L)**			**Nitrite (mg/L)**			**Nitrate (mg/L)**			**Phosphate (mg/L)**			**Sulphate (mg/L)**		
Sample	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Event 1	54.0	63.9	0.54	0.15	n.d.	n.d.	283	351	0.89	0.36	0.36	0.31	17.8	21.8	0.59
Event 2	9.55	12.8	0.18	0.26	0.3	n.d.	3.14	3.38	0.54	0.59	0.54	n.d.	5.10	9.15	0.46
Event 3	1.61	3.25	0.25	n.d.	n.d.	n.d.	0.20	0.16	0.7	1.01	0.78	n.d.	3.88	3.3	0.42
Event 4	3.99	2.89	0.32	n.d.	0.04	n.d.	0.50	0.64	0.53	0.63	0.31	n.d.	2.32	2.39	0.41
Event 6	18.6	4.39	0.24	n.d.	n.d.	n.d.	4.47	0.14	0.57	0.96	0.45	n.d.	9.83	3.53	0.18
Event 7	4.61	3.66	0.54	0.58	n.d.	n.d.	7.32	1.59	1.62	0.7	0.36	n.d.	6.33	3.02	0.69
Event 8	2.88	4.25	1.16	n.d.	n.d.	n.d.	0.17	0.13	0.18	n.d.	n.d.	n.d.	3.79	2.73	0.36
Event 9	9.18	9.88	1.33	n.d.	n.d.	n.d.	9.99	n.d.	n.d.	0.57	0.19	0.52	1.98	2.09	0.30

Sample 1 green roof with Callisia repens, sample 2 green roof with Sedum rupestre and sample 3 reference sample, n.d. not detected

Regarding the chemical parameters, one can see that both green roofs act as sources of Phosphate, Nitrate, Chlorine, Sulphate and Nitrite - the last one at very low levels, when it is detected. One can also see the difference after beginning the decomposition of the organic matter of Turtle Vine (Event 6). After July, Sample 1 (*Callisia Repens*) contains high levels of Chlorine, Nitrate and Sulphate, disassociating from Sample 2 (*Sedum rupestre*), because in the same events the green roof with Sedum appears to be even more efficient in the capture of Nitrate than in the past months.

It is noted that the levels of Chlorine, Nitrate and Sulphate tended to decrease with the maturity of the green roof, by stabilization of the planting medium, and of the vegetation. The Nitrite contents are quite varying, when detected. In Events 3 and 6, it can be seen that the green roof with *Sedum*-type vegetation has abducted part of the Nitrate present in the atmosphere, considering that the content of this nutrient in Sample 2 (SR) is considerably lower than in Sample 3 (reference). The same can be observed for Sample 1 (CR) in Event 3. Event 9 proves that, if there is no Nitrate present in the atmosphere, it will also not be present in water samples from the green roof with *Sedum*. The results from the samples collected on the green roof with *Callisia repens* are disregarded in this case, since with the death of the plants there was an intense release of Chlorine, Nitrate, Phosphate and Sulphate into the water (mainly in Events 6 and 7). Event 8 does not seem significant; however, as it was an event with high rainfall, there was a greater dilution of the nutrients. In Table 4, the total values of the chemical compounds (mg) lost in each precipitation event by the Sedum green roof are presented. The rainfall volume in liters can be calculated from the bench area of 1.6 m².

Table 4: Total amount of chemical compounds in the *Sedum* green roof water samples

Event	**Rainfall (mm)**	**Rainfall (L)**	**Chlorine (mg)**	**Nitrite (mg)**	**Nitrate (mg)**	**Phosphate (mg)**	**Sulphate (mg)**
1	50.5	80.8	5,160	0	28,325	29.1	1,760
2	10.6	16.9	218	5.09	57.3	9.16	155
3	26.5	42.4	138	0	6.78	33.1	140
4	18.5	29.6	85.5	1.18	18.9	9.18	70.7
6	24.2	38.7	170	0	5.42	17.4	137
7	18.3	29.3	107	0	46.6	10.5	88.4
8	48	76.8	326	0	9.98	0	210
9	14.5	23.2	229	0	0	4.40	48.5

Some authors (Pessoa, 2016; Macmillian, 2004) attributed the presence of Phosphate in the water mainly to the planting medium of the green roof, pointing at as an important source of Phosphorus and with the potential to release Phosphate during the rain events. Studies (Glass, 2007; Macmillian, 2004) indicate that concentrations of Phosphorus and Total Nitrogen decrease over time, concluding that the age of the structure may interfere with their concentrations. The present study did not run long enough to verify such statements. However, it can be observed that with the death of the species *Callisia repens*, there was a significant increase in the release of

Phosphate into water. In the last recorded event, it had tripled its content comparing with the values of Sample 2.

It was also observed that, except for the first rainfall (Event 1), when the particles were still quite loose (and the loss of chemical components was incredibly high), there was a chemical dilution effect in the Sedum rupestre water. That is, in the lower rainfall volumes, the highest levels of the components were detected into the water samples. Nitrite level could reach zero (or not detectable) in precipitations of 18 mm or more. Still regarding the chemical parameters, the amount of analysis was not enough to characterize the green roofs' interference in the pH. However, it is noticeable that the green roofs presented slight influence in neutralizing the pH of rainwater. The reference sample (3) has pH levels always below 7, that is, it has an acid character, and it could be seen an increase in pH in 62% of cases. A long-term monitoring could verify this issue.

Other parameters that were verified in this study are Total Coliforms and Thermotolerant Coliforms (indicators of *Escherichia Coli*). The presence of coliforms in the water is given from the soil type used, however, other contaminating sources are not eliminated. Regarding Total Coliforms, the results obtained during the monitoring revealed that the most probable number of organisms was always higher than 2,420 MPN, and there was no change during the investigation. Data for *E. coli* and rainfall events can be seen in Table 5.

One can see that the presence of *E. coli* in Sample 1 (CR) is similar to that of Sample 2 (SR); and it should be noted that the amounts of these coliforms decreased with the age of the green roof, reaching numbers less than 1 in the last sample. However in Event 6, there is a peak of *E. coli* in Sample 2, specifically. In this way, it is suspected an external contamination between events 5 and 6, since the analysis does not show compliance with Sample 1 like as in other events. These data with Total Solids and Nutrients content help to verify that the age of the roof influences the quality of drained water (Pessoa, 2016).

Table 5: Thermo-tolerant coliforms measured after rainfall events

Rainfall event	**Thermo-tolerant coliforms (MPN)**	
	CR	**SR**
1	710	740
2	1.00	2.00
3	5.20	6.30
4	3.00	1.00
6	2.00	248
7	1.00	3.10
8	2.00	2.00
9	1.00	1.00

CR (Callisia repens) and SR (Sedum rupestre)

From the qualitative evaluation of the green roof water samples analyzed, it was possible to deduce that they contributed to the increase of rainwater pH, approaching neutrality. The amount of solids present in green roof samples is significant and, consequently, the loss of nutrients by leaching as well. The samples are rich in Chlorine, Nitrate, Phosphate and Sulfate from the green roofs, and the Nitrite content is very low and only found in samples from the green roofs.

Potential water use

Currently, there is no specific legislation in Brazil on green roofs, much less on the use of its water for domestic use. However, the Brazilian norm NBR 15527: 2007 of the Brazilian Association of Technical Standards (ABNT) (Associação Brasileira de Normas Técnicas, 2007) presents requirements for non-potable uses of rainwater. This legislation is very similar to the standards adopted by the United States in the *"Guidelines for water reuse"* (USEPA, 2012) for use of roof water in urban areas for irrigation, vehicle washing, sanitary discharges, air conditioning systems, among other uses. According to these regulations, water pH can vary from 6 to 9; however, there should be a total absence of coliforms in the water.

Water to be sent to non-potable uses must be evaluated case by case, comparing the water quality with that required for its use. For example, if the green roof water is going to be used for irrigation of vegetable gardens, it cannot contain high levels of calcium, chlorine and others, or the plants will not develop properly and may even die (USEPA, 2012). In this case, the green roof water in this study is not suitable for crop irrigation due to its high levels of chlorine and nitrate, unless by receiving some specific treatment.

Also, green roof water could be used after appropriate treatment of Coliforms in discharges of sanitary basins, irrigation of lawns and ornamental plants, washing vehicles, cleaning sidewalks and streets, cleaning patios, and industrial uses. Additional volumes could be obtained from mixing with other waters, from rainwater collecting systems, for example. In addition, waters from green roofs with similar qualities to those evaluated in this work could be redirected to irrigation of the same green roof in periods of drought without any treatment needed.

4 Conclusions

Green roofs made with Tetra Pak® structures are sustainable, low-cost, affordable systems that do not depend on skilled labor. Choosing a modular system allowed the assembly by parts, facilitating storage during assembly. It is also a project that could be carried out in schools as a form of education and environmental awareness, with children and teenagers, who can help collecting Tetra Pak® boxes for the assembly and installation of the structure.

The evaluated green roofs did not contribute to the improvement of water quality regarding physical, chemical and biological aspects, compared with water samples collected directly from the atmosphere. The amount of solids present in green roof samples was significantly high and, as a consequence, the loss of nutrients by leaching. Chemical analyses showed the presence of high contents of chlorine, nitrate, nitrite, sulphate and phosphate, although in some rainfall events they have been reduced by the action of green roofs. A longer study period might show more conclusive results.

There is a possibility of using water collected from these structures for non-potable purposes, but preliminary treatment (filtration and chlorination) should be carried out, if the water is not intended for irrigation of gardens, lawns or the green roof itself.

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REGULATION OF HYDROGEN PEROXIDE DOSAGE DURING LIGNIN DEGRADATION BY THE HETEROGENEOUS PHOTO-FENTON PROCESS

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Keywords: Vinasses, tequila, cachaça, recalcitrant organic compounds, degradation, heterogeneous photo-Fenton process, hydrogen peroxide, automatic dosage, discrete control of dissolved oxygen

Abstract

The production of tequila in Mexico and cachaça in Brazil generates wastewater called vinasses, which contain recalcitrant compounds (RCs), whose degradation is difficult by using conventional wastewater treatment methods. If they are not properly treated they can cause negative effects in the environment. The heterogeneous photo-Fenton process is efficient in the degradation of RCs, where a ferrite catalyst, visible light and hydrogen peroxide (H_2O_2) are used. However, H_2O_2 can be consumed in scavenger reactions. Therefore, the objective of this study was to dose this compound in an automatic way using a control approach with the aim to improve the degradation of RCs. The degradation of lignin, one of the RCs most commonly found in vinasses, was performed. Experiments were divided in two types: open-loop and closed-loop modes. The open-loop experiment was carried out by applying a feed of a constant H_2O_2 flow. By using the obtained data and applying the reaction curve method a first-order transfer function model was achieved. The input variable was the H_2O_2 flow, and the output variable was the dissolved oxygen measured as oxygen saturation percent (%DO). The closed-loop experiment was performed with an automatic regulation of the H_2O_2 flow, using a discrete time direct synthesis approach. Thus, the obtained results showed that it is possible to model and to control the degradation of lignin applying a heterogeneous photo-Fenton process, which improved the TOC reduction performance using a lower H_2O_2 dosage.

1 Introduction

Problem statement

About 30% of drinking water in Mexico and 30% in Brazil is used in agro-industrial processes, which contaminate a significant proportion of this invaluable resource and generate large quantities of wastewater. It must be taken into consideration that wastewaters that come from industry have a large amount of pollutants, which have shown increasing difficulties to be eliminated. New Wastewater Treatment Processes (WWTP) have been developed in the last decades in order to face this challenge, and countries with emerging economies such as Mexico and Brazil should invest in these new technologies. Subsequently, topics related to alcoholic beverages like tequila and cachaça will be addressed, because they produce a large amount of wastewater with an important content of Recalcitrant Compounds (RCs), which cannot be degraded by conventional wastewater treatment methods (Comisión Nacional del Agua, 2016; de Azevedo-Soares, 2010).

Tequila is a traditional alcoholic beverage in Mexico that is obtained from distillation of fermented wort of *Agave Tequilana* Weber (blue variety). Based on data of Tequila Regulatory Council, Mexico has produced in average 248 million L of tequila per year from 2012 to 2017. It is exported to 102 countries, which has been increasing every year since 1995 (Macías & Valenzuela, 2009; Coelho, 2007). On the other hand, Cachaça is a typical distilled drink of Brazil, made by the fermentation of sugar cane juice. In 2008, the production of cachaça in Brazil was 1,300 million L (Borboletto, 2015). Although the production of cachaça is high, only an amount less than 1% is exported due to lack of standardization (Bortoletto, 2015; Cardoso et al., 2004). The wastewaters generated by the ethyl alcohol production processes are called vinasses, which are classified depending on their origin *"tequila vinasses"* or *"cachaça vinasses"*. For each liter of tequila, 10-12 L of vinasses are generated. In Mexico in 2008, 227 million L of vinasses were generated, whose treatment is equivalent to the generation of pollution produced by 6.2 million people (López-López et al., 2010). Concerning Cachaça, its production generates between 4 and 10 L of vinasses per liter of product obtained. In a general way, vinasses share several characteristics but differ in their concentration and composition. Concerning RCs contained in vinasses, it is common to found mainly phenols and polyphenolic compounds (tannic and humic acids), lignins and melanoidins (these last compounds giving them a characteristic dark brown color). Due to the content of potassium, calcium, magnesium and organic matter present in vinasses (España-Gamboa et al., 2011), they have been used in of agave or sugarcane fields in partial or total substitution of mineral fertilizers. But the unregulated application of vinasses on the ground is related with the salinization of soil and the contamination of surface and groundwaters (Ferreira et al., 2010). Furthermore, this type of compounds has a negative effect on the microbial flora of soil and plants, so the development of new processes for their degradation in this wastewater is crucial (España-Gamboa et al., 2011; López-López et al., 2010). In addition, phenolic and polyphenolic compounds present in vinasses can inhibit germs seed destruction and damage crops as well as adversely affect the microbial activity in the soil (Robles-González et al., 2012).

Heterogeneous photo-Fenton process

Advanced oxidation processes (AOPs) are systems, where the hydroxyl radical (•OH) is used as the main oxidizing agent. Hydroxyl radicals can be generated by reactions that use strong oxidants, such as ozone (O_3) or hydrogen peroxide (H_2O_2), semiconductors, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), and ultraviolet radiation (UV) (Peralta-Zamora, 2014). The AOPs have been used for the treatment of wastewater and have shown to be effective in the degradation of pollutants such as pesticides, surfactants, dyes, and pharmaceuticals. In addition, this type of reaction is usually carried out at ambient temperature, and it is able to oxidize organic matter to carbon dioxide (Prousek, 1996, Oturan & Aaron, 2014). The photo-Fenton process is an AOP that has shown to be efficient in the degradation of organic matter present in wastewater, and has also degraded RCs. The photo-Fenton process uses UV or solar light for the reduction of Fe (III) to Fe (II). The rate of degradation of organic pollutants is significantly improved, when UV-visible light is added to the reaction at wavelengths greater than 300 nm (Huang et al., 1993; Rahim-Pouran et al., 2015; Kavitha & Palanivelu, 2004). In the Fenton process, degradation is directly proportional to the amount of H_2O_2 added at the beginning. However, in the heterogeneous photo-Fenton process, when hydrogen peroxide was dosed at different flows, better degradations were obtained. Nevertheless, it has been observed that in batch experiments, the addition of a stoichiometric H_2O_2 quantity does not reach the expected degradation, so the process will require a greater amount of H_2O_2, because this compound can be consumed by other parallel running scavenger reactions. An acid pH favors the formation of hydroxyl radicals, so the recommended pH range for the heterogeneous photo-Fenton process is 2.8 to 3.5. However, a disadvantage of this process is that the use of UV light and H_2O_2 can raise the operating costs. H_2O_2 is a compound that is rapidly consumed in the process. If it is added at the beginning, its concentration decreases because of the occurrence of the scavenger reactions (Ortega-Gómez et al., 2012). Because of this, the optimization of the heterogeneous photo-Fenton process is based on the proper dosage of H_2O_2.

Modeling and control

Concerning dynamical models for the heterogeneous or homogenous photo-Fenton processes, only empirical methods, where their mass and energy balance equations are not based on the exact phenomenon or process description, have been developed, but they have been validated by experimental data (Ortega-Gómez et al., 2012; Herney-Ramirez et al., 2010; Sanino et al., 2016). On the other hand, H_2O_2 is related with the dissolved oxygen in the reaction system, and its measurement has been proposed to optimize the photo-Fenton process (Santos-Juanes et al., 2011). Taking this into account, some authors have chosen to use the method of reaction curve to model the homogenous photo-Fenton process (Ortega-Gómez et al., 2012). This method consists of the application of a step jump, observing the changes of the interested variables in the system, to calculate the transfer function and to apply later a classical control technique (Smith & Corripio, 1985).

As aforementioned, the photo-Fenton process is able to degrade the recalcitrant compounds present in vinasses. Previous studies have also shown that some compounds have been degraded in the homogeneous photo-Fenton process in batch reactors (Rahim-Pauran, 1994). But, the modeling of the system by the reaction curve method is necessary to perform the degradation of pure recalcitrant compounds by a heterogeneous photo-Fenton process in a batch reactor with an H_2O_2 input and then to propose a control approach for the regulation of the H_2O_2 dosage (Gernjak et al., 2006; Santos-Juanes et al., 2011; Ortega-Gómez et al., 2012). Once an empirical or kinetic model is adjusted for the degradation of recalcitrant compound, it will be possible to proceed to the regulation by classical control with the objective of making the degradation of these compounds more efficient in closed-loop experiments. This also searches to reduce the use of reagents, such as H_2O_2 and the catalyst, which can raise the operation costs.

2 Material and Methods

Reagents

A zinc ferrite catalyst that was prepared at the Research Center on Advanced Material and Energy, São Carlos Federal University, Brazil (Souza et al., 2018), and H_2O_2 (50% V/V, Fermont^R) were used. Synthetic samples of lignin were elaborated using low sulfonated lignin, soluble in water (Sigma^R). $TiSO_4$ was synthesized by the digestion of titanium dioxide (Sigma^R) with sulfuric acid (Sigma^R).

Reactor

A batch reactor of 0.5 L was used with a water jacket that maintained the temperature at 30 °C. The reactor was put inside of a box to keep the irradiance constant, and the reactor installed on a magnetic stirring plate. The sources of light were strips of LEDs, which concentrically surrounded the reactor, providing a constant flow of photons. The dissolved oxygen sensor was positioned at the center of the reactor, and a peristaltic pump was installed in the upper part that allowed to feed the H_2O_2 into the reactor.

Analytical methods

Contaminant concentration was determined by using an UV-Vis spectrometer operating at 280 nm, with lignin being a colored compound used without previous treatment. H_2O_2 concentration was determined by UV-Vis through the formation of the colored $TiSO_4/H_2O_2$ complex that has an absorption band at 420 nm, forming a yellow to red color depending on its concentration. The total organic carbon (TOC) concentration was determined by a Shimadzu^R TOC analyzer.

Experimental procedure

The pH of a solution containing 200 ppm of lignin was adjusted to 2.8. In all the experiments, the temperature was 30 °C and the initial concentration of H_2O_2 was zero. The stirring was fixed at 400 rpm. 10 min before starting the reaction, the catalyst was added and left on agitation, and also, the light source was turned on 5 min before starting. The reaction began, when the flow of H_2O_2 was activated. Subsequently, samples were taken approximately every hour in order to analyze the concentrations of lignin and H_2O_2, and to determine the TOC.

Instrumentation

A peristaltic pump and a sensor of dissolved oxygen were used, both Atlas-Scientific devices, which were connected to a data acquisition card (Arduino-Mega). The card sent to the computer the data of dissolved oxygen in saturation percentage and the H_2O_2 volume dosed into the reactor. To apply the controller, a program in Python was used. Pump flows (the control input) were calculated by this program. Time and dissolved oxygen data were stocked in a file at every second.

Modeling

The reaction curve method was used to model the system as a first order transfer function in the Laplace domain. This method is based on making a step jump in the input variable, which in this case is the flow of H_2O_2. Dissolved oxygen in the reactor was defined as the output variable. The transfer function is given by Equation (1).

$$G(s) = \frac{K}{(\tau s+1)} \qquad (1)$$

where K, is the system (static) gain, and it is the relationship between the output variable and the input variable at the steady state, while τ, is the system time constant, when the output variable reaches 63% of its steady state value.

Control by direct synthesis

Control by direct synthesis is model based approach, in which it is defined the path (see Equation 2) that the controller must follow (Ogunnaike & Ray, 1994).

$$q(s) = \frac{1}{\tau_r s+1} \qquad (2)$$

If the trajectory is defined by a function q(s) and the transference function is a first order system (see Equation 1), then the controller equation in the Laplace domain is expressed by Equation (3).

$$G_c(s) = \frac{\tau}{K\tau_r}\left(1 + \frac{1}{\tau s}\right) \qquad (3)$$

Equation (3) represents the characteristic equation of a PI controller, where the parameters are $K_c = \tau / (K\tau_r)$ *and* $\tau_r = \tau$.

3 Results and Discussion

Open loop experiments

Lignin degradation in an open-loop reactor was carried out with a 0.1 mL/min H_2O_2 flow and with an input H_2O_2 concentration of 1,000 ppm. Figure 1 shows the results. As it can be seen, due to the entry of H_2O_2 flow, this compound was accumulated in the system, and the dissolved oxygen tended to decrease. After 2.5 hours, the %DO was stabilized at 71.7%.

The degradation of lignin in this experiment was 28%; the TOC reduction was 21.5%. On the other hand, the consumed H_2O_2 in this experiment was only 20% of the amount in the whole experiment. The objective of this type of experiment was not to achieve a high degradation of lignin, but to apply a minimum input of H_2O_2, to be able to observe the effect that it has on the %DO variable in order to model the system and to obtain the transfer function.

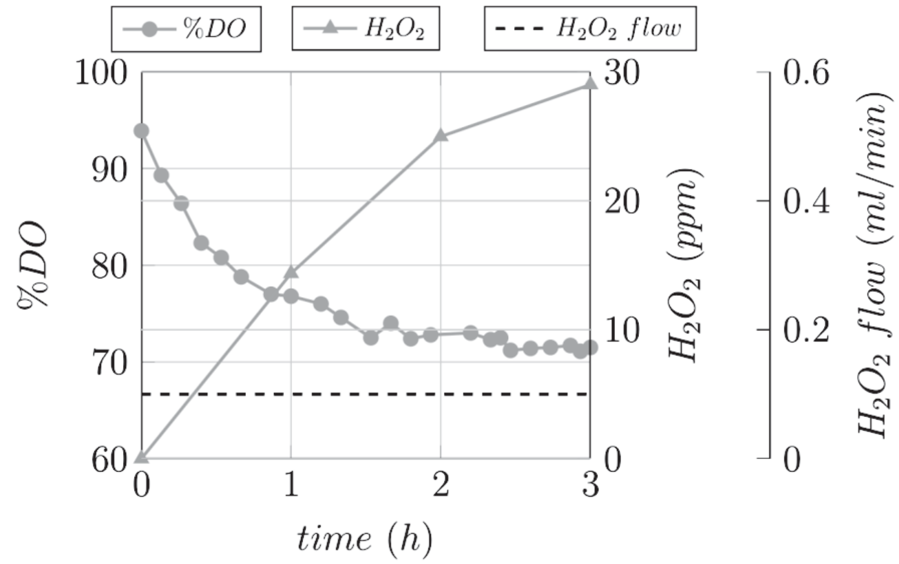

Figure 1: Closed-loop experiment, %DO response to a flow of H_2O_2

Modeling of lignin degradation

With the data obtained by the open-loop experiment, the degradation of lignin was modeled by the reaction curve method, where the output variable was %DO and the input variable was the H_2O_2 flow. With this method, a first-order transfer function (see Equation 4) was obtained. Figure 2 shows the high fit of the %DO data with the obtained model.

$$G(s) = \frac{-3.7}{(0.57[h]s+1)} [\%DO\ h/mL] \qquad (4)$$

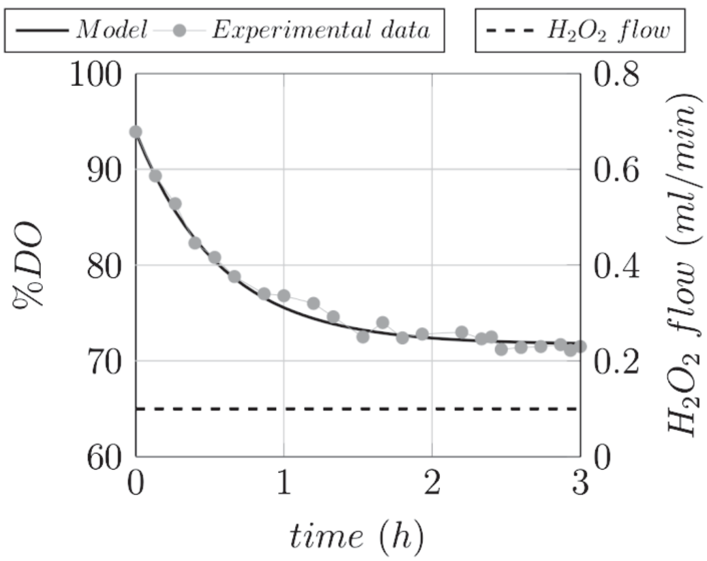

Figure 2: Simulation of the transfer function

Closed loop experiments

The parameters of the discrete PI controller were calculated by the direct synthesis technique, which were: K_c= -1.542 mL / (% DO h), τ_I=0.57 h and τ_r = 0.1 h, with a 5 min sampling time. The results of the closed loop lignin degradation related to TOC reduction, lignin degradation and H_2O_2 consumption were 39%, 37% and 36%, respectively.

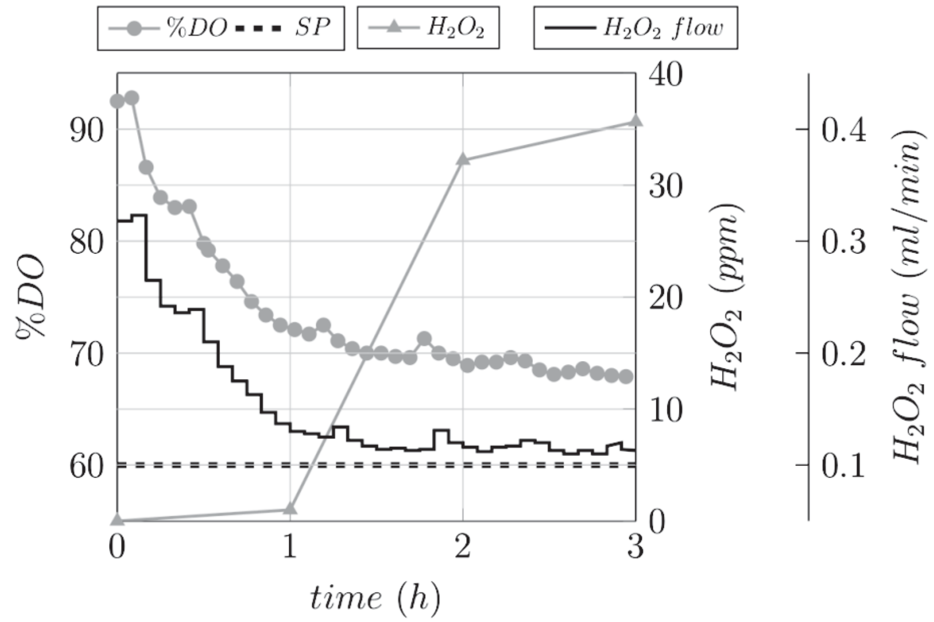

Figure 3: Closed-loop experiment with automatic regulation of H_2O_2 flow

The set-point (SP) in this experiment was 60% DO. As it can be observed in Figure 3, the %DO did not decrease to a final value of 68% DO, but it is possible that the system reaches the SP in a longer time. However, the time was limited to 3 h to avoid diluting the solution in the reactor, because the system had the limitations of the reactor volume (0.5 L) and the lower possible flow dosed by the pump was 0.1 mL/min. Besides, this time also guaranteed that the catalyst activity remained constant.

4 Conclusions

The regular dosing of H_2O_2 into the reactor during the used heterogeneous photo-Fenton process had a direct impact on the degradation of organic matter. With the regulation of the H_2O_2 dosage in the closed loop experiment compared with the open-loop one, it was possible to remove a higher amount of organic carbon, which reached a value of about 80%. The application of the reaction curve method was a viable option for modeling the degradation of a recalcitrant compound like lignin during the heterogeneous photo-Fenton process, and the use the measurement of dissolved oxygen as an output control variable was useful for the automatic regulation of the H_2O_2 dosage. Calculating the controller parameters with the direct synthesis technique provided a quick way of tuning the controller. Although the calculated controller did not allow reaching the set-point in a relatively short time, it showed a very good and acceptable performance.

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