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IDENTIFICATION, OCCURRENCE, ENVIRONMENTAL AND HUMAN HEALTH RISK OF PHENOLIC COMPOUNDS IN AQUEOUS MATRIX

Ramatisa Ladeia Ramos

Belo Horizonte
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Orientadora: Dr. Míriam Cristina Santos Amaral Moravia

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FOLHA DE APROVAÇÃO

Identification, Occurrence, Environmental And Human Health Risk Of Phenolic Compounds In Aqueous Matrix

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“Por vezes sentimos que aquilo que fazemos não é senão uma gota de água no mar.
Entretanto o mar seria menor se lhe faltasse uma gota.”

Madre Teresa de Calcutá

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RESUMO

Nos últimos anos a ocorrência de micropoluentes, como os compostos fenólicos, tem se tornado uma preocupação em todo mundo devido à complexidade dos compostos e ao risco para o meio ambiente e para saúde humana. Dessa forma, o presente trabalho teve como objetivo investigar a ocorrência de 17 compostos fenólicos em águas superficiais e uma água tratada em estação de tratamento de água convencional (WTP). Além disso, foi realizada avaliação de risco ambiental (coeficiente de risco - HQ) e para a saúde humana (margem de exposição - MOE) desses compostos na água bruta e sua redução pelo processo de tratamento convencional e pela destilação por membrana de contato direto (DCMD). A metodologia para a quantificação dos fenóis baseou-se na técnica de extração em fase sólida (SPE) (cartucho C_{18}) seguida por cromatografia gasosa com detector por ionização de chama (FID). Os ensaios demonstraram que houve influência da matriz na eficiência da SPE, mas o grau de recuperação para todos compostos fenólicos foi superior a 50% e houve maior recuperação dos compostos hidrofóbicos. Em geral, o método analítico utilizado foi capaz de determinar os fenóis nas amostras apresentando boa repetitividade, precisão, sensibilidade e limites de quantificação e detecção compatíveis com os apresentados na literatura. Dos 17 compostos fenólicos analisados 16 foram encontrados nas amostras coletadas no ano de monitoramento. Em relação à eficiência de remoção da WTP, ela não foi capaz de remover completamente os micropoluentes e, ao contrário, foi responsável pela geração de novas substâncias. Em geral, a avaliação de risco realizada para os compostos na água superficial foi altamente tóxica a qualquer nível trófico e apresentou um risco significativo para a saúde humana. Posteriormente, os resultados da redução do risco pela WTP não foram efetivos, visto a alta taxa de risco para a maioria dos compostos. No que se refere ao desempenho da DCMD, o fluxo de permeado ao longo do tempo teve uma queda de aproximadamente 0,7, sendo recomendado trabalhar com uma taxa de recuperação antes do decaimento do fluxo (RR <63%) para evitar incrustações e perda de desempenho. Porém, a condutividade permaneceu constante indicando a ausência de impurezas iônicas no permeado. Apesar dessa diminuição no fluxo, as taxas de retenção dos compostos fenólicos na água bruta foram superiores a 80%. A redução do risco também foi avaliada para a DCMD, provando que a tecnologia tem potencial para a remoção desses compostos.

Palavras-chave: compostos fenólicos; cromatografia gasosa; águas superficiais; tratamento convencional; avaliação de risco; destilação por membrana de contato direto.

ABSTRACT

In the recent years the occurrence of micropollutants, such as phenolic compounds, has become a worldwide concern due to the complexity of the compounds and the risks to the environment and to human health. Thus, the present work had as objective to investigate the occurrence of 17 phenolic compounds in surface waters and a water treated by a conventional water treatment plant (WTP). In addition, the environmental risk (hazard quotient - HQ) and human health (margin of exposure - MOE) assessments of these compounds in raw water and their reduction by conventional treatment process and by direct contact membrane distillation (DCMD) were performed . The methodology for the quantification of phenols was based on the solid phase extraction technique (SPE) (C_{18} cartridge) followed by gas chromatography with flame ionization detector (FID). The tests showed that was matrix influence on the efficiency of the SPE, but the degree of recovery for all phenolic compounds was higher than 50% and there was a greater recovery of the hydrophobic compounds. In general, the analytical method used was able to determine the phenols in the samples presenting good repeatability, precision, sensitivity, limits of quantification and detection compatible with those presented in the literature. In between the 17 phenolic compounds analyzed, 16 were found in the samples collected during the monitoring year. Regarding the WTP removal efficiency, it was not able to completely remove the micropollutants and, on the contrary, was responsible for the generation of new compounds. In general, the risk assessment for the compounds in surface water was highly toxic at any trophic level and posed a significant risk to human health. Subsequently, the results of WTP risk reduction were not effective, since a high-risk rate for most compounds was found. Concerning the performance of DCMD, the permeate flux over time dropped with the ratio of approximately 0.7. It is recommended to work at a recovery rate equivalent to the point before the flow decay (RR < 63%) to prevent fouling and loss of performance. However, the conductivity remained constant indicating the absence of ionic impurities in the permeate. Despite this decrease in flow, the retention rates of the phenolic compounds in the raw water were greater than 80%. The risk reduction was also evaluated for DCMD, proving that the technology has potential to remove these compounds.

Keywords: phenolic compounds; gas chromatography; surface water; conventional treatment; risk assessment; direct contact membrane distillation.

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A_m – Membrane Area

ABNT – Associação Brasileira de Normas Técnicas

ACN – Acetonitrile

AF – Factor Assessment

AGMD – Air Gap Membrane Distillation

ANVISA – Agência Nacional de Vigilância Sanitária

APHA – Standard Methods for the Examination of Water and Wastewater

BPA – Bisphenol A

CF – Concentration Factor

CONAMA – Conselho Nacional do Meio Ambiente

CV – Coefficient of Variation

DBP – Disinfection Byproducts

DCM – Dichloromethane

DCMD – Direct Contact Membrane Distillation

DLM – Detection Limit of the Method

DWEL – Safe Exposure Level

EA – Ethyl Acetate

ECD – Electron Capture Detector

EC50 – Mean Effect Concentration

EPA – Environmental Protection Agency (United States)

ERA – Environmental Risk Assessment

FAPEMIG – Fundação de Amparo à Pesquisa do Estado de Minas Gerais

FID – Flame Ionization Detector

GC – Gas Chromatography

HPLC - High Performance Liquid Chromatography

HQ – Hazard Quotient

HRA – Human Health Risk Assessment

ICH – International Council for Harmonization of Technical Requirements for Pharmaceutical Products for Human Use

INMETRO – Instituto Nacional de Metrologia, Qualidade e Tecnologia

ITD – Ion Trap Detector

J_0 – Initial Permeate Flux

J – Permeate Flux

LC/APCI – Liquid Chromatography Atmospheric Pressure Chemical Ionization

LC50 – Lethal Concentration 50

LDO/HS – Layered Double Oxide Hollow Spheres

LEP – Liquid Entry Pressure

LLE – Liquid Liquid Extraction

LOAEL – Lowest Observed Adverse Effect Level

LSE – Liquid Solid Extraction

m_d – Distillate Mass

MBR – Membrane Bioreactor

MD – Membrane Distillation

MDL – Method Detection Limits

MEC – Measured Environmental Concentration

MEF – Matrix Effect Correction

MeOH – Methanol

MOE – Margin Of Exposure

MS/SIM – Mass Spectrometry in Selective Ion Monitoring Mode

MPV – Maximum Permitted Value

NOAEL – No Observed Adverse Effect Level

NOEC – No Observed Effect Concentration

NPD – Nitrogen and Phosphorus Detector

PNEC – Predicted No Effect Concentration

PPESK – Polypiperazine Amide

PTFE – Polytetrafluoroethylene

PVDF – Polyvinylidene Difluoride

QLM – Quantification Limit of the Method

R – Resolution

RD – Recovery Degree

RR – Recovery Rate

RSD – Relative Standard Derivation

RW – Raw Water

SPE – Solid Phase Extraction

SPME – Solid Phase Microextraction

STS – Sewage Treatment Station

TDI – Total Daily Intake

TN – Total Nitrogen

TOC – Total Organic Carbon

TS – Total Solids

TSS – Total Suspended Solids

TW –Treated Water

VMD – Vacuum Membrane Distillation

WHO – World Health Organization

WTP – Water Treatment Plant

α – Separation Factor

2CP – 2-Chlorophenol

2MP – 2-Methylphenol

2NP – 2-Nitrophenol

24DMP – 2,4-Dimethylphenol

24DCP – 2,4-Dichlorophenol

26DCP – 2,6-Dichlorophenol

234TCP – 2,3,4-Trichlorophenol

235TCP – 2,3,5-Trichlorophenol

2356TCP – 2,3,5,6-Tetrachlorophenol

2346TCP – 2,3,4,6-Tetrachlorophenol

246TCP – 2,4,6-Trichlorophenol

245TCP – 2,4,5-Trichlorophenol

345TCP – 3,4,5-Trichlorophenol

3MP – 3-Methylphenol

4C3MP – 4-Chloro-3-methylphenol

CHAPTER I

THEME PRESENTATION

1.1 BACKGROUND

The quality of water resources is deteriorating over time due to the continuous addition of undesirable chemicals from sewage, industrial dumping and environmental disasters (BASHEER, 2018), which reduce the resilience of the entire watershed and increase the bioavailability of these substances (FERNANDES et al., 2016). Studies have given more attention to emerging contaminants, such as pharmaceutical compounds, pesticides, hormones and industrial residues, as phenolic compounds (MAGI et al., 2018). This can be attributed to the analytical development of recent years. The phenolic substances were detected in water at concentrations of ng L^{-1} and μg L^{-1} (FATTA - KASSINOS et al., 2011). However, they are very damaging, since they accumulate in living beings and can present chronic and even acute effects.

In addition, the presence of many pollutants could cause unexpected synergistic effects (MAGI et al., 2018). The phenolic compounds together with classical pollutants, such as heavy metals, are widespread in the environment and in the drinking water. However, their identification in the rivers are not simple, because the variations in the levels of chemical elements in water environments are affected by several factors, such as pH, dilution due to flow with other rivers, seasonal changes (wet and dry seasons), resuspension of sediments, among other physical-chemical variations (SEGURA et al., 2016). Therefore, very sensitive methodologies are required to detect them in water and the choice of appropriate preconcentration methods and analytical technique are crucial to obtain satisfactory results (RICHARDSON & TERNES, 2014).

A successful approach can be represented by the combination of passive sampling with sensitive analytical techniques, such as Solid Phase Extraction (SPE) and Gas Chromatography (GC). The SPE was introduced in 1976 (YOSHIMURA et al., 1976) to address the disadvantages presented by liquid-liquid extraction and is now the most popular method of sample preparation used in most routine analyzes. The main objectives of the SPE are concentration, analytes isolation and removal of interferents from the matrix. The concentration factor is obtained by the ratio of the initial sample volume in the cartridge to the final volume of the concentrated solution. The concentration can be increased by a factor of 100 to 5000, making qualitative and quantitative analysis of traces elements possible (JARDIM, 2010).

The determination of phenolic compounds in different sample matrices is generally performed using GC (WONG et al., 2003; SHAMSIPUR et al., 2016). GC is an analytical technique for separating components from a mixture, wherein a volatile liquid or gaseous substance is charged by a gaseous (inert) mobile phase onto a stationary phase inside a capillary column or a solid support. The technique has advantages as high efficiency in the separation of the analytes, high resolution and also high sensitivity (JÁUREGUI & GALCERAN, 2001). It can be coupled to high selectivity detectors such as the Electron Capture Detector (ECD), Nitrogen and Phosphorus Detector (NPD), Mass Spectrometry in Selective Ion Monitoring Mode (MS/SIM) and Flame Ionization Detector (FID) to aid in the identification of interest compounds. Several articles report the presence of phenolic compounds in aquatic environments and drinking water as shown in Table 1.1 (p. 4 – 6).

Table 1.1: Occurrence of phenolic compounds in different parts of the world

Compounds	Source	Analytical method	Concentration	Country	Refenrence
pentachlorophenol, trichlorophenol and dichlorophenol	water reservoir	GC/DCE	0.010 - 0.022 μg L^{-1}	Brazil	CARMO, 2000
trichlorophenols, tetrachlorophenols and pentachlorophenol	drinking water	GC/MS	0.008 - 0.238 ng mL^{-1}	Brazil	SARTORI et. al, 2012
2,4-dichlorophenol, 2,4-dichlorophenol	drinking water and surface water	HPLC/UV; SPE (C_{18}); acetonitrile	0.2 - 2.4 ug L^{-1}	Canada	KUESENG & PAWLISZYN, 2013
bisphenol A	river water	HPL/MS; microwave assisted extraction	17.0 - 62.3 ng L^{-1}	England	PETRIE et al., 2016
phenol, p-cresol, 2,3-dimethylphenol, 2,6-dimethylphenol, 2,5-dimethylphenol, 3,4-dichlorophenol, 3,5-dichlorophenol, 2,4-dichlorophenol and pentachlorophenol	influent of an urban wastewater treatment plant	GC/MS; SPME	0.055 - 2.1 ng mL^{-1}	Spain	LLOMPART et al., 2002
pentachlorophenol, phenol and trichlorphenol	ground water and surface water	HPLC; LSE; methanol	0.1 - 5 ug L^{-1}	Spain	PUIG & BARCELÓ, 1996
Pentachlorophenol, 2-chlorophenol, 2,6-dichlorophenol, 2,4-dimethylphenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol	Wasterwater treatment plant	GC/QqQ /MS/MS; SPE; dichloromethane	0.04 - 0.2 ug L^{-1}	Spain	PADILLA-SÁNCHEZ et al., 2011
o-chlorophenol, o-nitrophenol, 2,4-dimethylphenol, 2,6-dichlorophenol, 4-chloro-3-methylphenol , 2,4-dibromophenol, 2,4,6-trichlorophenol	river water	HPLC; SPE (C_{18}); methanol and acetonitrile	0.12 - 2.04 ug L^{-1}	Spain	JAUREGUI & GALCERAN, 1997
bisphenol A	Treated wastewater	GC/MS; stir bars	282 - 346 ng L^{-1}	Spain	QUITANA et al., 2007
phenol, cresol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4-chloro, 3-methylphenol, 2,4,6-trichlorophenol and pentachlorophenol	urban storm water and sewage effluent	GC/MS; LLE; dichloromethane	0.5 μg L^{-1} - 114.0 μg L^{-1}	Australia	JENNINGS et al., 1996
phenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dimethylphenol, 2,4-	lake water and ground water	GC/MS; stir bars	43 - 138 μg L^{-1}	Germany	MONTERO et al., 2005

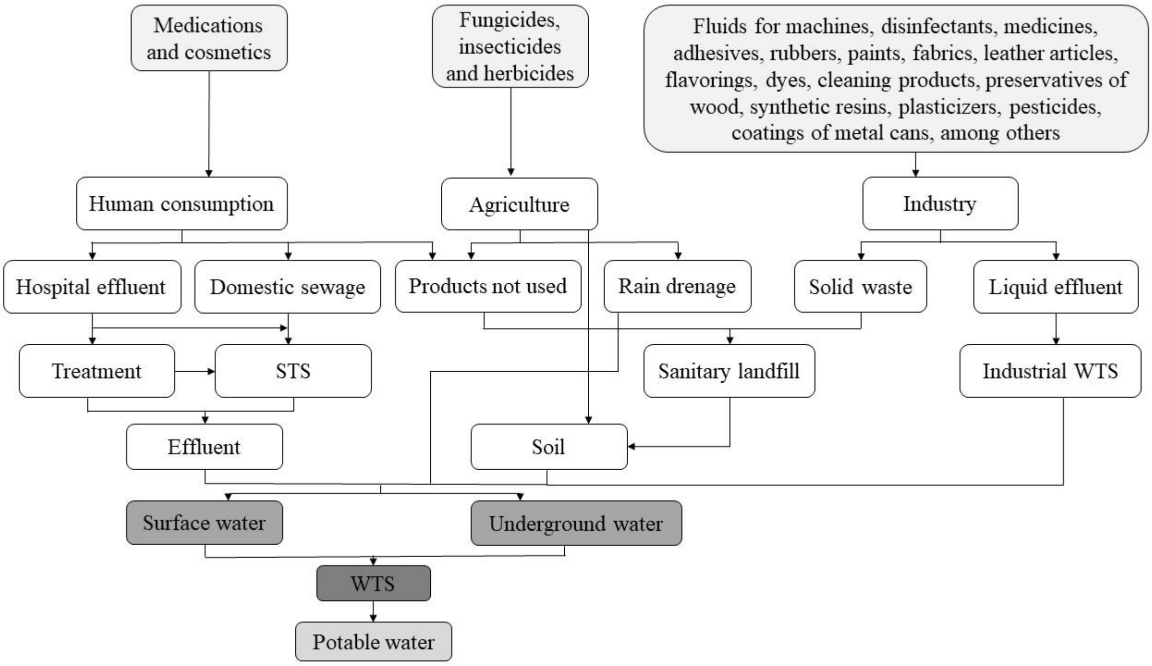
Compounds	**Source**	**Analytical method**	**Concentration**	**Country**	**Refenrence**
dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol					
phenol, m-cresol, p-cresol, 2-ethylphenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol	surface water	CG/MS; SPE (polypropylene); Methanol, tetrahydrofuran and acetonitrile	7.8 - 0.03 μg L^{-1}	Germany	SCHMIDT-BAUMLER et al., 1999
4-nonylphenol, 4-*t*-octylphenol, bisphenol and 2-hydroxybiphenyl	surface water	HRGC/LRMS adn GC/MS; SPE (ENV+); acetone	47 - 458 ng L^{-1}	Germany	BOLZ et al., 2001
phenol, 4-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,5-tetrachlorophenol and pentachlorophenol	surface water	GC/MS;SPE (C_{18}); diethyl ether and methylene chloride	7.07 - 0.02 μg L^{-1}	Poland	MICHALOWICZ et al., 2011
2,6-dichlorophenol, 2,3,6-trichlorophenol, pentachlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol	surface water	-	0.02 - 0.07 μg L^{-1}	Netherlands	HOFMAN et al., 1997
2,4,6-trichlorophenol	river water	GC/MS and LC/APCI/MS; SPE; acetonitrile and dichloromethane	0.02 - 2.3 μg L^{-1}	Portugal	AZEVEDO el at., 2000
2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol	drinking water	GC/ECD and GC/ITD/MS; SPME	3.01 - 69.1 μg L^{-1}	Italy	BIANCHI et al., 2002
dinoseb, 2-nitrophenol, 4-nitrophenol and bisphenol A	river water	GC/MS/MS; SPE (Strata-X and C18); hexane, dichloromethane and ethyl acetate	<LOQ	Greece	TERZOPOULOU et al., 2015
phenol and chlorophenols	river water	HPLC with amperometric detection; SPME	0.9 - 10.8 μg L^{-1}	Russia	FILIPOV et al.,2002
phenol, 2-chlorophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-nitrophenol	river water	HPLC; LDO−HSs	0.12 - 0.59 μg L^{-1}	Singapore	TANG et al., 2013

Compounds	Source	Analytical method	Concentration	Country	Refenrence
bisphenol A	surface water and drinking water	GC/MS ;SPE (C_{18}); acetone and hexane	1.3 - 215 ng L^{-1}	Malaysia	SANTHI et al., 2012
4-chloro-3-methylphenol, m-cresol, p-cresol, o-cresol, 2,4,5-trichlorophenol, 3,4,5-trichlorophenol, 2-nitrophenol	rivers	GC/MS; SPE (C_{18}); dichloromethane	35.9 - 1547 ng L^{-1}	China	ZHONG et al., 2010
2-cresol, 2,4-xylenol, 2-sec-butylphenol, 2-naphthol, 3-cresol, p-chloro-m-xylenol, 4-cresol, 3-cresol, 2,3,6-trimethylphenol, phenol, nitrophenol and 2-biphenylol	rivers	GC/MS; SPE (C_{18}); dichloromethane	0.18 - 1355 µg L^{-1}	China	WANG & WANG, 2018
2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol	surface water	GC/MS; MDL and RSD; dichloromethane, ethyl acetate, acetone and methanol	1.1 - 28650.0 ng L^{-1}	China	GAO et al., 2007
phenol	lake water	HPLC; LLE	35 ng mL^{-1}	China	ZHANG et al., 2011
phenol, 2-chlorophenol, 2,4-dimethylphenol, 4-chloro,3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and, pentachlorophenol	river water	GC/MS; SPE (CDS); methanol	0.03 - 0.15 µg L^{-1}	Iran	FARAJI et al., 2012
bisphenol A	surface water	-	2.1 - 881 ng L^{-1}	Canada, China, Germany, Greece and Korea	LUO et al., 2014

The concentrations of phenolic compounds vary greatly among the studies conducted depending on the compound properties and the analytical technique adopted. Considering the minimum concentration of phenolic compounds found as 1.3 ng L^{-1} in Malaysia and the maximum value as 1,355,000 ng L^{-1} in China, for drinking water and surface water respectively. Water containing phenolic compounds presents a serious problem due to its low biodegradability, high toxicity, persistence in the environment and carcinogenic properties (JIN et al., 2007). Thus, cause of great concern for all those involved in the production of drinking water due to the potentially adverse effects of these substances on human health, even at small concentrations (KENNEDY et al., 2007; KARABELAS et al., 2011; ACOSTA et al., 2018; ZHONG et al., 2018). Specifically, potential health hazards identified in toxicological and epidemiological studies include cancer, genetic malformations, damage to the immune system, protein degeneration, tissue erosion, central nervous system paralysis and damages the kidneys, liver and pancreas in humans (MERINI et al., 2007; MCKINLAY et al., 2008; MOHAMMADI & KAZEMI, 2014).

Phenols and their derivatives are introduced into the aquatic environment through natural degradation, agricultural practices and discharges of industrial effluents, such as rubber processing, glues and adhesives, resins, electrical components, plastics, steel, paper and cellulose, dyes, gas, textile, tannery, pharmaceutical and petroleum (JIN et al., 2007; WANG & WANG, 2018). In Figure 1.1 it is possible to verify a schematic diagram of the main routes that these compounds can be introduced in nature by human origin.

Figure 1.1: Main routes of introduction of phenolic compounds into the environment



***STS (Sewage Treatment Station); WTS (Water Treatment Plant).**

The occurrence of phenolic compounds in the aquatic environment has become a matter of international concern. Table 1.2 (p. 9) shows some phenolic compounds that already have maximum permitted concentration for surface and drinking water in the national Brazilian legislation and international legislation. The World Health Organization (WHO) has established a permissible concentration of phenolic content in drinking water of 1μg L^{-1} (WHO, 2017) and because of their toxicity, phenolic compounds have been included in the Environmental Protection Agency (EPA) list of priority compounds, which determines concentrations ranging from 0.03 μg L^{-1} to 4,000 μg L^{-1}, depending on the compound (EPA, 2015).

Table 1.2: National and international standards for phenolic compounds

Compounds	National Legislation				International Legislation		
	CONAMA 357(a)			Ordinance N° 2914(b)	WHO(c)	EPA(d)	European Commission (e)
	Class I e II - Sweet water	Class I - Sweet water for fishing and cultivation of organisms	Class III - Sweet water	Water for human consumption	Water for human consumption	Humam health for the consumption of water + organims	water for human consumption
2-chlorophenol	0.1 µg L^{-1}	0.1 µg L^{-1}				30 µg L^{-1}	
2,4-dichlorophenoxyacetic	4 µg L^{-1}	4 µg L^{-1}	30 µg L^{-1}	30µg L^{-1} (2,4-D + 2,4,5-T)	30 µg L^{-1}	1300 µg L^{-1}	
2,4,5-trichlorophenoxyacetic	2 µg L^{-1}	2 µg L^{-1}	2 µg L^{-1}	30 µg L^{-1} (2,4-D + 2,4,5-T)	0.009 mg L^{-1}		
2,4,5-trichlorophenoxypropionic	10 µg L^{-1}	10 µg L^{-1}	10 µg L^{-1}			100 µg L^{-1}	
2-methyl-4,6-dinitrophenol						2 µg L^{-1}	
dinitrophenols						10 µg L^{-1}	
2,4-dinitrophenol						10 µg L^{-1}	
2,4-dimethylphenol						100 µg L^{-1}	
2,4-dichlorophenol	0.3 µg L^{-1}	0.3 µg L^{-1}				10 µg L^{-1}	
4-chloro-3-methylphenol						500 µg L^{-1}	
2,4,6- trichlorophenol	0.01 mg L^{-1}	2.4 µg L^{-1}	0.01 mg L^{-1}	0.2 mg L^{-1}	0.2 mg L^{-1}	1.5 µg L^{-1}	
2,4,5- trichlorophenol						300 µg L^{-1}	
pentachlorophenol	0.009 mg L^{-1}	3.0 µg L^{-1}	0.009 mg L^{-1}	0.009 mg L^{-1}	0.009 mg L^{-1}	0.03 µg L^{-1}	
polychlorinated biphenyls	0.001 µg L^{-1}	0.000064 µg L^{-1}	0.001 µg L^{-1}			0.000064 µg L^{-1}	
phenol	0.003 mg L^{-1*}	0.01 mg L^{-1*}	0.01 mg L^{-1*}		1µg L^{-1}(phenolic compounds)	4000 µg L^{-1}	1µg L^{-1}(phenolic compounds)

(a)BRASIL, 2005;(b)BRASIL, 2011;(c)WHO, 2017;(d)EPA, 2019;(e)EUROPEAN COMMISSION, 2006. * total phenols - substances that react with 4-aminoantipyrine.

The European Union is in the process of revising the COUNCIL DIRECTIVE 98/83/EC - on the quality of water intended for human consumption, which has few established standards, but is intended to include 18 new or revised parameters such as emanating contaminants as three disinfection by-products and endocrine disrupting compounds such as bisphenol A (EUROPEAN PARLIAMENT, 2018). However, the legislation in general to regulate the concentration of phenolic compounds in water does not yet cover all the compounds that are found in surface and treated waters, which is still an important path to be achieved.

In this sense, the attention has been focused on identifying and removing these compounds from the environment to prevent their presence in drinking water. Different physical, chemical and biological methods, such as activated carbon adsorption, chemical oxidation and aerobic and anaerobic biological degradation, were used for the removal of phenols in water. However, these methods have many limitations, such as incomplete treatment, high cost, generation of toxic by-products and instability (JIN et al., 2007; MOHAMMADI & KAZEMI, 2014).

Studies done in Greece and Spain have shown that only about 68% of phenolic compounds are removed by effluent treatment processes (STASINAKIS et al., 2008; SANCHEZ-AVILA et al., 2009), while the rest ends up in the rivers letting the water treatment plants (WTP) in charge to remove them. In conventional WTP to remove these compounds would be necessary the optimization of chemical oxidation and / or the addition of activated carbon, being that the organic and inorganic matrices of the water greatly affect the performance of these processes. In many situations it is necessary to resort to unconventional techniques such as membrane technologies (ROSA et al., 2009).

The membrane processes are reliable and economically feasible to treat water with phenols and have many advantages such as low power consumption, high quality effluent, small ecological footprint, and easy scaling up with membrane modules (VILLEGAS et al., 2016). The most important membrane technologies used to remove these compounds from water and wastewater are extractive membrane bioreactors and hollow fiber membranes; photocatalytic membrane reactors; high-pressure membrane processes such as nanofiltration, reverse osmosis, and pervaporation; and membrane distillation (KHAZAALI et al., 2014; LOH et al., 2016; RAZA et al., 2018).

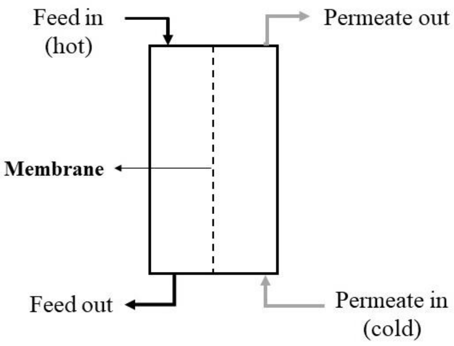
Membrane distillation (MD) has attracted attention to applications with more complex water and in different situations, in particular direct contact membrane distillation (DCMD), that produces high quality water, is a stable system and when associated with residual heat or renewable energy source, as solar power, the process cost decreases effectively (ASHOOR et al., 2016). The MD is a thermally driven separation process in which a hydrophobic microporous membrane separates a hot feed stream and a cold receiving phase (ALKHUDHIRI et al., 2012). The driving force of heat transport is the temperature gradient, which results in a water vapor pressure differential that causes the vapor transport through the membrane pores.

The main competitive advantage of MD is that distillation occurs below the normal boiling point of the feed solution (BANAT et al., 2007). The feed temperature may typically range from 60 to 90 °C (ASHOOR et al., 2016), although a temperature gradient around 30 °C is sufficient to promote separation. This separation method is based on the equilibrium between the vapor and liquid molecules of the liquid mixture (QATARISH et al., 2013). One of the most attractive features of MD technology is the theoretical rejection of 100% to non-volatile components, such as salts, inorganic compounds and macromolecules (THOMAS et al., 2017).

In addition, this technology can concentrate solutions to their saturation point without significant loss of permeate flux (FRANCIS et al., 2014). The main disadvantage of the MD process is the wettability of the membrane, which is due to three main factors, the surface tension of the process solution, the material, and the membrane structure. However, many researches are developing new membranes to overcome this disadvantage (El-BOURAWI et al., 2006; KHAYET & MATSUURA, 2011; SUSANTO, 2011).

Among the MD processes, there are variations how the vapor is recovered by the permeate side, since it migrated through the membrane. Figure 1.2 (p. 12) shows the configuration for DCMD. It being the oldest and most used MD process (ASHOOR et al., 2016), having liquid phases in direct contact with both sides of the membrane, where there is simultaneous heat and mass transfer determined by the heat flux and transfer coefficients in the feed and permeate sides (QATAR et al., 2008; PHATTANAANA et al., 2003). This configuration is easy to operate, easy to use, is simpler, does not require the use of an external condenser in the permeate gathering, and if it operated in the correct conditions can obtain a high flow (KHAYET & MATSUURA, 2011; EL BOURAWI et al., 2006).

Figure 1.2: DCMD configuration



It is noteworthy, that in the DCMD configuration, heat losses through conduction in the membrane matrix are greater than other configurations due to the existence of a continuous contact between the membrane surfaces and the hot feed and cold permeate (QATARISH & BANAT, 2013). This energy inefficiency is cause of worry in many DCMD applications, but the partial vapor pressure of the feed can be improved by using renewable energy, especially solar thermal power (ASHOOR et al., 2016).

Among the applications for DCMD, water treatment with phenolic residues challenges MD, which has applications as a uniform focus on the separation of non-volatile components. An understanding of the transport of volatile components present in water treatment is necessary even if the treatment aims are focused on non-volatile contaminants (SALLS et al., 2018). It is generally assumed that the volatile compounds will be poorly rejected by MD and may even be concentrated in the distillate stream relative to the feed stream if the contaminants have higher vapor pressures than water (WIJEKOON et al., 2014).

Some studies have examined the MD treatment for volatile and semi-volatile organic pollutants, noting that the rejection is related to the volatility and hydrophobicity of the contaminant (WIEKON et al., 2014; KUJAWA et al., 2015, SALLS et al., 2018). Rejection rates varied widely from 95% to 54% in these surveys, showing the need to study the behavior of each compound with the technology (WIJEKOON et al., 2014). In Table 1.3 (p. 13) it is possible to verify some research done using MD for the retention of phenolic compounds, however few studies have been found.

Table 1.3: Studies related to MD in the retention of phenolic compounds

Module configuration	Membrane configuration	Membrane material	Application	Analytes	Retention of each analyte in MD	Analyte identification method	Limit detection method	Country	Reference
DCMD	Flat sheet	PTFE	Water and wastewater treatment	bisphenol A; pentachlorophenol; 4-tert-butylphenol; 4-tert-octylphenol	bisphenol A (95%); pentachlorophenol (98%); 4-tert-butylphenol (72%); 4-tert-octylphenol (54%)	Described by HAI et al., 2011	1 - 20 µg L^{-1}	Australia	WIJEKOON et al., 2014
AGMD	Flat sheet	PTFE	Removal of contaminant	phenol; 2-nitrophenol; 4-nitrophenol	96 - 88%	EPA 8270 D	1 - 10 µg L^{-1}	EUA	SALLS et al., 2018
MD-EMBR + DCMD	Flat sheet	PTFE	Degradation	bisphenol A; 4-tert-butylphenol; 4-tert-octylphenol	94 - 99%	Described by HAI et al., 2011	1 - 20 µg L^{-1}	Australia	ASIF et al., 2018
MDV	Hollow fiber	PPESK	Wastewater removal	2,4-dichlorophenol	-	SPE-GC	-	China	JIN et al., 2007
DCMD	Flat sheet	PVDF + TiO_2	Removal	phenolic compounds	99.90%	-	-	Malaysia	HAMZAH et al., 2016
DCMD	Flat sheet	PTFE	Treatment and concentration of wastewater	polyphenols	99.90%	Colorimetry (Folin Ciocalteau reagent)	-	Morocco	EL-ABBASSI et al., 2009

Even if the identification and quantification of phenolic compounds in surface waters is done and the performance of different processes to removal them is evaluated, knowing these extents of contamination alone is not enough to determine if their presence in the concentrations which they are found in the water put in risk the environment and the human health. Thus, toxicological risk assessments must be carried out and consequently determine whether these compounds should be regulated by environmental legislation and improve risk control.

Environmental risk assessment (ERA) can be defined as a stepwise procedure to estimate the adverse effects of an environmental stressor (toxic chemical or pollution mixture) on an ecosystem or its components with a known degree of certainty (BEYER et al., 2012; LIU et al., 2012). The use of ERA has become increasingly important in studies of environmental pollutants effects (BEYER et al., 2012). The guidelines for ERA of new and existing chemicals from the European Medicines Agency (EMEA) and the US Food and Drug Administration (FDA) are based on the relationship between exposure and effect. It is expressed by the hazard quotient (HQ), given by the ratio between the measured environmental concentration (MEC) and the predicted non-effect concentration (PNEC). The higher the HQ value, the greater the probability that the chemical will present toxicological effects (FDA, 1998; EMEA, 2006).

The studies of phenolic compounds about toxicological risk assessment are still scarce in the literature, although these studies have become the scientific and important basis of the environmental risk management and environmental decision-making (LIU et al., 2012). Since these compounds persist in the treated water, in addition to ERA, the risk assessments for human health (HRA) should also be performed. The evaluation of such risk methods involves the margin of exposure (MOE) determination. MOE is obtained through the ratio between the safe exposure level and the highest concentration detected in the evaluated environment. The safe exposure level can be estimated by tolerable daily intake (TDI) (derived from the no-observed adverse effect level - NOAEL and safety factors) (WHO, 2017). Low risk is implied when MOE value is more than 100 for NOAEL-based assessments (EPA, 2012). Few recent articles that have exposed the risk assessments offered by phenolic compounds in natural waters are presented in Table 1.4 (p. 15). It is showing that China is the country that in its recently research has focused on the subject.

Table 1.4: Articles related to risk assessments offered by phenolic compounds

Compound	Risk analyzed	Source	Results	Country	Reference
50 phenolic compounds (phenol, 2-cresol, 4-CP, 4-cresol, 3-cresol, 2,5-DCP, pyrocatechold, 2-NP, 2-naphthol, 2-CP, 2,3,6-TMP, 2,4-xylenol, hexanoesd, 2,4-dichloro-3-ethyl-6-nitrophenol, 2-secbutylphenol 2-naphthol, 2,4-DCP, resorcinol, PCP, 2,6-DCP, para-chloro-meta-xylenol (PCMX), 2,4,6-TCP, 3,4,5-TCP, 2-biphenylol, 4-CP, 4-NP, among others)	Ecological risk - quotient method	Surface water	Five kinds of phenolic compounds were identified as priority phenolic compounds in Beitang Drainage river, and the order of risk was 2-cresol, 2,4-xylenol, 2-sec-butylphenol, 2-naphthol, 3-cresol. Six kinds of phenolic compounds were identified as priority phenolic compounds in e Dagu Drainage river, and the order of risk was 2-naphthol, p-chloro-m-xylenol, 4-cresol, 3-cresol, 2,4-xylenol, 2,3,6-Trimethylphenol. In Yongdingxin river, only phenol, 2-naphthol and 2,4-xylenol were identified as priority phenolic compounds.	China	ZHONG et al., 2018
polybrominated diphenyl ethers (PBDEs), 2,4,6-tribromophenol (TBP), pentabromophenol (PeBP), tetrabromobisphenol A (TBBPA), bisphenol A (BPA)	Estrogenic activity assessment; Eco-toxicity assessment	Water and soil samples	BPA was detected in the water and sediment samples collected at all sites except the control, and its concentrations were much higher than those of TBBPA at most sites (not detected to 8.6 × 102 ng L^{-1}). Estrogenic activity assessment showed that no estrogenic risk could be expected from the water and sediment based on TBBPA and BPA estrogenic activity, while eco-toxicity assessment at three representative trophic levels showed that different risks were present at most sampling sites.	China	XIONG et al., 2014
4-nonylphenol (4-NP), 4-tert-octylphenol (4-t-OP), bisphenol A (BPA), triclocarban (TCC), triclosan (TCS), galaxolide (HHCB) and tonalide (AHTN), musk xylene (MX), musk ketone (MK), clofibric acid, ketoprofen, naproxen, diclofenac, indometacin, ibuprofen, meclofenamic acid, mefenamic acid, fenoprofen, gemfibrozil, tolfenamic acid	Environment risck - quotient method	Surface water and sediment samples	Risks assessment showed that 4-NP and TCS had RQs > 1 in > 70% of samples and might pose various ecological risks to aquatic ecosystems, especially for algae. Possible risks were only occasionally found for 4-t-OP and BPA in the urban rivers in Guangzhou (one of the sample areas). Further investigations of ecotoxicological effects and potential ecological risks of these chemicals are therefore required to protect aquatic ecosystems and biodiversity in urban rivers of megacities in China.	China	PENG et al., 2017
nonylphenol (NP) and 4-tert-octylphenol (4-OP), 4-tert-butylphenol, 2,4-di-tert-pentylphenol, 4-n-heptylphenol, 4-butylphenol, 4-n-hexylphenol, TBBPA, bisphenol A (BPA)	Environment risk - quotient method	Surface water, suspended particulate matter	Risk assessment revealed greater risk associated with the surface water than the sediment, indicating that the discharge of industrial wastewater and domestic sewage poses a serious threat to aquatic ecosystems.	China	LIU et al., 2016

Compound	Risk analyzed	Source	Results	Country	Reference
phenol, 2-nitrophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol	Ecological risk - risk quotient; Human health risk - hazard quotient and Incremental lifetime cancer risk	Surface water and sediment samples	The results for risk quotient indicated that there were low ecological risks from the five phenolic compounds in water. However, there were high ecological risks of the total phenolic compounds in sediment. Based on the results for hazard quotient and incremental lifetime cancer, there were low risks of phenolic compounds to human health in the Yinma river basin.	China	ZHOU et al., 2017
4-tert-octylphenol, 4-n-octylphenol, 4-n-nonylphenol, nonylphenol, bisphenol A (BPA)	Environmental risk - risk quotient method and estrogenic activity	Surface water, sediment, and biota samples	The presence of BPA in the river could be mainly associated to punctual sources of contamination from industrial discharges. Calculated risk quotients showed low and moderate risk for the aquatic environment from the presence of the target compounds at all sampling points. The estimation of the daily intake of the studied compounds via water and biota ingestion indicated no risk for human health.	Spain	SALGUEIRO-GONZÁLEZ et al., 2015
4-tert-Octylphenol (OP), nonyphenol (NP), Bisphenol A (BPA), tetrabromobisphenol A (TBBPA), 4-tert-butylphenol (4-TBP), 4-butylphenol (4-BP), 4-hexylphenol (4-HP), 2,4-di-tert-amylphenol (2,4-DTAP)	Ecological risk - quotient method	Surface water and suspended particulate matter	Risk assessment based on the calculated risk quotients (RQ) showed that low and moderate risk for the aquatic environment from presence of the target compounds at all sampling points with exception of 4-TBP and NP which might pose a high risk to aquatic organisms.	China	LIU et al., 2016
octylphenol (OP), nonylphenol (NP), bisphenol A (BPA)	Ecological risk assessment - USEPA (1998); Aquatic health risk - hazard quotient; Human health risk assessment - standard methods	Surface water	The concentrations of OP, NP and BPA ranged from ND (not detected) to 16.3 ng L^{-1}, ND to 2200 ng L^{-1}, and 2.8 to 136 ng L^{-1}, respectively. The phenolic compounds in rivers are expected to cause potential toxicity to aquatic organism including crustaceans, mollusks, insects and fish. In respect to aquatic risk assessment, NP showed a greater hazard quotient (HQ) than did OP and BPA, and the highest HQ (62) was observed for fish in the Kaveri river. The backwater and estuarine NP levels may pose a risk to larvae of oysters and barnacles.	India	SELVARAJ et al., 2014
4-nonylphenol, bisphenol A (BPA), 4-t-OP	Ecological risk - quotient method; Human Health Risk - hazard quotient	Surface water, sediment, and biota samples	Taking co-exposure into account, the phenolic EDCs surveyed in the Pearl river estuary are probably not harmful to aquatic organisms or human health. However, further investigation of phenolic EDCs in the Pearl river estuary needed to improve regulation for man-aging and monitoring the usage of phenolic EDCs.	China	DIAO et al., 2017

Compound	Risk analyzed	Source	Results	Country	Reference
2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP)	The risk assessment - tiered approach	Surface water	The results show that the risks of three chlorophenols are ranked PCP>2,4-DCP≈2,4,6-TCP. PCP posed little ecological risk while 2,4-DCP and 2,4,6-TCP posed negligible or de mini risk in Chinese surface water. However, the risks varied with different river basins, for example, PCP posed some ecological risk in the Yangtze, Huaihe, and Pearl rivers.	China	JIN et al., 2011
bisphenol analogues (bisphenol A, bisphenol S, bisphenol F, among others)	Ecological risk - quotient method	Surface water and sediment samples	For both Taihu lake and Luoma lake, the risk assessment at the sampling sites showed that no high risk in surface water and sediment.	China	YAN et al., 2017
estrone (E1), 17b-estradiol (E2), estriol (E3), 17a-ethinylestradiol (EE2), bisphenol A (BPA)	Ecological risk - quotient method	Surface water	The concentrations of these compounds in the sediments of the Yellow river were relatively low comparing with the reported data in some other regions, mainly due to poor adsorption of these compounds on the sandy sediments. These results imply that harmful ecological effects might happen in some rivers.	China	YUAN et al., 2014

Given the background, this work, which is part of a project funded by Research Development Foundation (FUNDEP), entitled Advanced Water Treatment for Supplying Emergency Response, aimed developed and validated a methodology for identification of phenolic compounds in surface water, as well as to quantify the presence of these compounds in rivers and in the water treated by a WTP over one year. The risk to environmental and human health of the compounds found was observed. Finally, the DCMD was also prior evaluated for the retention of the studied compounds. It is worth noting that the project is very large and covers other aspects of MD, such as the retention mechanisms of pharmaceuticals and heavy metals, design, efficiency and economic aspects of a solar drive MD unit.

1.2 JUSTIFICATION

Increased contamination of water resources by different types of complex pollutants, such as phenolic compounds, is an issue directly related to public health because put in risk the human and the environment. These emerging contaminants are present in the waters in very low concentrations and the improvement of analytical techniques that allow their detection in this level of concentration deserves special attention from the scientific community, since from the identification and quantification environmental management measures can be taken.

However, even in countries where surveys related to the contamination of rivers are more advanced than Brazil, there is still little information available on the quality of water related to these contaminants. Nevertheless, knowing the extent of contamination and the concentration of phenolic compounds is not enough to determine whether their presence in water put in risk the environment and the human health. Thus, toxicological risk assessments, which are still scarce in the literature, are necessary.

Further, the evaluation of phenolic compounds removal by conventional processes currently used in the treatment of surface water, which has inherent problems and is ineffective in the retention of many micropollutants, and the study of an alternative technology, the DCMD, provide an important insight into the future of water treatment scenario. In this sense, the relevance of this work can be highlighted, since few studies have been published on the occurrence of these compounds in surface water and in national systems of water supply, in order to verify if they present environmental toxicological and human health risk, being an important step for the construction of national knowledge.

Therefore, this work is justified by contributing to the improvement of these micro-pollutant's identification and quantification techniques and to verify their occurrence in important rivers and in the drinking water of a water treatment plant, that supplies a large population. In addition to providing a better understanding of the toxicological risks to the environment and human health, due to the presence of phenolic compounds in surface and supply water. It also provides an alternative treatment through a robust and compact process, the DMCD.

1.3 OBJECTIVE

1.3.1 General objective

Investigate the occurrence of phenolic compounds in surface water and one supply water. In addition, to evaluate the environmental and human health risk of these compounds in the raw water, and its reduction by conventional and DCMD process.

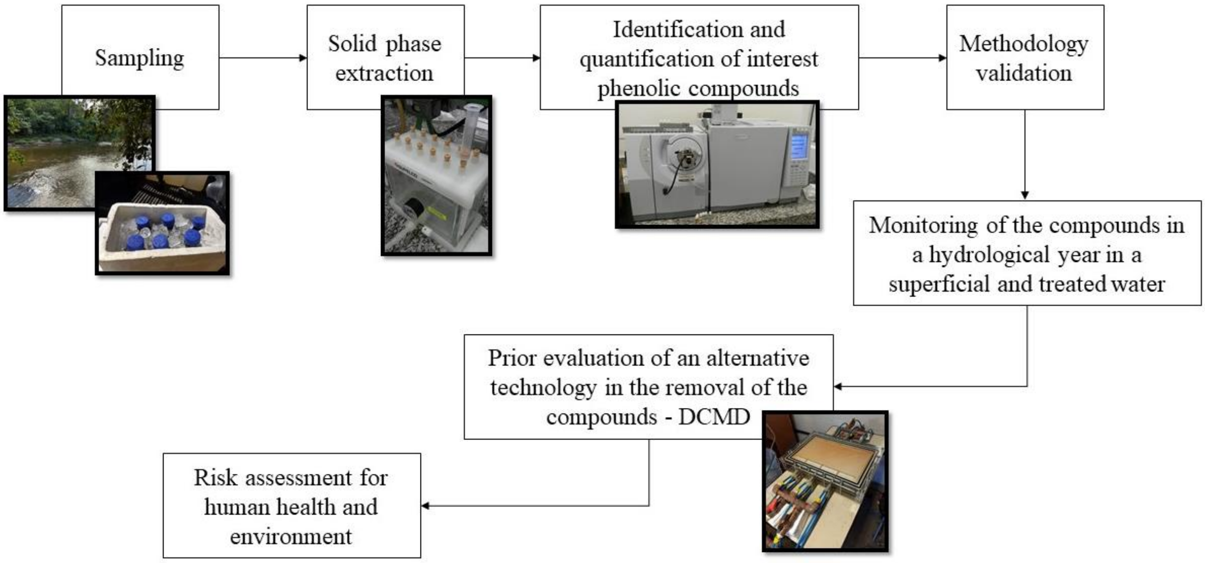
1.3.2 Specific objectives

- Develop and validate an analytical methodology for the identification and quantification of phenolic compounds studied;
- Identify, quantify and verify the most recurring phenolic compounds in the raw water and in the treated water from one WTP throughout a year;
- Evaluate the removal of the phenolic compounds in the studied WTP and by DCMD;
- To develop the environmental and human health risk assessment of these compounds in the aqueous matrices and to analyze the risk reduction capacity of the treatment systems studied.

1.4 DOCUMENT STRUCTURE

This master thesis was divided into five chapters in an article format with the structure described by Figure 1.3 (p.20). Each chapter has been named: Chapter I) Theme presentation; Chapter II) Identification and quantification of phenolic compounds in aqueous matrix: methodology, validation, and occurrence; Chapter III) Risk assessment and phenolic compounds occurrence in a surface water and their removal by conventional treatment; Chapter IV) DCMD as an alternative in the removal of phenolic compounds in water and risk reduction; Chapter V) Final considerations. The article format indicates that the chapters are independents.

Figure 1.3: Research structure



Within this arrangement, Chapter I aims to introduce and contextualize the whole theme discussed in the study, presenting a review of the literature on phenolic compounds in water and the process of direct contact membrane distillation as an alternative technology for the water treatment. It also shows the goals to be accomplished and demonstrates the relevance of the work developed. Chapter II aims to answer the first objective, showing the development and validation of the methodology used for the identification and quantification of phenolic compounds and it analyzes the surface and treated water in order to describe the actuality.

Chapter III deals with the evaluation of the occurrence of phenolic compounds over a year in the raw and treated water of a WTP. Answering the second goal. Chapter IV corresponds to the third objective of this research, in which the DCMD is prior analyze as an alternative to remove the studied compounds from water. The fourth target is answered through Chapters III and IV, where the analysis of the environmental and human health risks related to the presence of the phenolic compounds in the superficial and the risk reduction by conventional and DCMD process are reported. Finally, in Chapter V, final conclusions of the previous chapters were discussed integrated.

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CHAPTER II

Identification and quantification of phenolic compounds in aqueous matrix: methodology, validation, and occurrence

2.1 INTRODUCTION

River monitoring studies have evidenced the presence of organic micropollutants of environmental and toxicological interest, among them phenolic compounds play an important role (ZHONG et al., 2018). It exists in bodies of water due to the discharge of polluted wastewater from industrial, agricultural, domestic activities and as a result of natural phenomena (ANKU et al., 2017). Besides, chlorination treatments in drinking water disinfection may form chlorophenols when phenolic compounds are already present in raw water. Its presence gives off an unpleasant smell and taste in ppb concentration (HUANG et al., 2018).

It is known that phenolic compounds cause severe and long-lasting effects in humans and animals due to their toxicity, persistence and bioaccumulation. They act as carcinogens and cause damage to red blood cells and liver, even at low concentrations (ASIF et al., 2018; FRÉDÉRIC & YVES, 2014; LI et al., 2018). In the list of priority compounds established by the United States Environmental Protection Agency (EPA) eleven compounds are classified as phenolic (2,4,6-trichlorophenol, parachlorometa cresol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-o-cresol, pentachlorophenol, and phenol), due to the frequency and the damages associated with the presence of these micropollutants in the environment. This list is a starting point to be considered in the development of effluent discharge regulation and water quality standards (EPA, 2014). The phenolic compounds are detected in surface water, groundwater and drinking water at concentrations ranging from ng L^{-1} to tens of $\mu g\ L^{-1}$ (ANKU et al., 2017; CAMPOS-MAÑAS et al., 2017; HERMES et al., 2018). Advanced analytical techniques have been developed for the identification and quantification of these micropollutants in order to evaluate the occurrence and efficiency of water treatments currently employed.

Among the analytical techniques, high performance liquid chromatography (HPLC) with ultraviolet (UV) detector, fluorescence detection, electrochemical detection or mass spectrometry (MS) and gas chromatography (GC) are the most used in the determination of phenols (SIMÕES et al., 2007). Historically, GC has been adopted in different studies in the analysis of phenolic compounds (TERZOPOULOU et al., 2014; BIANCHI et al., 2002; DAVÌ & GNUDI, 1999; RODRÍGUEZ et al., 2000), besides being considered in several standard procedures developed by EPA, for example in the methods 604, 635, 8041, and 8270D (EPA, 1984a; EPA, 1984b; EPA, 1995; EPA, 2015). The technique has advantages as high efficiency in the separation of the analytes, high resolution, and also high sensitivity (JÁUREGUI & GALCERAN, 2001; FRIAS et al., 2014). It can be coupled to high selectivity detectors such as electron capture detector (ECD), nitrogen and phosphorus detector (NFD), mass spectrometry in selective ion monitoring mode (MS/SIM), and the flame ionization detector (FID).

However, none of these combinations of technics can reach the required limits of quantification for the phenols direct determination in surface and drinking water, making a preconcentration stage essential. For aqueous matrices, the frequently used techniques are liquid-liquid extraction (LLE) and liquid solid extraction, also known as solid phase extraction (SPE) (JÁUREGUI & GALCERAN, 2001). One of the most widely used extraction systems is SPE, due to its known advantages over LLE, as low sample handling and contamination, low solvent volume, higher efficiency, and good specificity with some polar adsorbent materials (TERZOPOULOU et al., 2014). Currently, a wide variety of adsorbent materials are available for SPE process, both in the form of cartridges and discs (JÁUREGUI & GALCERAN, 2001).

However, in the case of phenolic compounds, several authors have verified the performance of silica materials (C_{18}) in the extraction process, which in general presented higher recovery rates and better reproducibility for more nonpolar phenolic compounds (tri-, tetra-, and pentachlorophenol) (HERMES et al., 2018; RODRÍGUEZ et al., 2000). Consequently, higher throughput volumes can be considered in the preconcentration step without there being an increase in detection limits. On the other hand, when it was used for more polar compounds (phenol, nitrophenol, and monochlorophenols), the material showed lower throughput volumes (< 20 mL) and consequently higher detection limits (RODRÍGUEZ et al., 2000). Therefore, it is still challenging a single-stage of SPE for the recovery of a broad spectrum of compounds with different physicochemical characteristics (TERZOPOULOU et al., 2014).

Another relevant point are the matrix components contained in the extracts that can influence the quantification of the analytes of interest, generating dubious results. The change in the chromatographic response (due to the presence of co-extractives) is called the matrix effect (HAJSLOVÁ et al., 1998). The occurrence of matrix-induced effects and their extent are influenced by several factors, such as analyte polarity, analyzed matrix type, history of the chromatographic system (deposition of substances in the insert), analyte concentration, and others (HAJSLOVÁ & ZROSTLIKOVA, 2003). The matrix effect may generate recovery percentages above 100%, in addition to causing other changes in the chromatographic analysis, such as masking of the analyte peak of interest, generating a false negative result (SALVADOR et al., 2006). This is an important variable to be evaluated during the process of extraction and quantification of micropollutants.

In this context, it is important to establish rapid, sensitive and reliable analytical method that allow the determination of a wide range of phenolic compounds in water at the low levels of concentration that they are found. These methods are particularly needed to support studies addressing the occurrence and toxicity of these compounds, as well as supporting research in the development and evaluation of remediation processes. Thus, this work aims to develop and evaluate a methodology to identify and quantify a variety of 17 phenolic compounds in samples of raw water obtained in two hydrographic basins and a treated water from a water treatment plant (WTP) that supplies a large population.

2.2 MATERIALS AND METHODS

2.2.1 Sample collection

Five samplings were carried out in two different watersheds as shown in Figure 2.1 (p. 36). Three samplings were done in the same watershed in different points (RW1, RW2, and RW3) and the other two in another river, upstream of a WTP (RW4) and the treated water from a WTP (WT1). With the purpose to analyze the effect of the aqueous matrix on the phenolic compounds identification and verify their occurrence at different points. Some characteristics of the collection sites are described in Table 2.1 (p. 36).

Figure 2.1: Schematic of sampling points

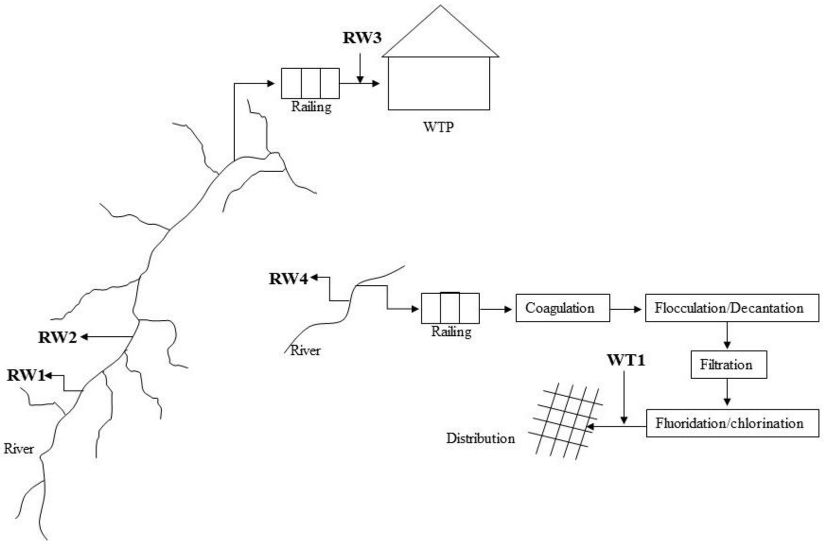


Table 2.1: Characteristics of the collection sites

Collection site	Water flow average	Climate	Other information
RW1	900 m^3 s^{-1}	temperature ranging from 21.6 to 26.9 °C; annual rainfall: 1109 mm	Rural supply
RW2	900 m^3 s^{-1}	temperature ranging from 21.6 to 26.9 °C; annual rainfall: 1109 mm	Rural supply
RW3	900 m^3 s^{-1}	temperature ranging from 21.6 to 26.9 °C; annual rainfall: 1109 mm	It feeds a conventional WTP that supplies an estimated population of 263 689 people
RW4	300 m^3 s^{-1}	temperature ranging from 18 to 27 °C; annual rainfall: 1390 mm	It feeds a conventional WTP that supplies an estimated population of 2.5 million people
WT1	300 m^3 s^{-1}	temperature ranging from 18 to 27 °C; annual rainfall: 1390 mm	TW that supplies an estimated population of 2.5 million people; WTP treatment type: coagulation, flocculation, sedimentation, sand filtration, disinfection (chlorination) and fluoridation

The collection was carried out taking into account the method of sampling, preserving and storing of NBR 9898 for phenol analysis (ABNT, 1987) and the recommendations of EPA 528 (EPA, 2000). Amber clean bottles (1 L) were immersed countercurrent in the rivers at about 15 to 30 cm below the water surface, to avoid the introduction of surface contaminants, in places that was no water stagnation or in places near the bank. After collection, these samples were immediately acidified to pH near to 3. All samples were refrigerated during transport so that the temperature did not exceed 10 °C. In the laboratory, these samples were kept at a temperature below 5 °C until the extraction time, which did not exceed 72 h.

2.2.2 Physicochemical characterization

The collected samples were characterized in terms of their physicochemical properties according to the recommendations of the Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The parameters and their respective methods are presented in Table 2.2.

Table 2.2: Physicochemical methodology for the sample's characterization

Parameter	Method	Parameter	Method
Turbidity (Hach 2100AN Turbidimeter)	2130B	*Determination of cations*	
pH (Qualxtron QX 1500 pHmeter)	4500B	Calcium (Ca)	3500-Ca
UV Absorption (254 nm) (Hach DR 2800 Spectrometer)	2120C	Magnesium (Mg)	3500-Mg
Apparent color (Hach DR 2800 spectrometer)	2120C	Sodium (Na)	3500-Na
Real Color (Hach - DR 2800)	2120C	Potassium (K)	3500-K
Total suspended solids (TSS)	2540D	Iron (Fe)	3500-Fe
Total Solids (TS)	2540B	Aluminum (Al)	3500-Al
Total organic carbon (TOC) (Shimadzu TOC-V CNP TOC)	5310	Arsenic (Ar)	3500-As
Conductivity (Hanna HI 9835 Conductivity Meter)	2510B	Lead (Pb)	3500-Pb
Alkalinity	2320B	Sulfur (S)	3500-S
Total nitrogen (TN)	4500-NC	Silica (Si)	4500-Si

2.2.3 Phenolic compounds assess

Seventeen phenolic compounds were studied, which seven of them are in the EPA priority compounds list (2-chlorophenol, 4-chloro-3-metylphenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichloropheno, 4,6-trichlorophenol, and 4-nitrophenol) (EPA, 2014). In addition to the compounds established by the EPA, bisphenol A was also considered due to its recurrence in industrial segments, as well as some isomers of the agency's compounds list and other phenolic compounds (2-metylphenol, 3-metylphenol, 2,6-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,3,6-trichlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and 3,4,5-trichlorophenol). The complete list of compounds considered along this study with their identification number, molecular formula, molecular structure and, some physical-chemical properties, is presented in the ANNEX I (p. 125 – 126).

2.2.4 Reagent and standards

The acetonitrile (J.T.Baker®), methanol (Exodus Scientif®), dichloromethane (Synth®) and ethyl acetate (Synth®) solvents were HPLC grade. Gases provided by White Martins were used with 99.999% purity. For pH adjustment a 0.01 mol L^{-1} hydrochloric acid solution (HCl) was used. The EPA 8040A Phenol Calibration Mix of analytical standard for the phenol compounds and Bisphenol A (99%) were purchased from Sigma-Aldrich®.

2.2.5 Solid phase extraction

The extraction methodology was based on the recommendation of the National Environmental Protection Agency of the United States through the EPA method 528, 3535A, and 8041. For the SPE, four different solvents proposed by the agency were evaluated. They were dichloromethane, acetonitrile, ethyl acetate, and methanol, opting for the one that presented the highest recovery degree for the analytes in question. In this work, C_{18} / 18% cartridges (500 mg / 6 mL - Applied Separations) were used, conditioned with 5 mL of solvent, after 5 mL of MilliQ water (ThermoScientific Smart2Pure 3 UV). Then, 1 L of the sample was percolated at pH 2, maintaining a constant flow and close to 20 mL min^{-1}. The cartridge remained under vacuum for 20 min after finalizing the concentration process for complete removal of moisture and the compounds were eluted using 2 times 1 mL of the solvent. The entire extraction procedure was performed with a manifold (Supelco-Visiprep ™).

2.2.6 Identification and quantification of phenolic compounds

The gas chromatography (GC 2010-Pus, Shimadzu) equipped with FID to increase the sensitivity of the method was used for the compound’s identification and quantification. A Zebron ™ MultiResidue ™ column (30 m x 0.32 mm x 0.50 µm) was utilized in the GC and helium as carrier gas. The optimum oven programming was 40 °C for 4 minutes, 4 °C min^{-1} to 240 °C and finally 240 °C for 5 minutes.

The injection volume of the samples was 2 μL in splitless mode, with the injector temperature at 275 °C. An automatic sampler (AOC-20i, Shimadzu) was used in all tests, programmed to perform a solvent wash (2 x) before and after each injection, in addition to settle the syringe with the sample (2 x). The FID detector temperature was maintained at 300 °C and an Air / H_2 mixture (400/40 mL min^{-1}) was used for the combustion while a N_2 / Air mixture (30 mL min^{-1}) was used as gas make-up to scan components through the detector in order to minimize the bandwidth of compounds. For the calibration curves, a stock solution at the concentration of 5,000 μg L^{-1} was prepared and from this, eighteen dilutions were performed at concentrations of 1 to 3,200 μg L^{-1}, all in isopropanol.

2.2.7 Validation of the analytical methodology

The methodology validation was based on the classical literature and standard methods defined by the International Council for Harmonization of Technical Requirements for Pharmaceutical Products for Human Use (ICH, 2005), and followed the requirements and recommendations of ANVISA (ANVISA, 2003) and INMETRO (INMETRO, 2007). The parameters evaluated were: selectivity, linearity, limit of detection and quantification, sensitivity, precision, accuracy, resolution, and matrix effect. The selectivity was evaluated by the resolution (R) and the separation factor (α) of the peaks. Equation 2.1 indicates that the resolution is the difference between the retention times divided by the mean width of the peak.

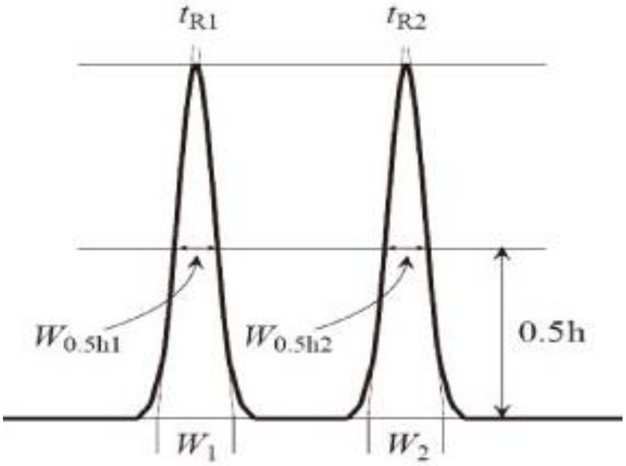
$$R = (t_{R2} - t_{R1}) \Big/ \frac{1}{2}(W_1 + W_2)$$ Equation 2.1

At a peak with Gaussian distribution, the peak width is W = 4σ (where σ is the standard deviation) and the peak length at half height is $W_{0.5h} = 2.354\sigma$. Substituting these relations into Equation 2.1 we get Equation 2.2.

$$R = 1.18 * (t_{R2} - t_{R1}) \,/ (W_{0.5h1} + W_{0.5h2})$$ Equation 2.2

Where t_{R1} and t_{R2} are the retention times for each peak ($t_{R1} < t_{R2}$); $W_{0.5h1}$ and $W_{0.5h2}$ the width corresponding to half the height (h) of each peak. A schematic drawing of these parameters is presented in Figure 2.2.

Figure 2.2: Peaks parameters used to calculate the resolution



Source: SHIMADZU, 2018a.

The separation factor (α) is defined as the ratio of the retention factors (k), as shown in Equation 2.3. Where t_0 is the dead time.

$$\alpha = (k_2/k_1) = (t_{R2} - t_0/t_{R1} - t_0) \qquad \text{Equation 2.3}$$

Accuracy was assessed by recovery degree. For these tests, the ultra-pure water, treated water and raw water were fortified with 0.4 μg L^{-1} of the analytical standards, and the experiments were performed in duplicate following the same procedure described for SPE. The extracts were analyzed and the recovery degree (RD) calculated according to Equation 2.4.

$$\%RD = 100 * (A - B)/C * MEF \qquad \text{Equation 2.4}$$

Where A corresponds to the concentration of the compound in the sample after fortification, B the concentration of the compound in the non-fortified sample, C the dosed concentration of the compound in the sample and MEF the matrix effect correction factor.

Precision was assessed through repeatability and intermediate precision expressed using coefficient of variation (CV%) and standard deviation. For this, the area of a standard injected three times on the same day and on three different days was compared to each other.

The matrix effect was evaluated from the samples obtained for the recovery degree added 200 µg L^{-1} of each compound, and compared with samples of ultrapure water, also fortified. The correction factor and the matrix effect were calculated from Equations 2.5 and 2.6.

$$MEF = (D - E)/F \qquad \text{Equation 2.5}$$

$$Matrix\ effect\ (\%) = (1 - MEF) * 100 \qquad \text{Equation 2.6}$$

Where D corresponds to the area of the compound in the fortified sample, E the area of the compound in the non-fortified sample and F the area of the compound in fortified ultrapure water.

The quantification limit (QL) and detection limit (DL) were determined based on the standard deviation of the intercept and the mean of the slope referring to three calibration curves, estimated by Equation 2.7 and 2.8 (ANVISA, 2003; IMOTO & FREITAS, 2008; SKOOG et al., 2006).

$$DL = 3.3 * DP/I \qquad \text{Equation 2.7}$$

$$QL = 10 * DP/I \qquad \text{Equation 2.8}$$

Where DP is the estimate of the standard deviation of the response or instrumental white (three curves) and I is the slope or angular coefficient of the calibration curve.

The limits of quantification and detection related to the method were obtained from Equations 2.9 and 2.10.

$$DLM = DL/(CF * R) \qquad \text{Equation 2.9}$$

$$QLM = QL/(CF * R) \qquad \text{Equation 2.10}$$

Where DLM is the detection limit of the method; QLM the quantification limit of the method; CF the concentration factor, and R the recovery index (R = %RD * 0.01).

The linearity for each compound was evaluated from the correlation coefficient (R^2) associated to its calibration curve, which correlates measured analytical signal and analyte concentration (SKOOG et al., 2006), described a linear equation (Equation 2.11).

$$y = ax + b$$ Equation 2.11

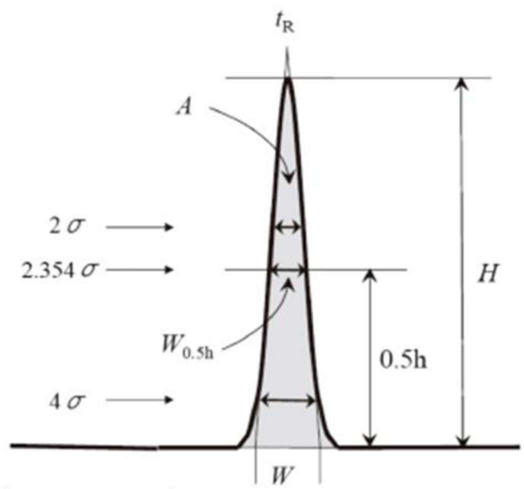
Where y is the analytic signal, x the analyte concentration, a is the angular coefficient, and b is the linear coefficient.

Besides these parameters, the quality of the peaks was also evaluated when considering the number of theoretical plates and the tail formation in the peaks, commonly called peak tailing. Assuming a Gaussian distribution (normal distribution), the number of theoretical plates is represented by Equation 2.12.

$$N = (t_R/\sigma)^2$$ Equation 2.12

Where t_R is the retention time and σ is the standard deviation. As shown in Figure 2.3, assuming a Gaussian distribution, the width of the peak W is 4σ and the length of the peak at half height ($W_{0.5h}$) is 2.354σ. Substituting these values into Equation 2.12 gives Equation 2.13 (p. 43).

Figure 2.3: Peaks parameters used to calculate the number of theoretical plates



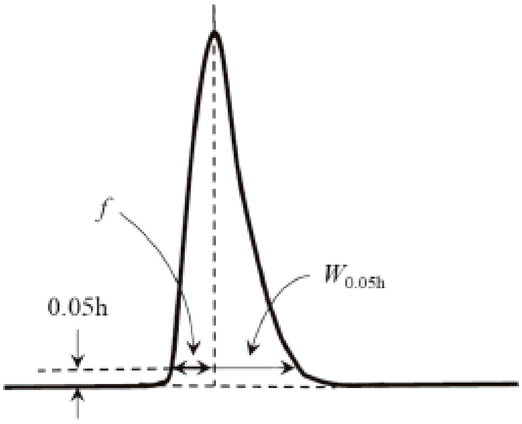
Source: SHIMADZU CORPORATION, 2018b.

$$N = 5.54 * (t_R/W_{0.5h})^2$$

Equation 2.13

The peak tailing was calculated through Equation 2.14 based on the measurements shown in Figure 2.4.

Figure 2.4: Peak parameters used to calculate peak tailing



Source: SHIMADZU CORPORATION, 2018b.

$$S = W_{0.05h}/(2 * f)$$

Equation 2.14

Where $W_{0.05h}$ is the peak width at 5% of height (h) and f is the distance between the beginning of the peak and the vertical line that intersects the top of the peak.

2.3 RESULTS AND DISCUSSION

2.3.1 Validation of SPE and chromatographic methodology

The recovery test results in the solid phase extraction step are presented in Figure 2.5 (p. 45) for the different solvents tested and in Figure 2.6 (p. 46) for the different matrices analyzed.

Figure 2.5: Compounds recovery in the SPE for the different solvents tested

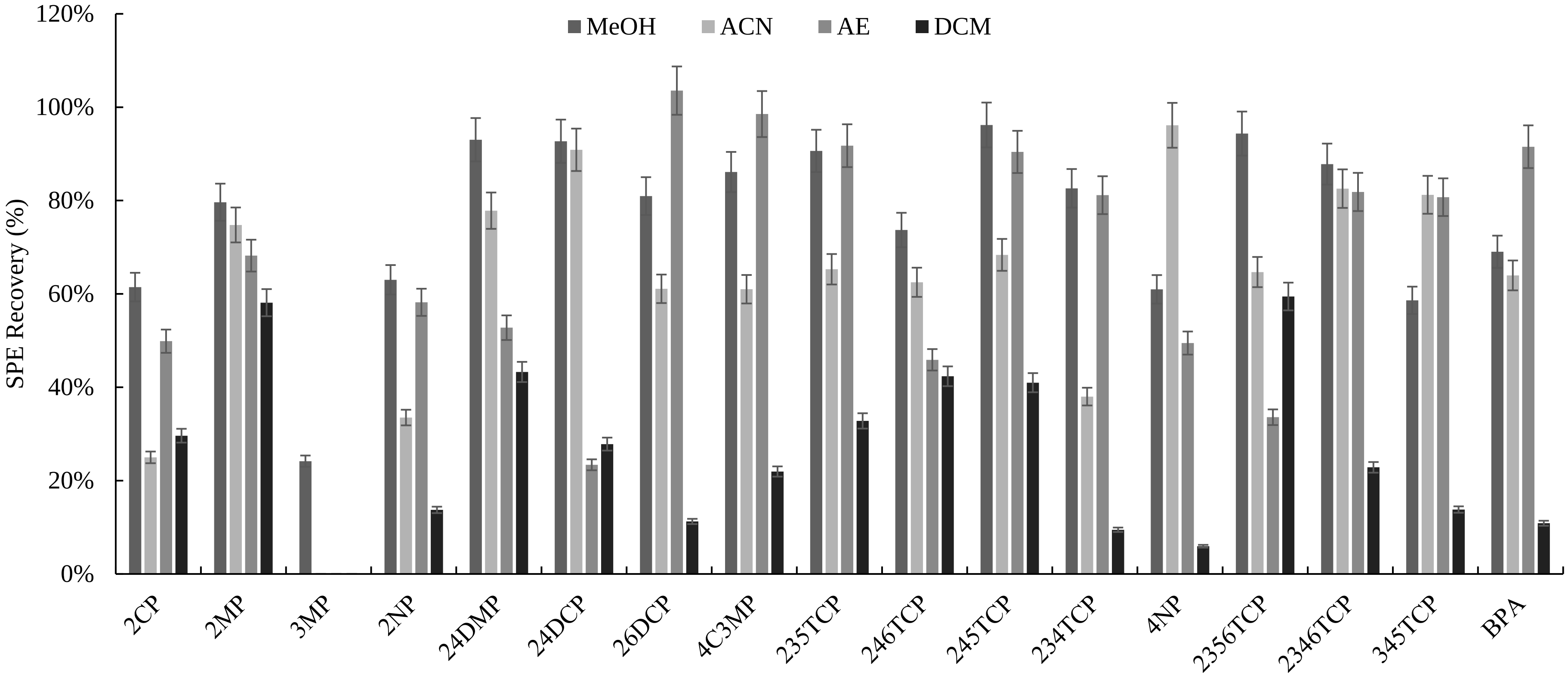
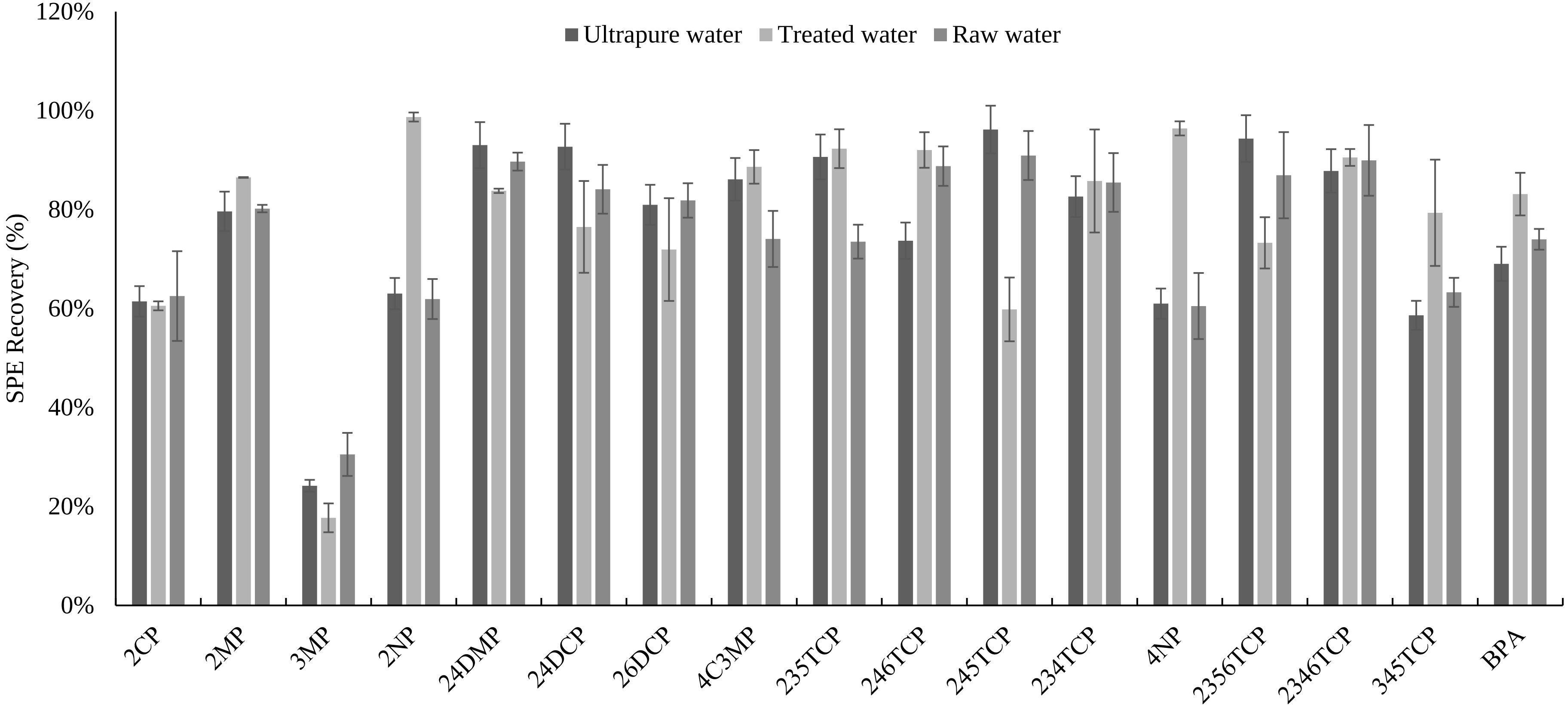


Figure 2.6: Compounds recovery in the SPE for the different matrices



From Figure 2.5 it is noted that the methanol (MeOH) solvent obtained a better performance, referring to the average recovery grade (76.18%), when compared to acetonitrile (ACN - 61.57%), ethyl acetate (EA - 64.74%), and dichloromethane (DCM - 26.13%). Since the separation process involves the difference of solubility between the analytes in the aqueous phase and in the stationary phase, the polarity of these compounds is determinant in the efficiency of the extraction process. The compounds 3MP, 4NP and 2NP showed recovery values below 70% when methanol was used in the extraction process. These compounds are hydrophilic in character and have a low octanol-water partition coefficient value ($1.31 < \log K_{ow} < 2.09$). For this reason, its affinity is lower for nonpolar adsorbents, such as C_{18}, that the functional groups bound to the solid phase attract the hydrophobic compounds present in the sample through the Van der Waals interactions and extract them from the aqueous solution. This implies lower production volumes and justifies the low rate of recovery of these compounds (RODRÍGUEZ et al., 2000).

On the other hand, compounds of lower polarity such as tri- and tetrachlorophenols have higher $\log K_{ow}$, and unlike the other compounds mentioned, presented a higher recovery degree. Results such as these were also observed by Jáuregui & Galceran (2001), which reported low levels of recovery for nitrophenols and monochlorophenols in general. The authors also estimated the transfer volume for these compounds, being this value less than 20 mL and much lower than the volumes considered in the evaluation of the recovery degree. Thus, it was decided to follow the studies using methanol as solvent since it presented the best result for most of the compounds studied and has been used in other studies that seek to identify different phenolic compounds in aqueous matrix (FARAJI et al., 2012; PETRIES et al., 2016).

In Figure 2.6 it is possible to analyze the influence of different matrices on the recovery degree with methanol as solvent. As predicted, the recovery degree for the phenolic compounds in the ultrapure water, accompanied by the treated water were higher. It is well knowing that the presence of organic matter and the presence of solid particles in the samples can also significantly affect the recovery of the analytes. Font et al. (1993) emphasized that the presence of these results in a competition for the active sites present in the adsorbent and results in a reduction of the recovery degree. Nonetheless, all compounds, except 3MP, had a recovery greater than 50%. According to Padilla-Sánchez et al. (2011), recoveries between 50 and 60% may be extraordinarily in environmental analysis whenever the accuracy values are adequate (< 30%).

The individual values of the parameters and correlation coefficients for the analytes are shown in Table 2.3. In relation to the linearity of the calibration curves, it was possible to reach regression coefficients greater than 0.99 for all analytes, in both concentration ranges, indicating a satisfactory adjustment of the analytical method employed according to Reis (2018).

Table 2.3: Parameters and correlation coefficient of the calibration curves used in the sample's quantification

Compounds	**1-400 µg L^{-1}**			**400-5000 µg L^{-1}**		
	a	b	R^2	a	b	R^2
2CP	6.21	-100.881	0.9995	3.661	-210.205	0.9987
2MP	9.018	-64.783	0.9984	8.002	-299.227	0.9996
3MP	16.951	526.581	0.9942	12.299	1148.41	0.9978
2NP	8.82	-69.997	0.9981	11.854	-681.888	0.9987
24DMP	4.05	76.077	0.9942	4.103	1979.756	0.9988
24DCP	4.026	45.684	0.9967	4.21	2714.654	0.9976
26DCP	6.476	-11.03	0.9971	5.103	35.133	0.9997
4C3MP	2.81	3.785	0.9991	2.983	36.141	0.9995
235TCP	2.939	-37.747	0.9955	3.282	-115.349	0.9991
246TCP	2.843	-56.373	0.9983	2.927	26.052	0.9979
245TCP	3.942	-121.672	0.9981	3.147	-13.098	0.9992
234TCP	3.352	-89.09478	0.9954	3.214934	-38.02707	0.9996
4NP	3.321	-11.206	0.9997	3.007	-256.297	0.9986
2356TCP	4.392	100	0.9929	4.27	-333.429	0.9981
2346TCP	2.266	105.198	0.9983	2.104	-215.622	0.999
345TCP	2.807	-14.569	0.9995	2.442	69.546	0.9986
BPA	3.097	459.844	0.9973	3.981	46.375	0.9993

From the analysis of Table 2.3 (p. 49) and Figure 2.7 (p. 49) it is possible to see that the 3MP, 2MP, 2NP, 2CP, and 26DCP compounds were the most sensitive to the method due to small variations in concentration result in higher response variation, in other words, higher values of the angular coefficient in the analytical curves (INMETRO, 2017). However, the tri- and tetrachlorinated compounds showed the lowest sensitivity as EPA warns, in its method 528 (EPA, 2000), that these compounds may present less sensitivity when compared to others in the list. This fact may be related to the pKa values of these phenols, which directly influence their ionization. The other compounds exhibited intermediate and similar sensitivity.

Figure 2.7: Analytical curves obtained for the analyzed compounds

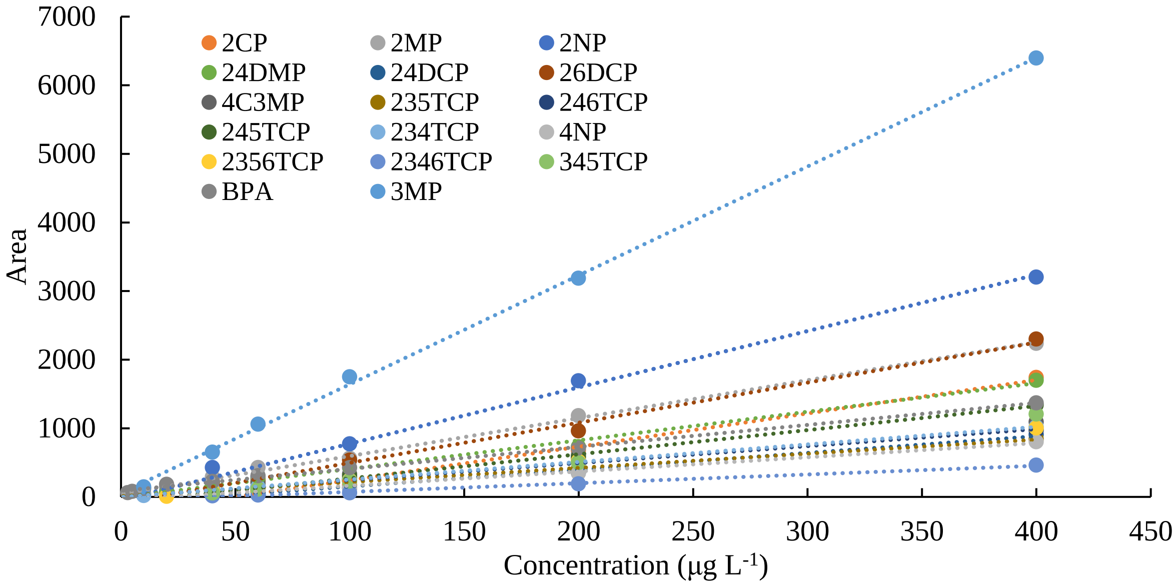


Table 2.4 shows the selectivity of the method, referring to the resolution and the peak tailing factor of the chromatographic peaks. The resolution and possible interference caused by the matrix were absent.

Table 2.4: Resolution, peak tailing and theoretical plates for the analyzed compounds

Compounds	Resolution	Peak tailing	Separation	Theoretical plates
2CP	0.665	1.935	1.062	2.27E+04
2MP	8.654	1.462	1.516	3.75E+04
3MP	3.344	1.152	1.155	2.91E+04
2NP	7.908	1.024	1.353	8.58E+04
24DMP	4.267	1.19	1.093	8.04E+04
24DCP	4.076	1.523	1.085	1.17E+05
26DCP	21.546	1.084	1.278	5.51E+05
4C3MP	14.285	1.117	1.104	6.02E+05
235TCP	7.768	1.101	1.052	6.46E+05
246TCP	1.225	1.153	1.008	7.37E+05
245TCP	2.986	1.137	1.018	6.82E+05
234TCP	5.988	1.089	1.037	7.29E+05
4NP	76.447	1.276	1.265	1.24E+06
2356TCP	2.771	1.206	1.015	5.89E+05
2346TCP	2.25	1.335	1.012	1.16E+06
345TCP	18.55	1.172	1.08	1.50E+06
BPA	69.896	1.93	1.315	2.82E+06

Reference values[(a)]	> 2	≤ 2	> 1	2.00E+06

(a)(SNYDER et al., 2012)

The values of resolution, peak tailing, separation and theoretical plates for most of the compounds met the reference values, indicating that the method can perform a good chromatographic separation and presents separate peaks and possible interferences caused were absent. The 2CP and BPA showed peak tailing values close to the limit, probably due to their high affinity for the column (FILHO et al., 2010). The 246TCP and 2CP presented resolution < 2, implying the presence of near-chromatographic peaks of these compounds. In contrast, the peak tailing, separation and theoretical plates presented satisfactory values.

The results concerning to quantification limit of the method (QLM) and detection limit of the method (DLM) are presented in Table 2.5 (p. 51).

Table 2.5: Quantification limit of the method (QLM), detection limit of the method (DLM), and precision for the considered compounds

Compounds	QLM (µg L^{-1})	DLM (µg L^{-1})	Intra-day[a]		Inter-day[a]		Matrix Effect (%)	Matrix Effect (%)
			Area[b]	CV(%)	Area[b]	CV(%)	Raw water	Treated water
2CP	0.276	0.091	20711.333 ± 185.823	0.90%	20099.000 ± 796.823	3.96%	-819.068	-724.576
2MP	0.012	0.004	30393.000 ± 130.885	0.43%	29728.333 ± 1012.588	3.41%	40.835	62.53
3MP	0.023	0.008	56877.333 ± 265.786	0.47%	54807.333 ± 2927.603	5.34%	26.460	39.12
2NP	0.035	0.012	30268.667 ± 142.290	0.47%	29507.667 ± 1165.631	3.95%	74.534	84.234
24DMP	0.012	0.004	16394.667 ± 89.092	0.54%	15585.000 ± 956.668	6.14%	44.205	69.15
24DCP	0.007	0.002	15993.333 ± 43.924	0.27%	15420.667 ± 620.519	4.02%	34.590	47.38
26DCP	0.017	0.006	19422.000 ± 244.514	1.26%	17645.000 ± 1472.404	8.34%	56.010	68.498
4C3MP	0.007	0.002	12308.000 ± 86.029	0.70%	11692.667 ± 693.170	5.93%	46.847	54.128
235TCP	0.044	0.014	12305.333 ± 497.150	4.04%	11504.667 ± 243.330	2.12%	45.531	66.899
246TCP	0.083	0.028	12207.667 ± 621.602	5.09%	11613.000 ± 1090.648	9.39%	53.800	65.054
245TCP	0.031	0.010	14260.333 ± 711.367	4.99%	12409.667 ± 962.367	7.75%	42.122	46.48
234TCP	0.053	0.018	12777.667 ± 94.320	0.74%	12009.667 ± 718.606	5.98%	55.582	73.979
4NP	0.170	0.056	9472.333 ± 261.514	2.76%	9449.667 ± 221.157	2.34%	32.690	59.064
2356TCP	0.016	0.005	5142.333 ± 159.177	3.10%	5219.667 ± 85.407	1.64%	15.224	29.676
2346TCP	0.030	0.010	6741.667 ± 550.572	8.17%	6010.333 ± 436.552	7.26%	26.068	163.931
345TCP	0.048	0.016	9731.333 ± 123.597	1.27%	9476.000 ± 614.388	6.48%	43.789	55.977
BPA	0.061	0.020	12013.333 ± 519.562	4.32%	11893.333 ± 902.826	7.59%	56.172	73.62

[a](n=3); [b]Average ± standard deviation; CV = Coefficient of variation.

In the methodology used, the QLM found ranged from 0.007 µg L^{-1} (24DCP and 4C3MP) to 0.276 µg L^{-1} (2CP) and the DLM ranged from 0.002 µg L^{-1} to 0.091 µg L^{-1} for the same compounds, respectively. SIMÕES et al. (2007) was developed and validated a methodology for the analysis of ten phenolic compounds in the raw and treated water in GC-MS, seven of them in common with the study (2CP, 245TCP, 246TCP, 2346TCP, 24DP, 26DP and, 43CMP). For these compounds the DLM ranged from 0.052 µg L^{-1} (245TCP) to 4.1 µg L^{-1} (2CP) and the QLM ranged from 0.16 µg L^{-1} (24 DP) to 12 µg L^{-1} (2CP). These limits values detect by Simões et al. (2007) were higher than those found in this study. To decrease the DLM and QLM it may be necessary to use a larger sample volume in the solid phase extraction step or to perform another concentration step after elution using a smaller volume of the same or a different solvent.

The accuracy of the method was evaluated through its repeatability and proven from the CV results (%), presented in Table 2.5. For the analyzes performed on the same day (n = 3), CV values (%) varied between 0.27% (24DCP) and 8.17% (2346TCP), lower than those observed by Simões et al. (2007), which varied between 8.3% (24DCP) and 32% (2346TCP). When the samples were evaluated on different days, the values observed varied between 1.64% (2356TCP) and 9.39% (246TCP). It is possible to attest to the validity of the proposed methodology for its accuracy for the level of concentration considered in the trials (3200 µg L^{-1}) and establishing as acceptance criteria 7 <CV% <11 as suggested by INMETRO (2007).

Furthermore, Table 2.5 shows the matrix effect for each analyte. According to several authors (AMATE et al., 2010; MORENO-GONZÁLEZ et al., 2017), matrix effects can be classified as weak (0 to ± 20%), medium (± 20 to 50%) and strong (> ± 50%). Positive values indicate that the raw water matrix has a suppressive effect on the compounds analytical signal and when negative values happen, an augmentative effect of the signal occurred. Most of the compounds studied had a matrix effect considered as medium and strong effects. In the case of raw water, this can be associated to the high organic matter present in this matrix (RODRÍGUEZ et al., 2000). In contrast, high values in treated water may be associated to ion suppression from another analyte, a metabolite or even from internal standard.

The 2NP and 2356TCP showed higher and lower matrix effects, respectively. The first one has more polar character compared to the others, probably associated preferentially to the organic material than to the adsorbent of nonpolar character. Consequently, in addition to a low recovery degree, the compound still has a higher matrix effect when compared to the others. One of the suggestions made by Reis (2018) to rectify the matrix effect is the use of compounds for the internal standardization of the analyzes. Although the internal standards were not used in the study, the values obtained for the matrix effect were considered in the quantification step to correct the observed values.

2.3.2 Physical-chemical characterization of the samples

After being collected, all surface water samples were characterized (RW1, RW2, RW3, and RW4). Table 2.6 presents the average values of the main physical-chemical parameters of the samples. In addition, it also has the respective maximum concentration allowed by Ordinance N° 2914/2011 / N° 5/2017 (consolidation), of the Ministry of Health for drinking water (BRASIL, 2011) and some requirements established by the National Council of the Environment, Resolution 357/2005, for river water classification (BRASIL, 2005).

Table 2.6: Physicochemical parameters for the sample collected in 2018

Parameter	RW1	RW2	RW3	RW4	Resolution 357/2005		Ordinance Nº2914 (MPV *)
					Class I	Class II	
Turbidity (NTU)	92.5	162	8.09	14.2	40	100	0.5***
pH	7.59	7.57	6.58	6.19	6 to 9	6 to 9	6 to 9.5
UV-Vis 254 nm	0.083	0.02	0.03	0.021			
Perceived color (mg Pt-Co L^{-1})	239	391	< DL	74			15
Real Color (mg Pt-Co L^{-1})	< DL	< DL	< DL	< DL		<75	
TSS (mg L^{-1})	94	68	11	16			
TS (mg L^{-1})	120	92	72	108			
TOC (mg L^{-1})	1.292	2.728	2.09	1.99			
Conductivity (µS cm^{-2})	47.05	63.78	108.5	121.3			
Alkalinity (mg $CaCO_3$ L^{-1})	21.34	24.25	22.3	29.3			
TN (mg L^{-1})	0.96	0.751	0.984	1.37	<2.18	<2.18	
Ca (mg L^{-1})	3.916	3.964	4.749	21.1			500****
Mg (mg L^{-1})	1.815	2.0128	1.816	6.4			500****
Na (mg L^{-1})	1.092	0.835	3.639	5.68			200
K (mg L^{-1})	2.153	1.393	1.967	1.07			
Fe (mg L^{-1})	1.321	0.847	<0.1	<0.1	0.3	0.3	0.3

Parameter	RW1	RW2	RW3	RW4	Resolution 357/2005		Ordinance Nº2914 (MPV *)
					Class I	Class II	
Al (mg L^{-1})	0.749	0.349	<0.1	<0.1	0.1	0.1	0.2
As (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	0.01	0.01	0.01
Pb (mg L^{-1})	<0.1	<0.1	<0.1	<0.1	0.01	0.01	0.01
S (mg L^{-1})	<0.1	<0.1	<0.1	2.69			
Si (mg L^{-1})	7.207	7.875	6.005	6.41			

* MPV (Maximum Permitted Value); ** DL (Detection Limit) *** Filtration rapid (conventional and direct filtration); **** Defines MPV 500 mg L^{-1} for Hardness (the sum of Mg and Ca concentrations).

The four samples presented some different characteristics such as pH, conductivity, solids, alkalinity, color, different concentrations of cations and the presence or not of some metals such as iron, aluminum, sulfur and silicon, which are important to analyze the influence of different matrices in the identification and quantification of phenolic compounds. To be classified as water type I or II in Brazil the sample must meet some requirements established by the National Council of the Environment, Resolution 357/2005. In river water classified as type I or II, human consumption is allowed after simple or conventional treatment. Treatment plants should be able to absorb differences in raw water quality and produce water in accordance with the parameters established in Ordinance N° 2914.

One of the main physicochemical indicators of water quality is pH and turbidity. In terms of pH, the studied rivers are classified in Classes I and II because they have pH between 6 and 9. The pH has a great influence on the biological action and hydrolysis of complex chemical compounds, as well as on the reducing the volatility of the constituents, affecting factors such as bioavailability, absorption and solubility of the phenolic compounds (ABNT, 1987). Thus, it is necessary that the monitoring of these compounds always consider the pH of the matrix which their occurred. Already the turbity evaluates the presence of suspended and colloidal particles present in the sample by the degree of attenuation of intensity that a lux beam suffers when crossing it. For the samples in question, the observed value of both pH and turbidity fits the class I or II, except for the sample RW2 that has a higher turbidity.

The UV absorption at 254 nm allows monitoring of the organic load and is associated with the total organic carbon (TOC) and dissolved organic carbon (COD), since organic compounds with aromatic structure or double carbon bonding are able to absorb the radiation ultraviolet at 254 nm (REIS, 2018). Although there is no value established by CONAMA 357/2005, the raw water sample presented values close to those observed by REIS (2018), who evaluated this parameter for six different raw water samples except the sample RW2 that has a higher absorption.

In addition to UV absorption at 245 nm, the real color of the sample was also evaluated. The parameter is associated with the ability of a sample to transmit visible light at a wavelength sensitive to the human eye and may be the result of natural action (organic matter and presence of iron and manganese) or anthropogenic (industrial waste and domestic sewage). The samples measured real color were lower than the detection limit of the method (5 mg Pt-Co L^{-1}), consequently less than the maximum established by the Council (75 mg Pt-Co L^{-1}) for type II.

The other parameters evaluated are not regulated by the National Environmental Council, or do not constitute a drinking standard, although their evaluation is important when considering the use of the sample in other processes. The presence of particulate matter may, among other things, decrease the efficiency in the extraction processes by saturating the adsorbent capacity with compounds in addition to the desired analytes. Moreover, the presence of organic matter may decrease the selectivity of the method and result in more complex chromatograms, making it difficult to analyze by chromatographic techniques (RODRÍGUEZ et al., 2000).

2.3.3 Identification and quantification of phenolic compounds

Through the SPE and the GC-FID injection of the samples it was possible to identify the phenolic compounds present in the samples evaluated with the purpose of verifying the availability of these compounds in a current scenario. Among the 17 phenolic compounds studied, 15 were identified and quantified in the samples collected as can be seen in the Table 2.7 (p.56).

Table 2.7: Concentration average of phenolic compounds found in RW1, RW2, RW3, RW4, and WT1 water samples collected in 2018

Sample	**2MP (µg L^{-1})**	**3MP (µg L^{-1})**	**2NP (µg L^{-1})**	**24DMP (µg L^{-1})**	**24DCP (µg L^{-1})**	**26DCP (µg L^{-1})**	**235TCP (µg L^{-1})**	**234TCP (µg L^{-1})**	**245TCP (µg L^{-1})**	**4C3MP (µg L^{-1})**	**4NP (µg L^{-1})**	**2356TCP (µg L^{-1})**	**2346TCP (µg L^{-1})**	**345TCP (µg L^{-1})**	**BPA (µg L^{-1})**
RW1		1.36 ± 0.195	1.42 ± 0.205			1.768 ± 0.255	1.912 ± 0.275				6.425 ± 0.925				3.009 ± 0.433
RW2			0.289 ± 0.074	0.731 ± 0.03	1.490 ± 0.064					24.162 ± 2.031		0.241 ± 0.008	5.611 ± 0.41		0.446 ± 0.092
RW3	0.519 ± 0.066		0.354 ± 0.09	0.647 ± 0.026	0.131 ± 0.056		0.308 ± 0.017	0.355 ± 0.038							2.877 ± 0.593
RW4			0.525 ± 0.134					0.292 ± 0.031							1.328 ± 0.274
WT1	0.381 ± 0.025		0.218 ± 0.04		0.114 ± 0.015				0.163 ± 0.099		0.138 ± 0.015			380.072 ± 8.04	0.04 ± 0.004

The 2-nitrophenol and bisphenol A were found in all samples. Studies have shown that between the nitrophenol isomers, the 2NP is found to be more toxic (LIU et al., 2009; KUPETA et al., 2018). Because of the aromatic ring in its structures, treatment through chlorination generates chlorinated byproducts that are stable and potentially toxic (CHAN et al., 2003). Concerning to bisphenol A, it is the most popular representative of bisphenol group and was first synthesized over 100 years ago. During the 1930's BPA was investigated and known as endocrine disruptor (ZHANG et al., 2019). Being an important industrial chemical, it is primarily used as an intermediate in the production of polycarbonate plastics and epoxy resins. They are widely used in different products of daily life, including digital media (typically CDs and DVDs), electronic equipment, automobiles, construction glazing, sports safety equipment, medical devices (e.g. dental sealants), tableware, reusable bottles (e.g. baby bottles), and food storage containers (LANE et al., 2015; ZHANG et al., 2019).

BPA is also common to municipal wastewaters and can exert toxicity to exposed organisms in the environment. Second Petrie et al. (2019), despite ≥ 90% of BPA could be removal during a correct wastewater treatment, but notable concentrations could remain in effluent (0.062 – 0.892 µg L^{-1}) leaving to the environment and water treatment stations their removal. In this study were found concentrations of 0.446 – 3.009 µg L^{-1} for BPA in the surface waters studied. These were higher values than that found by Petrie et al. (2019). Regarding to the treated water (WT1), the BPA was detected in the average concentration of 0.04 µg L^{-1}. Another problem related to this compound is the formation of chlorinated BPA by-products in the chlorination process performed in WTP when the compound is already in the raw water as was observed during the kinetic studies done by Lane et al. (2015). However, knowledge on the occurrence of bisphenols in the aquatic environment, especially in source and drinking water, is still limited (PETRIE et al., 2019).

The 4-chloro-3-methylphenol showed the highest concentration among the samples studied with 24.162 µg L^{-1}. In Germany from a natural water this compound was identified at three different levels of a water surface with the average concentration of 6 µg L^{-1} (MONTERO et al., 2005). The 4C3MP is in the list of priority pollutants of EPA (EPA, 2014) and in the directive on environmental quality standards in the field of water policy of the European Union (EU) (EU, 2008). This phenol is a disinfectant used to control slime-forming bacteria and fungi that might develop in industrial adhesives, coatings, emulsions, leather processing liquors, metal cutting fluids, paints (in can), specialty industrial products, oil drilling muds/packer fluids, and wet-end adhesives/industrial processing chemicals (ZANG et al., 2010). Nonetheless, it is not classified as a possible carcinogen by IARC (IARC, 1999).

The 4-nitrophenol also had higher concentration between the samples (6.425 µg L^{-1}). Nthunya et al. (2019), also found concentrations of this compound very similar to that identified in this study in some surface water monitoring samples in South Africa (6.25 µg L^{-1}). The 4N is a class of phenolic pollutant extremely widespread in the environment due to it is broad array of utility in the manufacture of plasticizers, pesticides, fungicide in leather industries, pharmaceutical, acidic pH indicator in chemical laboratories, explosives, and dyes (MULCHANDANI et al., 2005; BALASUBRAMANIAN et al., 2019). It also is formed in the reaction of phenol with nitrite ions in water. In contrast, a trace level consumption of 4NP would cause severe health hazards such as liver, kidney damages, nausea, cyanosis, drowsiness and, headache (MULCHANDANI et al., 2005). The higher solubility of 4NP in water impose major thread to the population towards of 4NP consumption (BALASUBRAMANIAN et al., 2019).

Of the compounds identified, five of them have a drinking standard established by the EPA (EPA, 2019) for water consumption. The 2NP, 4NP, 2,4DMP, and 2,4,5TCP showed concentrations in all samples below EPA seated, 10 µg L^{-1}, 10 µg L^{-1}, 100 µg L^{-1} and, 10 µg L^{-1} respectively. Although the 2,4DCP concentrations in all samples were lower than that established by the EPA (10 µg L^{-1}), the RW2 concentration (1.49 µg L^{-1}) was much higher than that established by the national legislation (BRASIL, 2005) for surface water class I or II (0.3 µg L^{-1}), which could be rivers destined to human consumption after conventional treatment.

The presence of this toxic and resistant to biodegradation compound in rivers can be a result of transformation the widely used group of diaryl-ether pesticides like nitrophen or dichlorodiphenyl (MICHAŁOWICZ & DUDA, 2007). Moreover, 2,4DCP together with 2CP and 2,4,6TCP are the most likely to occur in drinking-water as possible by-products of disinfection (WHO, 2003). Chlorine is the most widely used disinfectant due to its excellent ability in inactivating pathogens (HUANG et al., 2018) and chlorophenols are present in drinking-water as a result of its non-removal in the water treatment and / or the chlorination of phenols during disinfection. The by-products are generated in the substitution of organic matter and low molecular weight compounds present in purified water (e.g. biocides and products of phenoxy herbicides) with chlorine atoms derived from inorganic chlorine oxidants (e. g. hypochlorite) (MICHAŁOWICZ & DUDA, 2007; WHO, 2003).

Comparing RW4 and WT1 results, which are from the inlet and outlet of a water treatment plant, it is possible to note a greater quantity of phenolic compounds identified in the treated water than in the surface water. Although it cannot be said that one sample is representative of the other, since the collection was carried out on the same day not taking into account the residence time of water in the WTP. The presence of the chlorophenols in the treated water can be attributed to non-removal in the treatment, but principally the formation of it in the chlorination process. Studies have shown that chlorination increased significantly the concentrations of these contaminants (WHO, 2003). The presence of the trichlorophenols in the WT1 sample is a point of concern since the International Agency for Research on Cancer (IARC) classifies polychlorophenols (including trichlorophenols) as possibly carcinogenic to be a human carcinogen (IARC, 2011).

The 2-chlorophenol and 2,4,6-trichlorophenol were not found in any of the samples analyzed. The non-appearance of the compounds may be related, besides the absence in the samples, to the steps of collection, storage, solid phase extraction and the infusion method used.

2.4 CONCLUSION

In this study, it was possible to identify and quantify the presence of different phenolic compounds in three different points of the same river belonging to an important national watershed and in the water from the entrance and exit of a treatment station that serves a large population. Of the compounds analyzed, 2-nitrophenol and bisphenol A appeared in all samples and 4-chloro-3-metilphenol had the highest concentration (24.162 µg L^{-1}). The presence of different chlorophenols in the analyzed treated water (24DCP, 245TCP, 345TCP) was also observed. These compounds are resistant, toxic and with carcinogenic potential. Regarding the physicochemical characterization of the samples, it was possible to verify differences between the quality of the surface waters evaluated, but in general the values were within the limits established by national legislation, CONAMA Resolution 357/2005, for Class II rivers, in which water can be distributed to the population after conventional treatment.

For the validation of phenolic compounds identification and quantification methodology developed in this work, the selectivity, linearity, detection and quantification limits, sensitivity, precision, accuracy, resolution, matrix effect and peak quality were taken into account. In the recovery grade trials for the solvent choice, methanol had a better performance than acetonitrile, dichloromethane and ethyl acetate. Demonstrating that the polarity of the compounds is determinant in the efficiency of the extraction process and was greater recovery of the hydrophobic compounds. With respect to the influence of the matrix on the efficiency of SPE, as expected compared to the other samples there was a lower recovery of the compounds in the raw water, which is the more complex matrix. However, all samples had the recover higher than 50%.

Concerning to the calibration curves linearity, it was possible to reach regression coefficients higher than 0.99 for all the analytes. The values of resolution, peak tailing, separation and theoretical plates of all the compounds met the reference values, indicating that the method can perform a good chromatographic separation and presents separate peaks and possible interferences as absent. The matrix effect evaluation was an important step to consider the suppression and increase of the signal in the quantification, being the highest suppression occurred for 2-nitrophenol (84.234%). In general, the analytical method used was able to determine the phenolic compounds in the samples presenting good repeatability, precision, sensitivity, and limits of quantification and detection compatible and even lower than those found in the literature.

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CHAPTER III

Risk assessment and phenolic compounds occurrence in a surface water and their removal by conventional treatment

3.1 INTRODUCTION

The presence of phenolic compounds in surface water may have a natural, industrial, domestic or agricultural origin, through treated sewage discharges, application of pesticides, and pharmaceutical drugs (ZHOU et al., 2017). In developing countries, such waste is commonly disposed directly into natural waters and has a significant impact on the environment. The monitoring of these compounds by means of appropriate analytical techniques has been a reason of great international concern, which can be demonstrated by the number of real-world studies (MICHALOWICZ et al., 2011; ZHONG et al., 2010; TANG et al., 2013; WANG & WANG, 2018), that evidenced the phenols presence in micro and nano concentrations in surface water.

Nevertheless, few studies have been found on the occurrence and monitoring of these compounds in the Brazilian natural water, despite some established standards for phenolic compounds exist in the national legislation at CONAMA Resolution N° 357. The phenolic compounds in surface water play an important role among the organic micropollutants due to the environmental and toxicological interest. They can cause toxicity, persistence, and bioaccumulation effects in animals, vegetable organisms and may be dangerous for human health (ZHONG et al., 2018).

Conventional methods for the treatment of drinking water, that still widely used, which comprise coagulation / flocculation, sedimentation, filtration and disinfection, are ineffective for the removal of many organic micropollutants, such as phenols (KARABELAS & PLAKAS, 2011; ROSA et al., 2009). Another undesirable feature is the byproducts formation in the drinking water chlorination stop. The reaction of phenolic compounds already in the water with chlorine produces chlorophenols and polychlorophenols that are carcinogenic, and their presence can give a nasty smell and taste to the water (QU et al., 2010; SANTANA et al., 2009).

The toxicity of phenols can be associated to the hydrophobicity of the individual compound and formation of free radicals. Hydrophobicity affects the solubility of phenol in the cell and, therefore, the possibility of interaction between the compound with the specified cellular and tissue structures (MICHAŁOWICZ & DUDA, 2007). For example, the increased hydrophobicity of chlorophenols is related to the increase in the number of chlorine atoms that increases the toxicity of the individual compound. For instance, chlorine atom substituted in ortho position in phenol molecule decreases its toxicity and meta substitution increases toxic action of the compound (BOYD et al., 2001)

The World Health Organization (WHO) has established a permissible concentration of phenolic content in drinking water of 1µg L^{-1} (WHO, 2017) and because of their toxicity, phenolic compounds have been included in the Environmental Protection Agency (EPA) list of priority compounds, which determines concentrations ranging from 0.03 µg L^{-1} to 4,000 µg L^{-1}, depending on the compound (EPA, 2015a). However, for the range of phenolic chemicals present in surface water have not been reported statutory standards in the legislation, drinking water guideline levels, or provisional guideline values based on toxicological (BAKEN et al., 2018). Therefore, environmental and human health risky studies can help in the determination of these standards and, consequently, in the proper management of the natural resource and potable water.

The environmental risk assessment (ERA) evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to site contamination. Risks may include survival, reproductive impairment, growth impairment and loss of habitat and they are estimated at the population level (populations on site) (EPA, 2015b). As natural and anthropogenic materials enter the environment on a regular basis, and it is also frequently the interest to estimate the probability or likelihood of adverse effects of a chemical to human health.

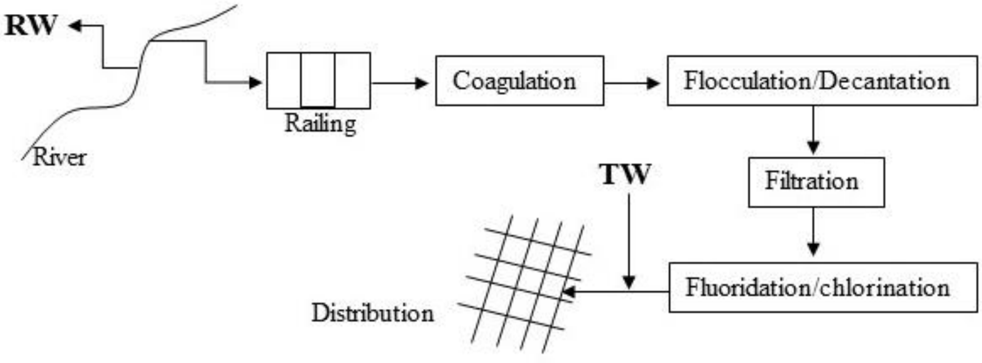
In this regard, the aims of this research were (I) to identify and quantify phenolic compounds in a river belonging to an important watershed and in the water produced by a conventional water treatment plant (WTP), which supplies a population of more than 2 million people, around a year in Brazil, and (II) to assess the environmental and human health risk posed by these compounds. The environmental risk was calculated based on the hazard quotient (HQ) and the human health risk according to the margin of exposure (MOE).

3.2 MATERIALS AND METHODS

3.2.1 Sampling

The samplings were carried out in two different points as shown in Figure 3.1, according to the method of sampling, preserving, and storing of NBR 9898 for phenol analysis (ABNT, 1987). The recommendations of EPA 528 (EPA, 2000) were also considered. The studied waters were withdrawn in the river at the treatment plant entrance (RW) and at the exit of a conventional water treatment plant after chlorination (TW).

Figure 3.1: Schematic of sampling points



The studied river average water flow is 300 $m^3 s^{-1}$. The climate at the collection point is hot and temperate, characterized by the occurrence of medium to high temperatures during most of the year, with an annual average temperature ranging from 18 to 27 °C. There is much more rainfall in the summer than in winter and the average annual rainfall is 1,390 mm. The WTP is responsible to water supply for 5 municipalities, this is an average of 2.5 million people. The adduction capacity of the WTP is 8,000 L s^{-1}, but its flow rate average is 6,750 L s^{-1}. Sampling was carried out over a hydrological year in order to identify and quantify the most recurrent phenolic compounds and to verify the influence of seasonality on the occurrence of them.

3.2.2 Selected compounds for monitoring

Seventeen phenolic compounds were monitored in a raw water and in a treated water from a conventional WTP, having as reference the EPA priority compounds list. Seven of them are in the list, which are 2-chlorophenol, 4-chloro-3-metylphenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4,6-trichlorophenol, and 4-nitrophenol (EPA, 2014). The bisphenol A and

2-metylphenol, 3-metylphenol, 2,6-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,3,6-trichlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and 3,4,5-trichlorophenol were also considered. The main characteristics of the compounds can be seen in Annex I (p. 125 – 126).

3.2.3 Water characterization

The raw water and the treated water were evaluated by pH, alkalinity, turbidity (Hach 2100AN turbidimeter), color (Hach DR 2800 spectrophotometer), and UV Absorption (254 nm - Hach DR 2800 Spectrometer) according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2012).

3.2.4 Instrumental analysis

The presence of phenolic compounds was monitored in the surface water and treated water. The methodologies proposed by EPA (528, 3535A, and 8041) were used as basis, but it was adapted according to the need found throughout the developed of the research and the tests for the analytical method validation were based on ICH (2005), ANVISA (ANVISA, 2003), and INMETRO (INMETRO, 2007), as can be seen in Chapter II.

In the solid phase extraction, the C_{18} / 18% cartridges (500 mg / 6 mL - Applied Separations) were used, conditioned with 5 mL of methanol, after 5 mL of MilliQ (ThermoScientific Smart2Pure 3 UV) water. Then, 1 L of the sample was percolated at pH 2, maintaining constant flow and close to 20 mL min^{-1}. The cartridge remained under vacuum for 20 min after finalizing the concentration process for complete removal of moisture and the compounds were eluted using 2 times 1 mL of methanol. The entire extraction procedure was performed with a manifold (Supelco-Visiprep ™).

The phenolic compounds identification and quantification were carried out using the Shimadzu CGMS-QP2010 SE equipment coupled to FID detector. Zebron ZB-MultiResidue column (30 m x 0.32 mm x 0.50 µm) and helium as carrier gas were used. The optimum oven programming was 40 °C for 4 minutes, 4 °C min^{-1} to 240 °C and finally 240 °C for 5 minutes. The injection volume of the samples was 2 µL in splitless mode, with the injector temperature at 275 °C. An automatic sampler (AOC-20i, Shimadzu) was used in all tests, programmed to perform a solvent (methanol) wash (2 x) before and after each injection, in addition to settle the syringe with the sample (2 x). The FID detector temperature was maintained at 300 °C and an Air / H_2 mixture (400/40 mL min^{-1}) was used for the combustion while a N_2 / Air mixture (30 mL min^{-1}) was used as gas make-up to scan components through the detector in order to minimize the bandwidth of compounds.

3.2.5 Risk assessment

3.2.5.1 Environmental risk assessment

Hazard quotient (HQ) was employed to calculate the potential environmental risks of each target pollutant, which is described as follows in Equation 3.1 (EPA, 1986).

$$HQ = MEC/PNEC \qquad \text{Equation 3.1}$$

where MEC is the measured environmental concentration and PNEC is the predicted no effect concentration. The value of PNEC water was obtained from the ratio between the acute toxicity data (Lethal Concentration 50 (LC50) or Mean Effect Concentration 50 (EC50)) and an assessment factor (AF) of 1000 or from the ratio between the no observed effect concentration (NOEC) data and an AF of 10. The LC50, EC50 and NOEC values used can be seen in the ANNEX II. The lowest PNEC values and the highest phenolic compounds concentration in the evaluated water were considered for HQ calculation in order to obtain a worst scenario. The risk was classified into high risk ($HQ > 1$), medium risk ($0.1 \leq HQ \leq 1$), low risk ($0.01 \leq HQ < 0.1$), and negligible risk ($HQ < 0.01$) (EMEA, 2006)

3.2.5.2 Human health risk assessment

Human health risk was characterized by the margin of exposure (MOE) determination (Equation 3.2).

$$MOE = DWEL/MEC \qquad \text{Equation 3.2}$$

MOE is obtained through the ratio between the safe exposure level (DWEL) and the highest concentration detected in the evaluated environment (MEC). The DWEL can be estimated by tolerable daily intake (TDI) (derived from the no-observed adverse effect level - NOAEL and safety factors), as shown in Equation 3.3.

$DWEL = (TDI * bm * f)/c$ Equation 3.3

Where b_m is the body mass (60 kg), f the contribution of water to exposure (10%), and c the daily water consumption (2 L) (WHO, 2017). The value of TDI was obtained direct from the literature or calculated from the ratio between the non-observed adverse effect level (NOAEL) or the lowest observed adverse effect level (LOAEL) and an AF of 100 and 10000, respectively. The data values used can be seen in the ANNEX III (p. 131 – 133). The low risk is implied when MOE value is more than 100 for NOAEL-based assessments (EPA, 2012).

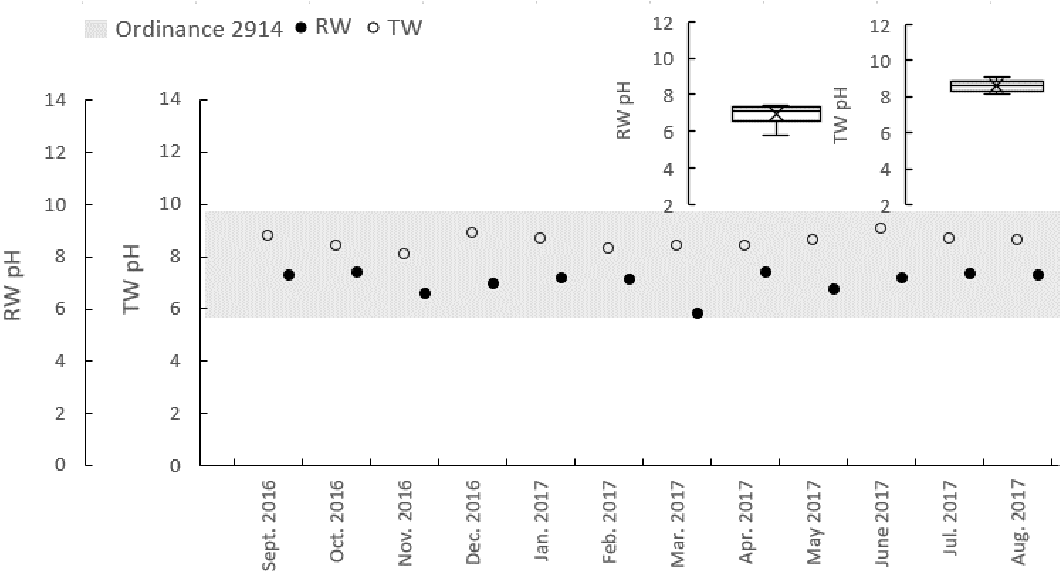
3.3 RESULTS AND DISCUSSION

3.3.1 Quality of the studied waters

From the physical-chemical characterization of the RW and TW monitored for one year, it is possible to verify the water quality according to the standards established by the Ministry of Health for drinking water (Ordinance N ° 2914/2011 / N° 5/2017 - consolidation), and the National Environmental Council for surface water (CONAMA 357).

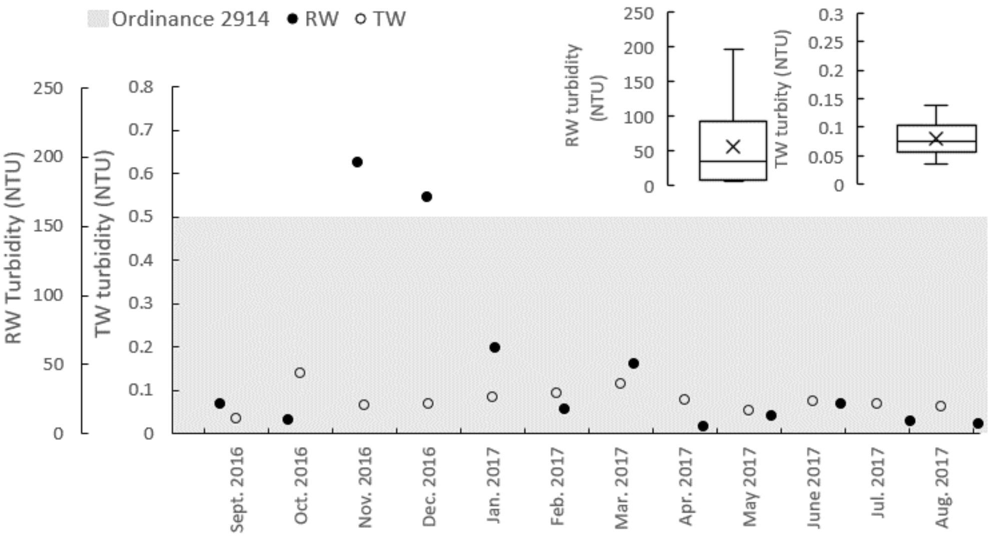
The CONAMA 357/2005 establishes that the rivers classified in to classes I and II, which can be used for human supply following simplified and conventional treatment, must have pH between 6 and 9. This happens most of the time in the monitoring, except for a minimum value of 5.8 found in a sample (Figure 3.2) (p. 76). However, the Ordinance N° 2914/2011 recommends that the pH of the water distributed to the population be maintained in the range of 6 to 9.5, which happened in all samples during the year of observation. The pH has great influence on the bioavailability, absorption and solubility of the phenolic compounds. In water, phenolics tend to become more soluble at high pH. Since they can come from polar salts and they are very weak acids, their ionization is pH dependent. This ionization is the main factor that governs solubility (MOTA et al., 2008).

Figure 3.2: pH of the raw and treated water collected in one year of monitoring



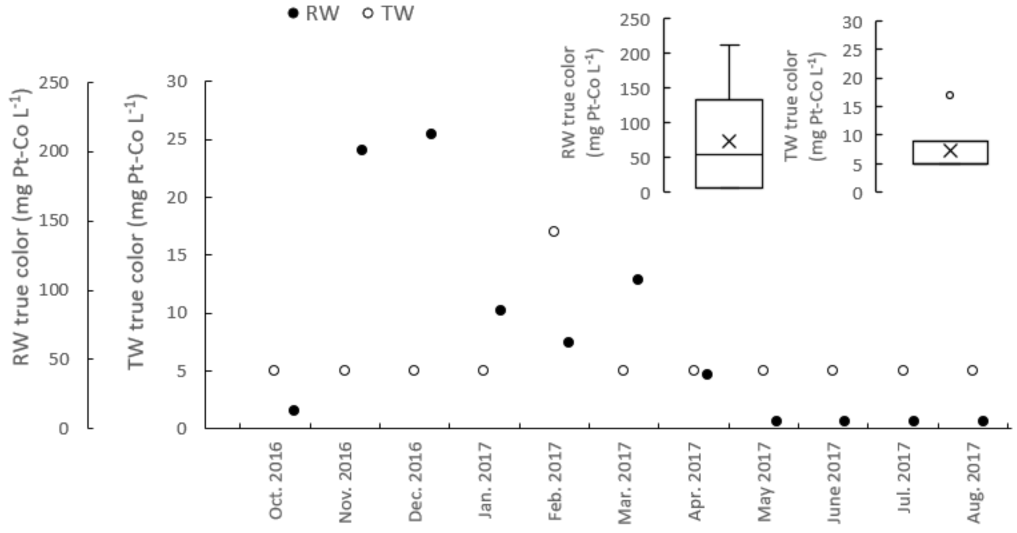
It is possible to notice that there are episodes in which the turbidity of the RW exceeds the values recommended by CONAMA 357/2005 for freshwater class I (40 NTU) and class II (100 NTU) (Figure 3.3) (p. 77). This increase is probably directly related to the watershed slopes and should be verified from the characteristics of the relief, soils, main channel, rainfall and land use. The measured turbidity values of the treated water were less than 0.5 NTU, which is in accordance with the Ordinance N° 2914 for treatments that use rapid filtration (conventional and direct filtration). The turbidity analysis is of extreme importance, because in the sediments transported can accumulate species of microorganisms and/or chemical elements that associate to the material in suspension, being transported in the dissolved form, or sometimes, colloidal.

Figure 3.3: Turbidity of the raw and treated water collected in one year of monitoring



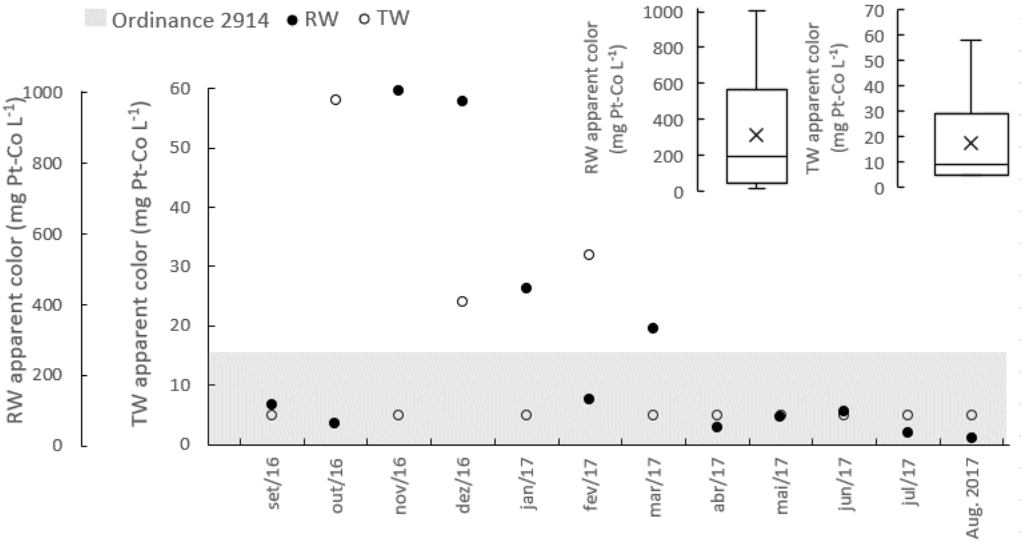
As can be seen in the Figure 3.4 (p. 78), the true color, most of the time, was within the range recommended by CONAMA 357/2005 for classification of freshwater in class II (up to 75 mg Pt L^{-1}). But in four rainy months presented values much higher (201, 212, 85 and 107 mg Pt L^{-1}) probably due to the impurity of rainwater, as sediments. This limitation is important because in natural waters the true color is associated with problems of aesthetics, difficulties in light penetration and the presence of recalcitrant compounds (not biodegradable or very low decomposition rates), which are generally toxic to organisms in the water. While there are more specific techniques for identifying toxic substances in water, the presence of true color may be indicative of this possibility. Already in the monitoring of this parameter in the treated water, all measured values were below the detection limit of the method (5 mg Pt-Co L^{-1}), except for one month with 17 mg Pt-Co L^{-1}.

Figure 3.4: True color of the raw and treated water collected in one year of monitoring



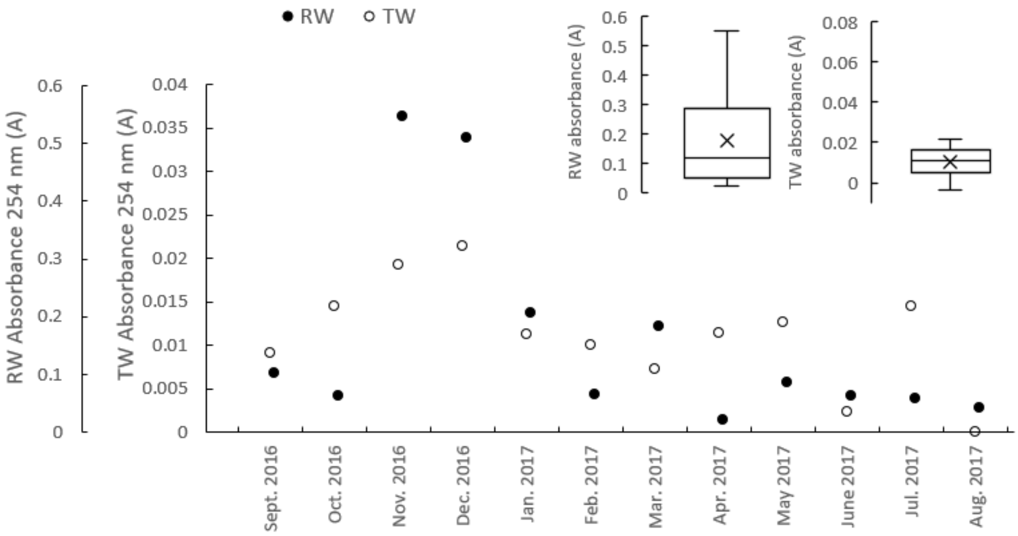
Regarding the apparent color, Ordinance N° 2914/2011 establishes limits for this parameter in the treated water of 15 mg Pt-Co L^{-1}, although it is an aesthetic attribute of water, not necessarily related to problems of contamination, is a standard of potability. As can be seen in the Figure 3.5 (p. 78), most of the values measured for TW were lower than the detection limit of the method (5 mg Pt-Co L^{-1}), except for three samples that presented higher values than those established by the legislation (58, 32 and 24 mg Pt-Co L^{-1}).

Figure 3.5: Apparent color of the raw and treated water collected in one year of monitoring



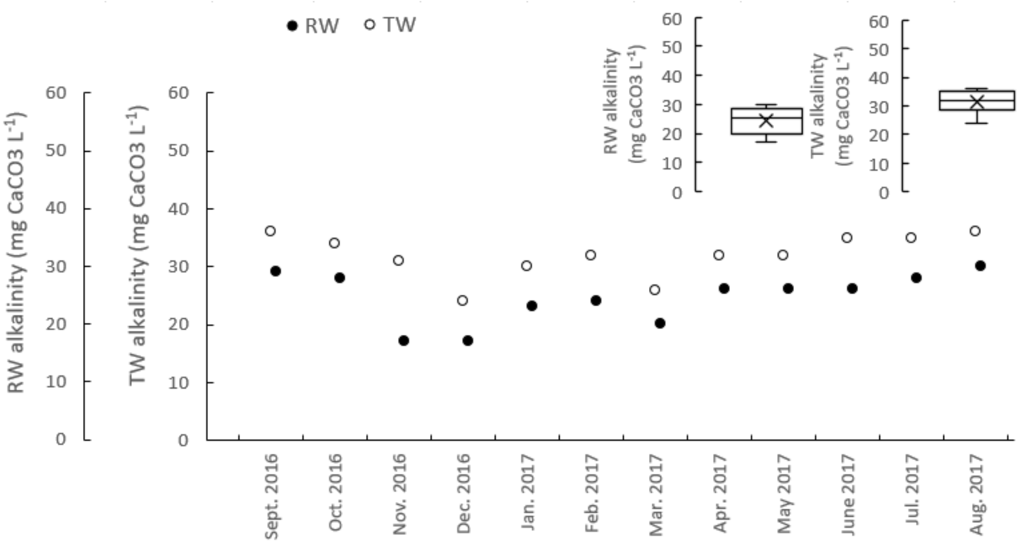
In addition to color, UV absorption was monitored at 254 nm. This parameter can be used as a representative of total organic carbon (TOC), because the organic compounds with aromatic structure or double bonds of carbon are absorbed by ultraviolet radiation at 254 nm. A decrease in absorbance occurs throughout the raw water after the water treatment, as expected (Figure 3.6) (p. 79). This removal is fundamental, since the presence of natural organic compounds in supply waters in concentrations above certain values has caused a series of problems in the water quality, being possible to mention the formation of total halogenated organic compounds when reacting with chlorine (GARZUZI et al., 1999).

Figure 3.6: UV absorption of the raw and treated water collected in one year of monitoring



It is possible to realize that alkalinity is increased from RW to WT (Figure 3.7) (p. 80). This increase, although not presenting a risk to human health, occurs because alkalinity is an important determination in the control of water treatment, being related to the steps of pH correction, coagulation, reduction of hardness, and prevention of corrosion in pipes.

Figure 3.7: Alkalinity of the raw and treated water collected in one year of monitoring



In this way, water is a precious and essential commodity for life and the physical-chemical characterization of the samples shows differences between water quality during the monitoring periods. Although we live in a world surrounded by water, very little of it is conducive to human consumption, being the determination of quality and verification of legal prerequisites an important tool of natural resource management.

3.3.2 Monitoring of phenolic compounds in the river and in the treated water by conventional process

3.3.2.1 Occurrence and concentration of phenolic compounds

As can be seen in the Table 3.1 (p. 81), sixteen phenolic compounds were detected at some point in the samplings between the seventeen investigated compounds in the raw and treated waters. The 3-methylphenol was the only one not observed in any of the samples evaluated. Probably, this compound was with concentrations below the limit of detection or was absence in the samples.

Table 3.1: Concentration analysis of phenolic compounds monitored for one year in a raw and a treated water from Brazil

Compounds	**Detection limit (µg L^{-1})**	**Raw water**				**Treated water**			
		Frequency of detection (n=12)	C (µg L^{-1}) Min-Max	C (µg L^{-1}) Avarege	C (µg L^{-1}) Median	Frequency of detection (n=12)	C (µg L^{-1}) Min-Max	C (µg L^{-1}) Avarege	C (µg L^{-1}) Median
2CP	0.091	1	2.433	2.433	2.433	1	1.741	1.741	1.741
2MP	0.004	3	0.064 – 6.555	2.229	0.0664	2	0.666 – 5.486	3.076	3.076
2NP	0.012	2	0.191 – 0.356	0.274	0.274	1	0.429	0.429	0.429
24DMP	0.004	6	0.248 – 2.194	1.038	0.726	0			
24DCP	0.002	3	0.422 – 1.003	4.764	3.838	2	2.94 – 3.328	3.134	3.134
26DCP	0.006	1	2.565	2.565	2.565	3	0.149 – 34.115	11.597	0.527
4C3MP	0.002	0				4	0.147 – 0.524	0.308	0.282
235TCP	0.014	4	0.216 – 5.712	0.374	0.354	2	0.453 – 3.712	2.083	2.083
246TCP	0.028	3	1.131 – 38.619	13.681	1.294	2	0.077 – 25.893	12.985	12.985
245TCP	0.01	1	0.257	0.257	0.257	1	0.225	0.225	0.225
234TCP	0.018	7	0.780 – 3.106	2.353	2.467	4	0.676 – 2.22	1.431	1.414
4NP	0.056	6	4.471 – 25.417	13.416	12.254	8	0.219 – 8.223	2.989	1.639
2356TCP	0.005	0				2	0.867 – 4.432	2.65	2.65
2346TCP	0.01	1	14.374	14.374	14.374	0			
345TCP	0.016	1	0.613	0.613	0.613	2	0.296 – 0.375	0.336	0.336
BPA	0.02	4	0.093 – 1.456	0.532	0.290	5	0.363 – 3.566	1.876	2.135

The mean concentration range of the phenolic compounds in raw water was 0.257 µg L^{-1} (245TCP) to 14.374 µg L^{-1} (2346TCP). The level of phenols in surface water determined by other authors vary in magnification in several studies. For instance, in rivers of Singapore, phenols were determined at concentrations ranging from 0.12 to 5.90 µg L^{-1} (TANG et al. 2013), and in Poland, from 0.02 to 7.070 µg L^{-1} (MICHAŁOWICZ et al., 2011). Another study revealed that phenols were present in Moscow River (Russia) at concentrations ranging from 0.90 to 10.80 µg L^{-1} (FILIPOV et al., 2002). Relatively high amounts of this compounds were determined in Germany, at concentrations of 43 to 13.80 µg L^{-1} (MONTERO, 2005), and in polluted China rivers, which were detected at concentrations ranging from 0.18 to 135.50 µg L^{-1} (WANG & WANG, 2018). The differences between the concentration's ranges indicate the variation in the consumption pattern of these phenolics compounds among different countries.

The most detected compounds in the studied raw water were 234TCP, 24DMP and 4NP. The prevalence of them can be explained by their widespread use in industry and their presence in common sewage, beyond their low degradability (BALASUBRAMANIAN et al., 2019) and hydrophilic characteristics (low values of log k_{ow}). Nthunya et al. (2019), also found with frequency the 4NP during a year of monitoring in a superficial water in South Africa with concentrations ranging from 0.85 to 12.16 µg L^{-1}. Besides, the highest concentration value was detected for 246TCP equal to 38.619 µg L^{-1}. Gao et al. (2008) also found high values of this compound in a river in China (28.65 µg L^{-1}). It must be noted that this concentrations of 246TCP detected in the raw water exceeded the admissible standard formulated by EPA (2019), which sets the maximum limit for human consumption in water equal to 1.50 µg L^{-1}.

Still in Table 3.1 regarding to the treated water, the mean concentration of the phenolic compounds was 0.225 µg L^{-1} to 12.985 µg L^{-1} for the same compounds detected in the raw water, 245TCP and 2346TCP respectively. Comparing this samples concentrations values observed in this study with those reported in the literature, the levels were in the range found for some compounds in the potable water in Italy (3.010 to 69.10 µg L^{-1}) (BIANCHI et al., 2002) and Poland (0.05 to 7.07 µg L^{-1}) (MICHAŁOWICZ et al., 2011). However, the average concentration was significantly higher than those found by Sartori et al. (2012) for another drinking water in Brazil (0.008 to 0.238 µg L^{-1}).

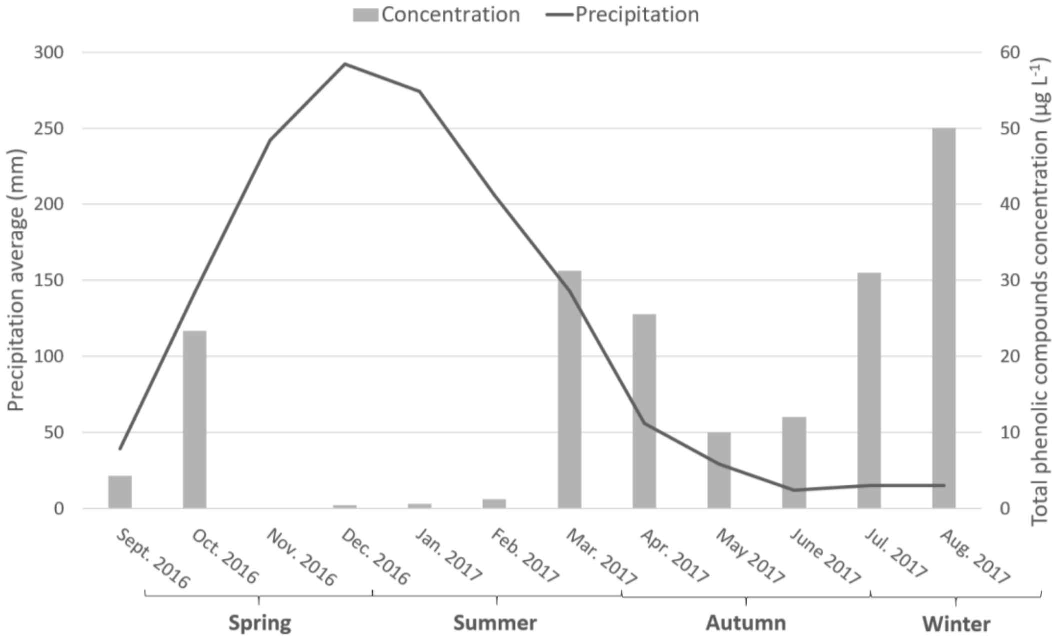
Moreover, the most detected compounds in the treated water were 4NP and BPA. There is a concern in respect to these phenols, since the BPA is known as endocrine disruptor (ZHANG et al., 2019), and trace level consumption of 4NP would cause severe health hazards such as liver, kidney damages, nausea, cyanosis, drowsiness, and headache (MULCHANDANI et al., 2005). The highest concentration value found for 26DCP (34.115 µg L^{-1}) is also a cause to stay tuned. This compound is used as a starting material for the manufacture of tri-chlorophenol, tetra-chlorophenols and pentachlorophenol, and it is used as sex pheromone with pesticide control (CPCB, 2016). It may be also generated as by-products during waste incineration, the bleaching of pulp with chlorine, and in the dichlorination of drinking water. The toxicity and persistence of chlorophenols can directly present a threat to humans through contamination of drinking water supplies (KANSAL et al., 2007).

Thus, to better understand the origin of these compounds in the water this analysis should be accompanied by a study of soil use and occupation in the river area, including the discharge of domestic effluents and industrial wastewater, since water quality is extremely dependent on the watershed preservation.

3.3.2.2 Seasonality influence on the concentration of phenolic compounds

Concerning to the concentration variation of the phenolic compounds during the year of monitoring in the raw water, in general, except for October and May, the highest values of total concentration are related to the months in which there was less precipitation, as can be seen in Figure 3.8 (p. 84). Wang et al. (2011) reported the same result indicating that micropollutant in summer water samples in wet weather showed lower occurrence levels than those in winter during dry weather conditions. This could be due to promoted biodegradation of the compounds in warmer temperature, and the elevated dilution during wetter summer (LUO et al., 2014).

Figure 3.8: Total phenolic compounds concentration for the raw water samples during the monitoring and their correlation with the monthly variation of the total precipitation



Nevertheless, rainfall did not always reduce the concentration levels of micropollutants released. In some cases, rainfall was identified as a contributor to the emission of micropollutants to surface water. For Zhong et al. 2018, the concentrations of total phenolic compounds in wet-season samples were higher than those in dry-season samples. They attribute this to the fact that the wet season is the busy farming period in which phenolic compounds are extensively used in pesticides; thus, the increased phenolic compounds might result from seasonal emissions. However, the region of the studied raw water sampling is not characterized by large agricultural activities. Some other studies revealed that the chemicals, as bisphenol A and biocides, used in building material (e.g. pavement materials, facades and roof paintings) were able to leach during precipitation and accumulate to remarkable levels in roof runoff and subsequently ended up in surface water (JUNGNICKEL et al., 2008; SAKAMOTO et al., 2007).

Being thus, the numerous surface waters variables, such as pH, temperature, sediments, microorganism's behavior, turbidity, organic matter, solar radiation, among others, and the use and occupation of the watershed make it a challenge to predict the comportment of the compounds in these environments.

3.3.2.3 Phenolic compounds removal by a conventional WTP

The WTPs that have a conventional treatment system control a wide range of substances, such as particulates, carbon elements, nutrients, and pathogens. However, removal of micropollutants, as phenolic compounds, is often insufficient and the mechanisms involved to removal these pollutants may be retention of size, biodegradation in the filtration step, adsorption, and chlorine oxidation (LUO et al., 2014). In these stages also, the formation of by-products could occurred, especially in the chlorination (BIANCHI et al., 2002). Figure 3.9 (p. 85) shows the removal efficiency of the phenolic compounds found in the raw water of the WTP evaluated. The results of 100% removal correspond to the samples where the compound was detected in the raw water but in the treated water was not found or was below the quantification limit. Thus, it is known that not necessarily the phenol has been completely removed, which may be present at concentrations below the limit of detection and quantification. In Figure 3.10 (p. 86), could be observed the concentration of phenolic compounds in the treated water that had negative removal or were not found in the raw water.

Figure 3.9: Removal of each phenolic compound per month by the conventional water treatment

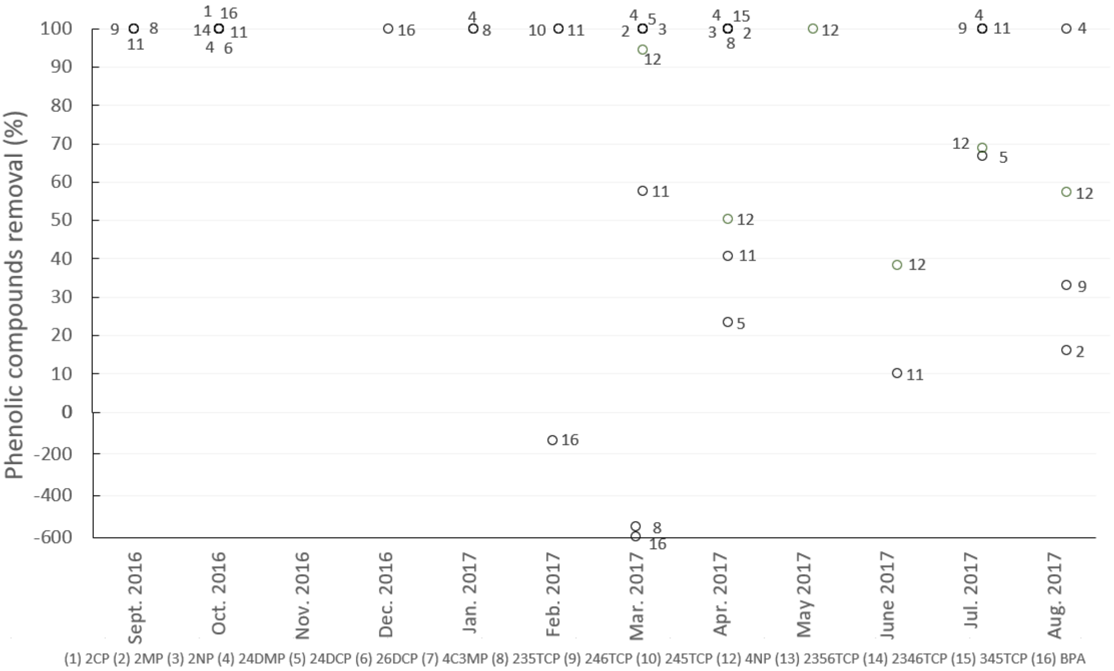
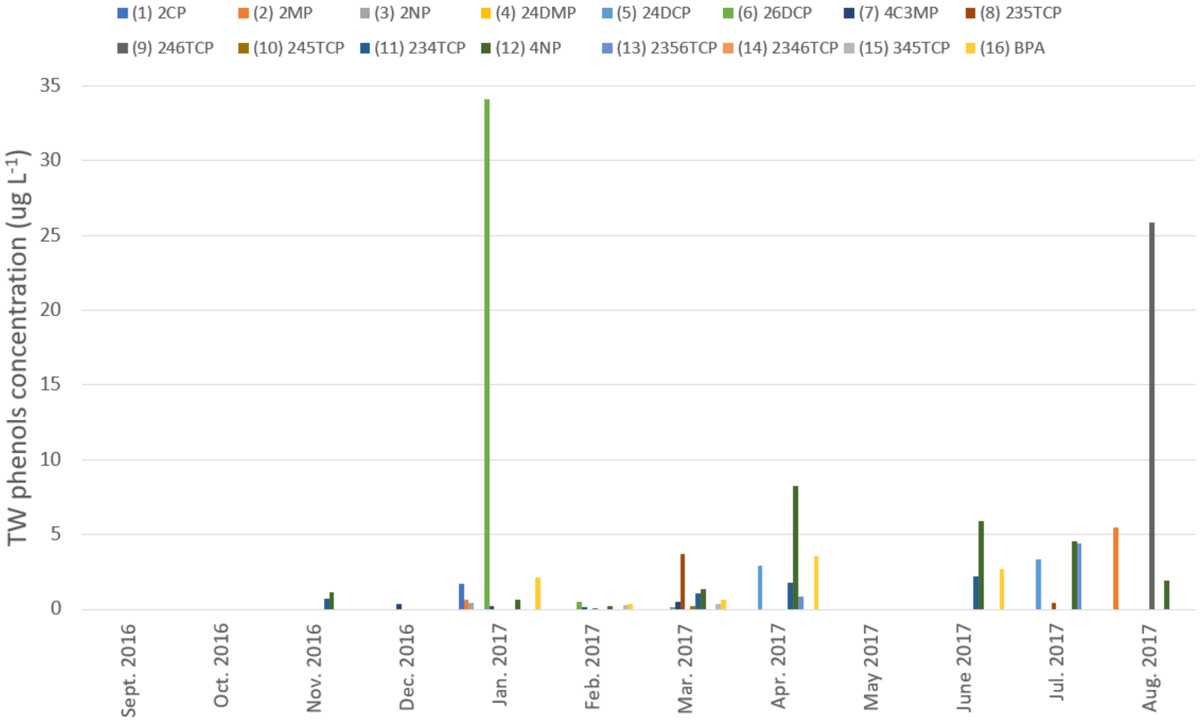


Figure 3.10: Concentration of phenolic compounds per month in the treated water that had negative removal or were not found in the raw water



In general, the removal efficiency of these compounds during the monitoring showed great variability as in other researches (Michałowicz et al.,2011; LUO et al., 2014). For example, 4NP showed removals ranging from 38.3% to 94.59%, some compounds had their concentration increased after the treatment, and others were only identified in the treated water. This variation can be related to the punctual collection of the samples, and the hydraulic holding time of the treatment which was not respected.

The 2346TCP (Log K_{ow} = 4.45) was the compound that had the highest removal efficiency and was not identified in any sample of the treated water. It removal may have occurred by adsorption in some part of the WTP. Suárez et al. (2009) observed a relatively high removals (around 80%) for the compounds with Log K_{ow} equal 4 due to sorption. The general rule for applying K_{ow} to the sorption estimation say that log $K_{ow} < 2.5$ indicates low sorption potential, $2.5 < \log K_{ow} < 4$ indicates medium sorption potential, and log $K_{ow} > 4$ indicates high sorption potential (ROGERS, 1996).

About the compounds that increase their concentration after the treatment (2MP, 2NP, 26DCP, 235TCP, and BPA), it supposed that this increase may have occurred due to external factors, such as penetration of contaminants in the water-supply systems, i.e., periodical contamination of sediments, soil, or rain water with the compounds, which were in contact with taken water (MICHAŁOWICZ et al., 2011). In addition, another factor is the use of aerated grit chamber in the treatment that could cause significant increase of phenolic compounds, specially BPA and nonylphenol, because the compounds originally attached to the grits could be peeled off due to air agitation (NIE et al., 2012). The negative removal can be also ascribed to the daily concentration fluctuations during the sampling period, the analytical uncertainty, or desorption of molecules from suspended particulate matter (KÖCK-SCHULMEYER et al., 2013).

Besides, the amounts of 26DCP and 235TCP in drinking water supplied significantly increased, the 4C3MP and 2356TCP were not detected in any raw water sample but were identified in the treated water. They are chlorinated compounds that may have appeared in the chlorination process due to substitution of organic matter and low molecular weight compounds (present in raw water) with chlorine atoms derived from inorganic chlorine oxidants (MICHAŁOWICZ & DUDA, 2007; BIANCHI et al., 2002). According to toxicological and epidemiological studies, the long-term consumption of drinking water containing low or trace levels (ng L^{-1} and µg L^{-1}) of disinfection byproducts (DBP) may have chronic adverse effects on human health, potentially leading to bladder cancer, colorectal cancer, birth defects, and many other health issues (LI & MICTH, 2018; FREEMAN et al., 20017).

These results of Figure 3.9 (p. 85) and Figure 3.10 (p. 86) show that compounds even in the same usage class were removed to fairly different degrees as was found by Michałowicz et al. (2011). In their studies were analyzed the presence of 2CP, 24DCP, 245TCP, 246TCP, and polychlorophenols in six different months comparing two rivers and two water treatment plants. The results did not show a logic in the removal or increase of the compounds by the conventional process of water treatment, since in some samples the phenolic compounds were totally removed and in others their increase or formation occurred. Generally, the removal difference among distinct compounds in WTPs could be ascribed to a number of factors such as micropollutant properties, operational conditions, and water quality, which makes it hard to define the exact causes of the removal or increase of phenolic compounds in the treated water.

As the raw water has different characteristics throughout the year and the WTP uses the same treatment technology independent of the water quality, it was sought to evaluate the correlation between the values of turbidity and true color measured in the raw water and the percentage of removal of the most recurrent phenolic compounds (4NP and 234TCP). Pearson's correlation coefficient was used for this, but no dependence was found. The correlation between the concentration of these compounds in the raw and treated water was also evaluated, however any correlation was detected.

3.3.3 Environmental and human health risk assessment

Figure 3.11 and Table 3.2 show the risk assessment for the two-water source studied, reminding that for the calculations were considered the highest measured environmental concentration (MEC) value of each compound during the monitored year. Using the HQ method, phenolic compounds for which HQ exceeded 1.0 were identified as potential stressors to the aquatic environment and the risk levels of the potential stressors were ranked according to the HQ values.

Observing the toxicological risk for the raw water, the acute risk for all compounds was between high and medium, while the chronic risk presented a greater degree variety, but the majority was high. Some recent studies found in the literature reported by Zhong et al. (2018), Peng et. al (2017), and Yan et al. (2017) also identified high ecological risks for phenolic compounds by the HQ method in surface water. The 2,3,4,6-tetrachlorophenol had the highest acute HQ (28.747) and the 2,4-dichlorophenol the highest chronic HQ (2.007) in the raw water. Jin et al. (2011) also identified these chlorophenols at three rivers in China, but both compounds presented minimal ecological risk. The chronic risk for the 3,4,5-Trichlorophenol was not calculate because its NOEC was not found in the literature.

Regarding the human health risk assessment (HRA), most of the compounds have a huge probability to offer risk in the raw water and after undergoing conventional treatment, demonstrating that the process used to treat the water in the WTP are not being totally efficient in removing the risk related to the phenolic compounds evaluated. Selvaraj et al. (2014) also investigated the HRA for some phenolic compounds in surface water, such as bisphenol A, which exhibited a significant risk as presented in this study. The only micropollutants that offered small risk in the treated water were 4-nitrophenol and 4-chloro-3-methylphenol. As well as 2,4-dimethylphenol and 2,3,4,6-tetrachlorophenol, that their concentrations in the treated water was below the method quantification limit and for the reason the water can be considered free of HRA.

Figure 3.11: Overall risk assessment

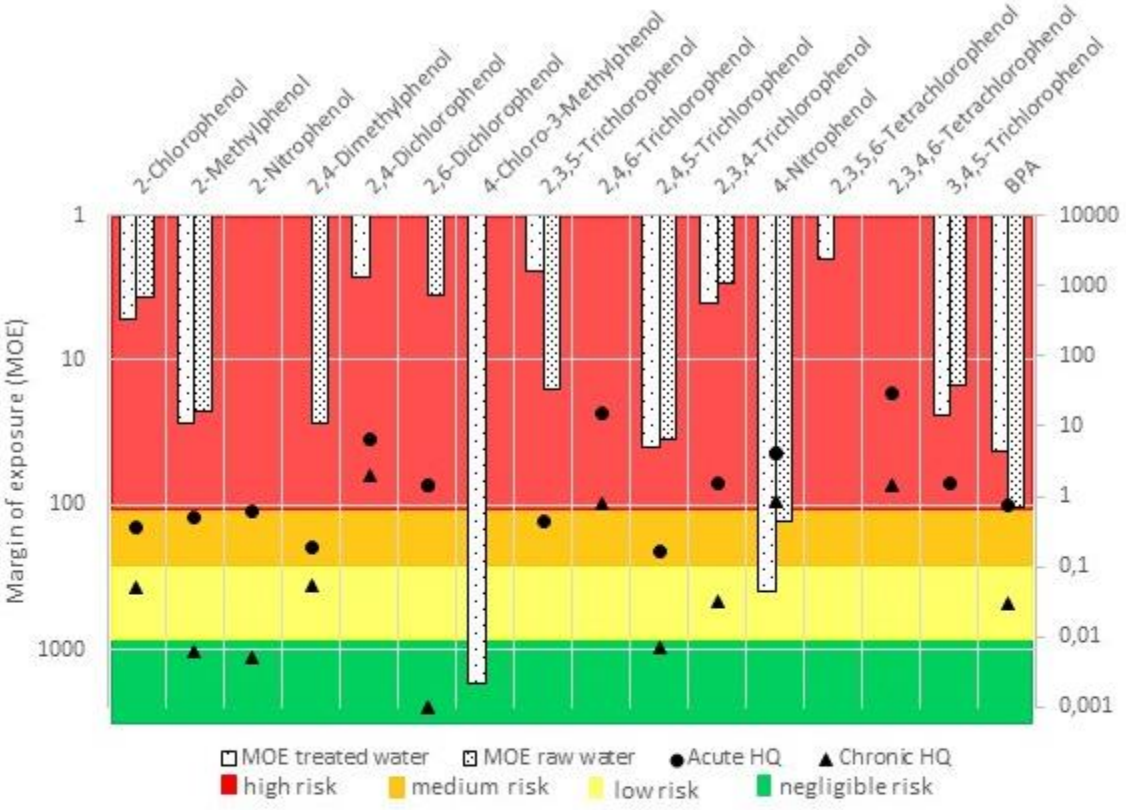


Table 3.2: Environmental and human health risk assessment of phenolic compounds in the raw water and treated water by conventional process

Compounds	Raw water						Treated water	
	ERA				HRA		HRA	
	Acute toxicity		Chronic toxicity		MOE	Classification	MOE	Classification
	HQ	Classification	HQ	Classification				
2-Chlorophenol	0.371	Medium risk	0.049	High risk	3.699	High probability of risk	5.168	High probability of risk
2-Methylphenol	0.504	Medium risk	0.006	Low risk	22.884	High probability of risk	27.344	High probability of risk
2-Nitrophenol	0.631	Medium risk	0.005	Low risk	0.0004	High probability of risk	0.0003	High probability of risk
2,4-Dimethylphenol	0.187	Medium risk	0.055	High risk	27.345	High probability of risk	**	**
2,4-Dichlorophenol	6.689	High risk	2.007	High risk	0.897	High probability of risk	2.705	High probability of risk
2,6-Dichlorophenol	1.481	High risk	0.001	Low risk	3.509	High probability of risk	0.264	High probability of risk
4-Chloro-3-Methylphenol	**	**	**	**	**	**	1,717.32	Small probability of risk
2,3,5-Trichlorophenol	0.443	Medium risk	0.0004	Low risk	15.756	High probability of risk	2.424	High probability of risk
2,4,6-Trichlorophenol	14.854	High risk	0.772	Medium risk	0.233	High probability of risk	0.348	High probability of risk
2,4,5-Trichlorophenol	0.163	Medium risk	0.007	Low risk	35.082	High probability of risk	40.022	High probability of risk
2,3,4-Trichlorophenol	1.553	High risk	0.031	High risk	2.897	High probability of risk	4.053	High probability of risk
4-Nitrophenol	4.236	High risk	0.847	Medium risk	129.833	Small probability of risk	401.292	Small probability of risk
2,3,5,6-Tetrachlorophenol	**	**	**	**	**	**	2.03	High probability of risk
2,3,4,6-Tetrachlorophenol	28.747	High risk	1.437	High risk	0.626	High probability of risk	**	**
3,4,5-Trichlorophenol	1.533	High risk	*	*	14.682	High probability of risk	24.015	High probability of risk
BPA	0.766	Medium risk	0.029	High risk	103.03	Small probability of risk	42.066	High probability of risk

*NOEC not found in the literature; **the compound was not detected.

Therefore, a significant point concerning to toxicological risk assessment is that the contamination with phenolic compounds in surface water and drinking water varies widely between different regions and countries, since it will depend on the amount of the compounds used, the generated effluents treatment and the technologies used to treat the water, besides the climate of each location. Thereby, the HQ and MOE values obtained for a phenolic compound in a specific region do not necessarily reflect the risks in other locations.

3.4 CONCLUSION

This work mainly investigated the seasonal distribution and the potential pollution of seventeen phenolic compounds in a water river and their removal by conventional WTP around one year. The risks assessments were also evaluated. The results indicated that sixteen phenolic compounds were detected at some point in the samplings between the seventeen investigated compounds in the raw and treated waters. The mean phenolic compounds concentration range in the one year of analysis for the raw water was 0.257 µg L^{-1} to 14.374 µg L^{-1} and in the treated water was 0.225 µg L^{-1} to 12.985 µg L^{-1} for the same compounds, being them the 245TCP and the 2346TCP respectively. The most detected compounds in the studied raw water were 234TCP, 24DMP, and 4NP and in the treated water were 4NP and BPA. In order to better understand the origin of these compounds in the study waters it was clear that the analysis should be accompanied by a study of soil use and occupation of the watershed.

Concerning to the concentration variation of the phenolic compounds in the surface water during the monitoring, in general, except for October and May, the highest values of total concentration are related to the months in which there was less precipitation, demonstrating that the presence of the phenolics was subject to seasonality. The removal efficiency results of the phenolic compounds by the conventional treatment process of the WTP did not show a logic in the removal or increase of the compounds, since in some samples the phenolic compounds were totally removed and in others their increase or formation occurred.

The risks assessments confirmed the toxicity potential concern regarding the phenolic compounds, since most of the evaluated compounds were highly toxic to any trophic level and posed a significant human health risk. Subsequently the risk reduction of phenolics using conventional WTP was low, requiring attention. It is necessary to think about more efficient technologies considering the increase in contamination of water source by complex chemicals.

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CHAPTER IV

DCMD as an alternative in the removal of phenolic compounds in water and risk reduction

4.1 INTRODUCTION

Clean water is a human need for many different activities. Due to population and economic growth, the rapidly intensifying production and use of chemicals, longer periods of reduced river discharge, and improved sensitivity of analytical techniques, the number of chemicals that is detected in the aquatic environment is increasing. Thus, water pollution with various chemical wastes, such as phenolic compounds, is a serious problem of contemporary society associated with an expectation of high-water consumption. Phenols are found in wastewater, as well as in all-natural aquatic systems (AHMARUZZAMAN, 2008), and are among the priority pollutants of the US Environmental Protection Agency (EPA), one of the world's leading environmental control, due to their unpleasant tastes, odors, and toxicity even at low concentrations (EPA, 2014).

However, removal of phenolic compounds from water is challenging, because of their high reactivity and solubility (BUSCA et al., 2008), thereby the development of effective methods for the removal of this compounds from contaminated water is still an important topic. For many years the main purpose of city water treatment was simply to reduce the number of suspended solids, oxygen-demanding materials, dissolved inorganic compounds and pathogenic bacteria. However, efforts are being done to adopt better water treatment conditions. Among the most common organic pollutants are phenol derivatives (THE & MOHAMED, 2011). The removal of these micro-pollutants has been possible as the water treatment progresses, due to the appearance of different techniques such as chemical precipitation, filtration, electrodeposition, ionic adsorption, membrane filtration, solvent extraction biodegradation, adsorption on activated carbon, organic polymers and inorganic compounds, electrochemical or photocatalytic oxidation, biochemical processes, among others (BO et al., 2008).

Some of these techniques have many limitations, such as incomplete treatment, high cost, generation of toxic by-products, and instability (JIN et al., 2007; MOHAMMADI & KAZEMI, 2014). For example, the chlorophenol biodegradation is not feasible because it has a slow and incomplete kinetics and the products formed are more toxic to the environment and humans than the precursors (AGHAV et al., 2011). Among these methodologies alternative, in the membrane separation processes the direct contact membrane distillation (DCMD) has attracted attention to applications with more complex water and in different situations, due to the high quality water produced, stability, and when associated with the renewable energy source the process cost decreases effectively. Furthermore, when compared to nanofiltration, reverse osmosis, and electrodialysis, membrane distillation has some advantages, such as: (a) low operating temperature, which allows its association to energy sources such as geothermal, solar and industrial residual heat; (b) operation at room pressure, which increases the system's security and decreases costs of equipment; (c) membrane fouling is less severe (MANNA & PAL, 2016).

The DCMD is a thermally driven separation process in which a hydrophobic microporous membrane separates a hot feed stream and a cold receiving phase (ALKHUDHIRI et al., 2012). The driving force of heat transport is the temperature gradient, which results in a water vapor pressure differential which causes vapor transport through the membrane pores. The temperature gradient around 30 °C is sufficient to promote separation. DMCD is the oldest and most used membrane distillation process, having liquid phases in direct contact with both sides of the membrane, where there is simultaneous transfer of heat and mass determined by the heat flow and transfer coefficients on the feed and permeate sides (ASHOOR et al., 2016). The heat losses by conduction through the membrane matrix are higher in the DCMD than in other membrane distillation configurations, due to the existence of a continuous contact between the membrane surfaces and the permeate and feed solutions (QATARISH et al., 2013).

Nonetheless, this configuration is easy to operate, widely used, is simple, does not require the use of an external condenser in the permeate collection, and a high flow can be obtained under the correct operating conditions. In addition, it has high rejection factor, with theoretical exclusion of 100% for non-volatile solutes (KHAYET & MATSUURA, 2011; EL BOURAWI et al. al., 2006). As a result to these features, membrane distillation has been recently widely studied, and it is promised to be a cost-effective technology to treat water and wastewater (BAPPY et al., 2016).

Among the applications of DCMD, water treatment with phenolic compounds is a task, since this technology has applications as a uniform focus on the separation of non-volatile components. Although understanding the transport of volatile components present in water treatment is necessary even if the treatment aims are focused on non-volatile contaminants

(SALLS et al., 2018). Some studies have examined the MD treatment for volatile and semi-volatile organic contaminants, noting that the retention is related to the volatility and hydrophobicity of the contaminant (WIJEKOON et al., 2014; KUJAWA et al., 2015, SALLS et al., 2018; RAZA et al., 2018) and the rejection rates varied widely from poor to high rejections, showing the need to study the behavior of each compound with the technology (WIJEKOON et al., 2014).

Knowing alone the performance of the DCMD in the removal of phenolic compounds is not sufficient to determine if the presence of this micropollutants in the concentrations which they are found in the permeate put in risk the human health. The lack of insight into the human health relevance of many chemicals appearing in the water cycle is a growing concern for drinking water utilities (BAKEN et al., 2018). Notably, environment (ERA) and human health risk assessments (HRA) must be carried to support decision making to mitigate risk where needed. The absence of risk investigation and management may thus unreliably regulate the quality of water resources and efficiency of treatment processes (WEE & ARIS, 2017).

As environmental legislation and health quality standards become increasingly restrictive, demands arise for the definition of strategies for the development of clean technologies, improvement of existing processes and development of robust water purification systems. In this way, seeking solutions to established problems and anticipating new sources of pollution, the present work addresses a preliminary study on the removal of phenolic compounds in an superficial water by the DMCD process and the reduction of risk.

4.2 MATERIALS AND METHODS

4.2.1 Sampling

The collecting point was in one river (RW) at the entrance of a WTP that provide water for an average of 2.5 million people. The average of water flow in the studied river is 300 $m^3 s^{-1}$, the annual average temperature ranging from 18 to 27 °C, and the average annual rainfall is 1390 mm. The water sample was collected in July of 2018, according to the technical specification requirements for monitoring phenol in surface water described by NBR 9898 (ABNT, 1987) and EPA 528 (EPA, 2000).

4.2.2 Physicochemical characterization of the water and flows

The pH, conductivity, alkalinity, turbidity (Hach 2100AN turbidimeter), and color (Hach DR 2800 spectrophotometer) were evaluated in the raw water and in the flows obtained during the operation of the DCMD unit, according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The Na^+, NH_4^+, K^+, Mg^{2+} ions concentrations (Ion Chromatograph ICS-1000 - Dionex) and total organic carbon - TOC (Shimadzu TOCV CNP) were measured. Furthermore, total solids and humic substances (APHA, 2012) were verified in the raw water.

4.2.3 Selected compounds and instrumental analysis

Seventeen phenolic compounds were monitored in the raw water and in the flows from the DCMD unit based on the list of EPA priority compounds. They were: 2-chlorophenol, 4-chloro-3-metylphenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4,6-trichlorophenol, 4-nitrophenol, bisphenol A, 2-metylphenol, 3-metylphenol, 2,6-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4-trichlorophenol, 2,3,6-trichlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, and 3,4,5-trichlorophenol. The characteristics of these compounds can be seen in ANNEX I (p. 125 – 126). Therefore, the methodologies proposed by EPA (528, 3535A, and 8041) were used as basis for identification and quantification of the compounds, while the validation was grounded on ICH (ICH, 2015), ANVISA (ANVISA, 2003), and INMETRO (INMETRO, 2007).

In the solid phase extraction, the C18 / 18% cartridges (500 mg / 6 mL - Applied Separations) were used, conditioned with 5 mL of methanol, after 5 mL of MilliQ (ThermoScientific Smart2Pure 3 UV) water. Then, 1 L of the sample was percolated at pH 2, maintaining constant flow and close to 20 mL min^{-1}. The cartridge remained under vacuum for 20 min after finalizing the concentration process for complete removal of moisture and the compounds were eluted using 2 times 1 mL of methanol. The entire extraction procedure was performed with a manifold (Supelco-Visiprep ™).

For the stage of identification and quantification, the Shimadzu CGMS-QP2010 SE equipment with the FID as detector, the Zebron ZB-MultiResidue column (30 m x 0.32 mm x 0.50 µm), and helium as carrier gas were used. The optimum oven programming was 40 °C for 4 minutes, 4 °C min^{-1} to 240 °C and finally 240 °C for 5 minutes. The injection volume of the samples was 2 μL in splitless mode, with the injector temperature at 275 °C. An automatic sampler (AOC-20i, Shimadzu) was used in all tests, programmed to perform a solvent wash (2 x) before and after each injection, in addition to settle the syringe with the sample (2 x). The FID detector temperature was maintained at 300 °C and an Air / H_2 mixture (400/40 mL min^{-1}) was used for the combustion while a N_2 / Air mixture (30 mL min^{-1}) was used as gas make-up to scan components through the detector to minimize the bandwidth of compounds.

4.2.4 Prior evaluation of DCMD in the removal of phenolic compounds

4.2.4.1 <u>Experimental set-up</u>

The DCMD assays were performed in a semi-pilot unit. Figure 4.1 (p. 104) shows a schematic diagram and a photo of the MD system, which contains a DCMD flat sheet module with three hydrophobic microporous polytetrafloroethylene (PTFE) membrane (total active filtration area of 0.3 m^2). In the unit were used two diaphragm pumps (one for feed and another for distillate flows, Provitec GA5200 MB), two supply tanks, a balance, two thermometers, an electric heating system, and a cooling system (AquaCooler, Australia) for the permeate. The membrane characteristics are shown in Table 4.1 (p. 105).

Figure 4.1: Semi-pilot DMCD unit: a) Schematic diagram and b) Unit photo

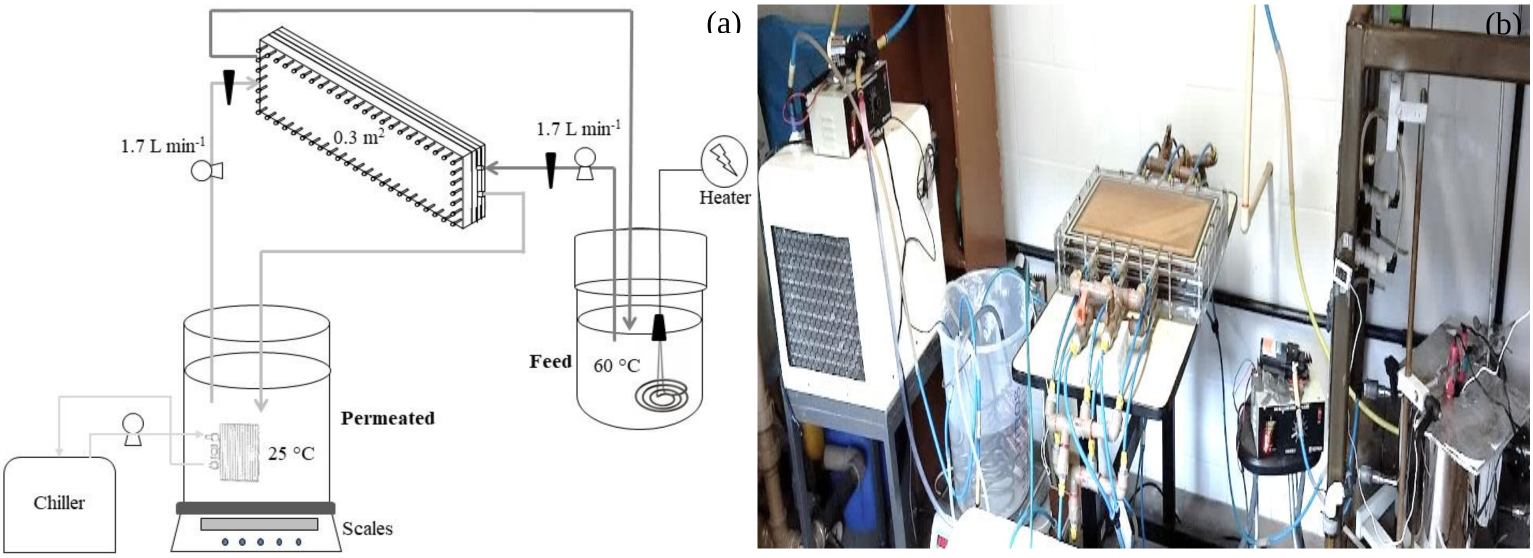


Table 4.1: Membrane characteristics based on supplier data

Membrane	Supplier	Material	Pore size	Porosity	LEP	Bubble Point
PTFE 023005	Sterlitech Corp.	PTFE	0.2 µm	60 - 80%	> 14.5 psi	> 10 psi

4.2.4.2 Experimental procedure

The volumes of raw water for feed and distilled water for cooling were 4 L and 8 L respectively. Both streams were recirculated in counter-current at 1.7 L min^{-1} up to a recovery rate of approximately 70% and the temperatures during the test were maintained at 60 °C and 25 °C in the feed and permeate respectively. As the configuration is DMCD, the permeate generated was incorporated into the initial distilled water. In the experiments the permeate mass and temperature of the currents were monitored every 5 minutes, while conductivity and pH of the permeate were checked every 10 minutes.

4.2.4.3 Calculations

The permeate flow of the DCMD process was continuously measured by means of a mass balance and the membrane flux was calculated from this value according to Equation 4.1.

$$J = \frac{m_2 - m_1}{(t_2 - t_1) \times A_m} \qquad \text{Equation 4.1}$$

Where J is the permeate flux; t_1 and t_2 are the time; $m_2 - m_1$ is the increase in the permeate mass (kg) between times t_1 and t_2; and A_m is the membrane area (m^2).

The permeate recovery rate (RR) was calculated by Equation 4.2.

$$RR = \frac{m_{df} - m_{di}}{m_{fi}} \qquad \text{Equation 4.2}$$

Where m_{di} and m_{df} correspond to the mass (kg) of the initial and final distillate, respectively, and m_{fi} corresponds to the initial feed mass (kg).

The retention of the compounds was calculated using Equation 4.3.

$$Retention\ (\%) = \frac{m_f - m_d}{m_f} x\ 100$$ Equation 4.3

Where m_f and m_d represents the mass of the compound in the feed and distillate streams, respectively. The system mass balances were performed to determine if there was loss of specific contaminants during experiments. It was defined by Equation 4.4.

$$M_s = M_i - (C_r * V_r) - (C_d * V_d)$$ Equation 4.4

Where M_s is mass lost (biodegradation/biotransformation/adsorption); M_i is total initial mass of given contaminant; C_r and C_d represents respectively the solute concentrations in the retentate and distillate streams; V_r and V_d are the volumes in the retentate and distillate sides, respectively.

4.2.5 Risk assessment

The potential environmental risks were calculated by hazard quotient (HQ), it is measured by dividing the environmental concentration of the compound found in the research (MEC) by the predicted no effect concentration (PNEC)(EPA, 1986). The value of PNEC was obtained from the ratio between the acute toxicity data (Lethal Concentration 50 (LC50) or Mean Effect Concentration 50 (EC50)) and an assessment factor (AF) of 1000, or from the ratio between the no observed effect concentration (NOEC) data and an AF of 10. The LC50, EC50 and NOEC values used can be seen in the ANNEX II (p. 127 – 130). The lowest PNEC values and the highest MEC were considered in the calculations in order to obtain a worst scenario. The risk was classified into high risk ($HQ > 1$), medium risk ($0.1 \leq HQ \leq 1$), low risk ($0.01 \leq HQ < 0.1$), and negligible risk ($HQ < 0.01$) (EMEA, 2006).

Whereas the human health risk was characterized according WHO (2017) by the margin of exposure (MOE) determination. MOE is obtained through the ratio between the safe exposure level (DWEL) and the highest concentration detected in the evaluated environment (MEC). The low risk is implied when MOE value is more than 100 (EPA, 2012). The DWEL can be estimated by tolerable daily intake (TDI), as exposed in Equation 4.5.

$$DWEL = (TDI * b_m * f)/c$$ Equation 4.5

Where b_m is the body mass (60 kg), f the contribution of water to exposure (10 %), and c the daily water consumption (2 L) (WHO, 2017). The value of TDI was obtained direct from the literature or calculated from the ratio between the non-observed adverse effect level (NOAEL) or the lowest observed adverse effect level (LOAEL), and an assessment factor of 100 and 10000, respectively. The data values used can be seen in the ANNEX III (p. 131 – 133).

4.3 RESULTS AND DISCUSSION

4.3.1 Flux and water quality

Table 4.2 (p. 107) describes the characteristics of the raw water used in the membrane filtration process and the permeate produced in the DCMD. For all parameters analyzed the removal was greater than 50% reaching 100% for some parameters. This result was already expected, as MD technology has a high rejection to non-volatile components, such as salts, inorganic compounds and macromolecules (THOMAS et al., 2017). It should be noted, that the removal could be even greater if the recovery rate was lower, since the tests were performed with a high recovery rate (70%). In addition, the temperature of 60 °C used was not enough to reach the volatile point of ions and organic matter. Therefore, most of the time, only water vapor probably was able to pass through the membrane.

Table 4.2: Characteristics of raw water and DCMD permeate

Parameter	RW	DCMD permeate	DCMD efficiency (%)
Turbidity (NTU)	14.2	0.338	97.62
pH	6.19	5.03	-
UV-Vis 254 nm	0.021	0.0027	87.14
Perceived color (mg Pt-Co L^{-1})	74	< DL	100
Real Color (mg Pt-Co L^{-1})	< DL	< DL	-
TSS (mg L^{-1})	16	0	100
TS (mg L^{-1})	108	27.6	74.44
TOC (mg L^{-1})	1.99	0.8553	57.02
Conductivity (µS cm^{-2})	121.3	4.75	96.08
Alkalinity (mg $CaCO_3$ L^{-1})	29.3	2.4	91.81
NT (mg L^{-1})	1.37	0.1564	88.58
Ca (mg L^{-1})	21.1	< 2.50	88.15
Mg (mg L^{-1})	6.4	< 1.25	80.47

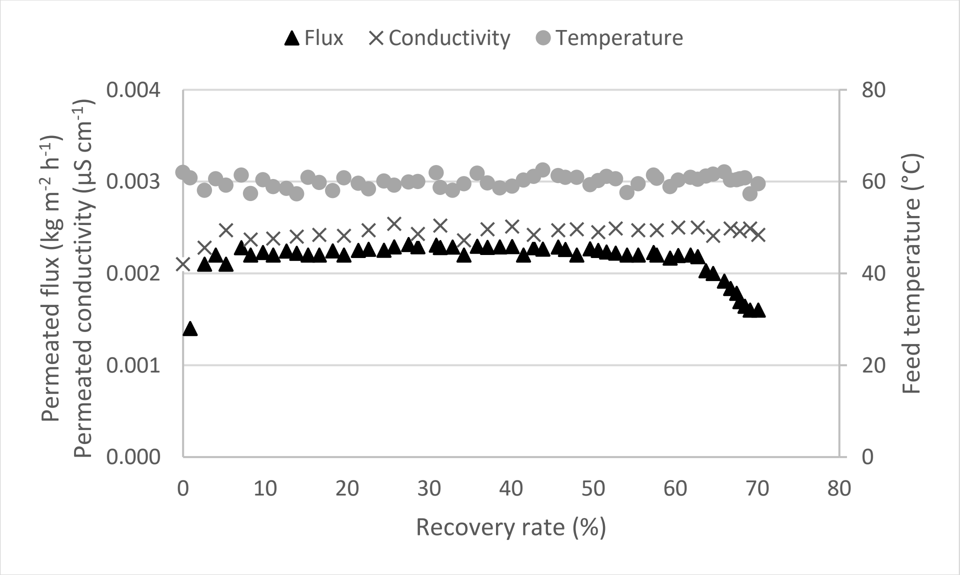
Parameter	RW	DCMD permeate	DCMD efficiency (%)
Na (mg L^{-1})	5.68	< 1.0	82.39
K (mg L^{-1})	< 2.50	< 2.50	-

The lowest removal for TOC can be associated with the interaction of the hydrophobic part of the organic matter with the membrane, whereas the hydrophilic part can bond to the water molecules to diffuse through the membrane (MENG et al., 2014; WANG et al., 2018).

4.3.2 DCMD performance

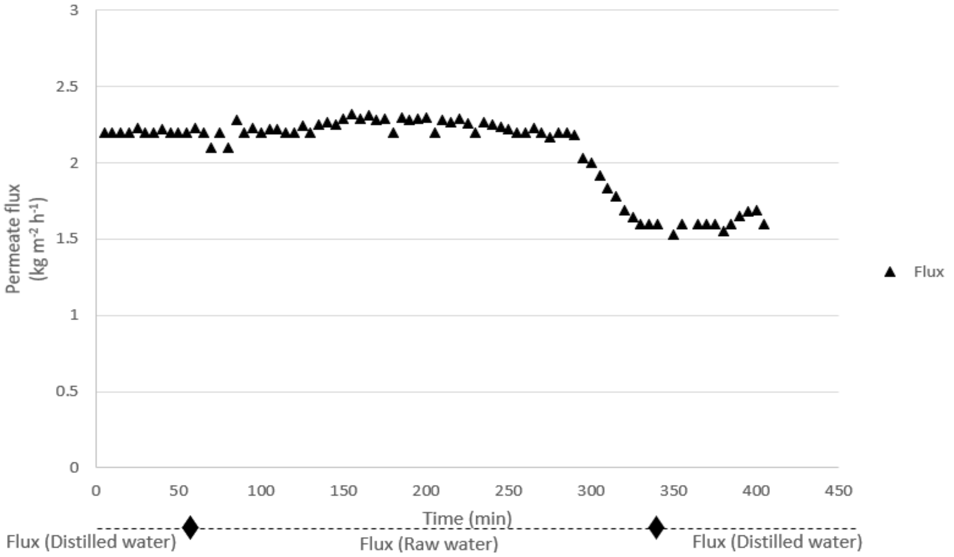
Figure 4.2 (p. 108) shows the permeate flux, the permeate conductivity, and the feed temperature over time for a prior assessment of the DCMD performance in the removal of phenolic compounds in a superficial water at a recovery rate of 70%. It is noted that the temperature variation of the feed remained constant at about 60 °C throughout the test, the flow dropped at the recovery rate of 63%, and despite this the conductivity remained constant. It could indicate the absence of ionic impurities in the permeate.

Figure 4.2: Permeate flux and conductivity, feed temperature, flow rate set at 1.7 L min^{-1} for DCMD preliminary test on phenols removal



The ratio between the initial and final flows was approximately 0.7, indicating a decrease in the performance of the DMCD, which may have occurred because of fouling during the process, since the permeate conductivity remained constant over the time it can be affirmed that membrane wetting not happened. Therefore, it is recommended to work at a recovery rate equivalent to the point before the flow decay (RR < 63%) to prevent fouling and loss of performance. After the raw water test, the flow was measured with distilled water and it can be seen in Figure 4.3 (p. 109) that the flow decay remained constant, highlighting the need to evaluate a chemical cleaning for the recovery of membrane permeability. As these are preliminary results it is still necessary to evaluate all the fouling mechanisms and the operational parameters to better evaluate the performance of this technology.

Figure 4.3: Decay of the flow by time with distilled and raw water, the feed temperature of 60 °C, with flow rate set at 1.7 L min^{-1}



4.3.3 DCMD in the removal of phenolic compounds

From Table 4.3 (p. 110) is possible to see that in the collected sample of the river water used in MD feed only three phenolic compounds were identified among the seventeen surveyed, being them: 2-nitrophenol, 2,3,4-trichlorophenol, and bisphenol A. These micropollutants are widely spread in the environment and many studies already report their presence in natural waters (SANTHIA et al., 2012; KUPETA et al., 2018). In a monitoring of phenolic compounds carried out over a year in this river, the 2NP, 234TCP, and BPA were detected in samples of two, seven and four months respectively (Chapter III). The bisphenol A is classified as endocrine disrupter

(WEE & ARIS, 2017), while the 2-nitrophenol and 2,3,4-trichlorophenol have a carcinogenic potential (JIN et al., 2012; KUPETA et al., 2018). The bisphenol A and 2-nitrophenol are manufactured chemicals that do not occur naturally in the environment, being therefore the consequence of river pollution.

Table 4.3: Removal of identified phenolic compounds in raw water by DCMD with 70% of permeate recovery and pK_H / log D ratio

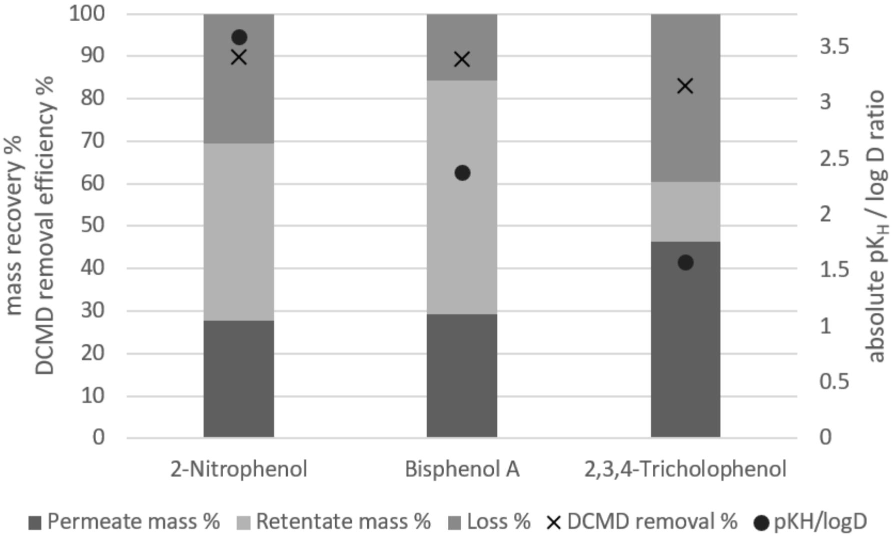
Sample	2-Nitrophenol ($\mu g\ L^{-1}$)	2,3,4-Tricholophenol ($\mu g\ L^{-1}$)	Bisphenol A ($\mu g\ L^{-1}$)
Feed (Raw water)	1.028	0.509	2.503
Permeate	0.105	0.087	0.268
Removal efficiency (%)	89.80	82.91	89.28
pK_H / log D	3.597	1.58	2.379

The results regarding to the removal of phenolic compounds from the raw water by the DCMD technology showed a removal efficiency greater than 80% for all compounds identified. Some researchers have reported the MD retention efficiency for different phenols ranging from 54-70% (WIJEKOON et al., 2014) to 99% (HAMZAH & LEO, 2016). It was found in a recent studies of trace organic contaminants removed in water by MD technology, that the rejection could be linked to the contaminant volatility and hydrophobicity (HUO et al., 2013; WIJEKOON et al., 2014; XIE et al., 2014).

The retention by the MD membrane of trace organic contaminants, as phenolic compounds, is governed by the vapor pressure (indicated by Henry's constant, H or, $pK_H = -\log H$) and the water partition coefficient (log D). Wijekoon et al. (2014) in a stand-alone MD system, suggested that a pK_H / log D ratio of the compound low than < 2.5 led to its poor removal. However, the interpretation of this result is complicated because of mass loss and incomplete mass balances, due to evaporative and sorptive losses during the test and biotransformation (SALLS et al., 2018).

Observing Figure 4.4 (p. 111), taking into account the pK_H / log D ratio of the studied compounds and the mass losses due to evaporation, adsorption, degradation or biotransformation, the 2-nitrophenol and bisphenol A have this rate higher than 2.5 and they presented the highest removal rates, according to the Wijekoon et al. (2014) results. Although, the 2,3,4-trichlorophenol had the pK_H / log D ratio less than 2.5 and it also attained a good removal. The 2-nitrophenol (pK_H=4.893) and 2,3,4-trichlorophenol (pK_H=5.153) compared to the bisphenol A (pK_H=8.66) had higher mass losses, probably due to its greater volatility.

Figure 4.4: Overall removal of phenolic compounds in DCMD, mass distribution, mass loss and pK_H / log D ratio



In this sense, predict the behavior of trace organic contaminants in MD technology is still a challenge and the few recent studies (SALLS et al., 2018; ASIF et al., 2018) with this theme show the need of understanding the transport of volatile and semi volatile components present in water treatment.

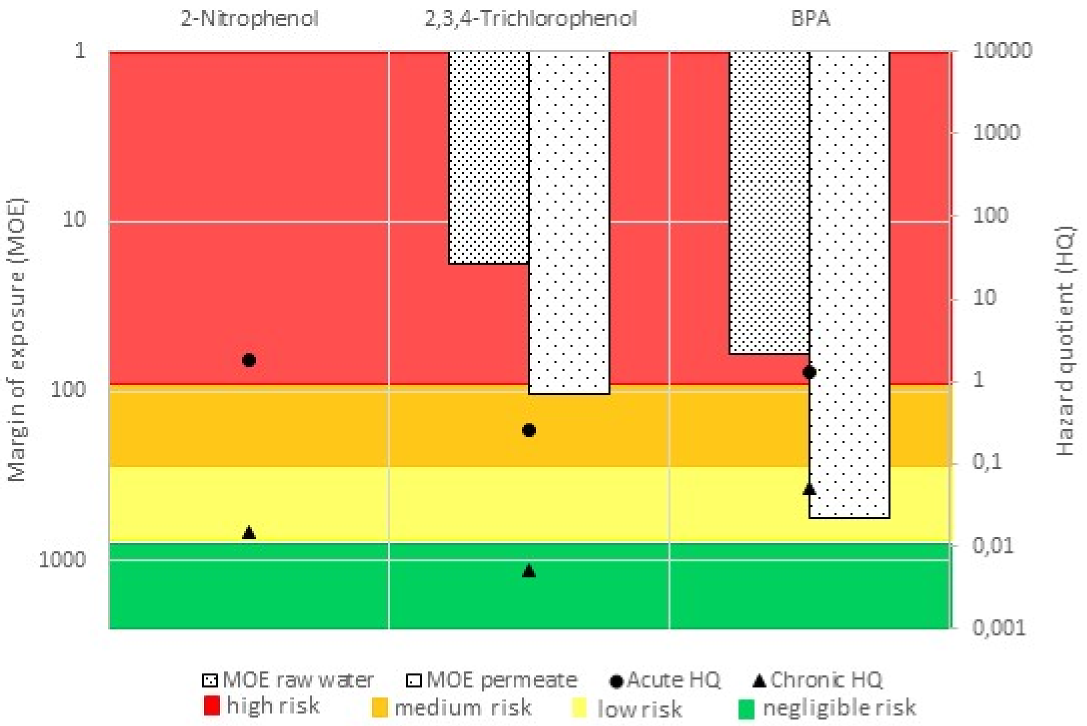
4.3.4 Risk reduction

The Table 4.4 (p. 112) and Figure 4.5 (p. 113) show the environmental and human health risk reduction by the DCMD processes when compared to the raw water. Observing the ERA for the raw water, the acute risk for 2-nitophenol and bisphenol A were classified as high risk, while 2,3,4-trichlorophenol was medium risk. Although the chronic risk for all compounds was low or negligible risk. Xiong et al. (2014) also found a high risk for bisphenol A in all surface water samples that they analyzed. Already Zhou et al. (2017), with respect to 2-nitrophenol in a river in China, identified a small ERA. Looking to the HRA in the raw water, the high removal of 2,3,4-Trichlorophenol and BPA by the DCMD leads to a consequent reduction of HRA. However, even with the greater retention of 2-nitrophenol by the technology it was not enough to reduce the risk offered by this compound. Therefore, the technology has proven to be efficient in risk reduction for most of the compounds found in raw water.

Table 4.4: Environmental and human health risk assessment of Phenolic compounds in the raw water and DCMD permeate

	Raw water						**DCMD permeate**	
Compound	**ERA**				**HRA**		**HRA**	
	Acute toxicity		Chronic toxicity		MOE	Classification	MOE	Classification
	HQ	Classification	HQ	Classification				
2-Nitrophenol	1.819	High risk	0.015	Low risk	0.0001	High probability of risk	0.001	High probability of risk
2,3,4-Trichlorophenol	0.254	Medium risk	0.005	Negligible risk	17.692	High probability of risk	103.528	Small probability of risk
Bisphenol A	1.317	High risk	0.05	Low risk	59.922	High probability of risk	558.728	Small probability of risk

Figure 4.5: Overall risk assessment



4.4 CONCLUSION

For all physicochemical parameters analyzed the removal by the DCMD unit was greater than 50% for TOC and reaching values close to100% for turbidity, solids, and ions, as was already expected. Since the MD technology has a high rejection to non-volatile components, such as salts, inorganic compounds and macromolecules.

The permeate flux over time in the MD test showed a dropped of flow, with the ratio between the initial and final flows of approximately 0.7. But the conductivity remained constant indicating the absence of ionic impurities in the permeate. Better studies need to be performed on operational issues to better understand and confirm this flow drop in the recovery rate of 70%. However, it is recommended to work at a recovery rate equivalent to the point before the flow decay (RR < 63%) to prevent fouling and loss of performance. Despite this decrease in permeate flux, the retention rates of the phenolic compounds in the raw water (2-nitrophenol, 2,3,4-Trichlorophenol, and BPA) shown to be of a great efficiency, more than 80% of all compounds were removed by the DCMD system.

In relation to risk assessment the technology has proven to be efficient in human health risk reduction for most of the compounds found in the raw water (2,3,4-Trichlorophenol and BPA).

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CHAPTER V

Final considerations

5.1 MAIN RESULTS AND CONCLUSIONS

In this research was developed and validate an analytical methodology for the identification and quantification of phenolic compounds in aqueous matrix at trace concentration, in order to investigated the occurrence of seventeen phenolic compounds in a surface water and a treated water by a conventional water treatment plant (WTP) in one year. In addition, the environmental (ERA) and human health risk (HRA) of these compounds in the raw water, and its reduction by conventional and direct contact membrane distillation (DCMD) processes were also evaluated.

In Chapter II, the methodology for the identify and quantify of a variety of 17 phenolic compounds was done using solid phase extraction (SFE) (C_{18} cartridge) and gas chromatography with FID. For the methodology validation, the selectivity, linearity, detection and quantification limits, sensitivity, precision, accuracy, resolution, matrix effect and peak quality were considered. In the recovery grade trials for the four solvent tested, methanol had a better performance and was used throughout all analyzes. With respect to the influence of the matrix on the efficiency of SPE, a lower recovery of the compounds was noted in the raw water compared with the treated water, but all samples had the recover higher than 50%. It was also possible shown in this chapter the presence of different phenolic compounds in three different points of the same river belonging to an important national watershed and in the water from the entrance and exit of a treatment station that serves a large population. In between the compounds analyzed, 2-nitrophenol and bisphenol A appeared in all samples. The presence of different chlorophenols in the analyzed treated water (24DCP, 245TCP, 345TCP) was also observed.

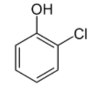
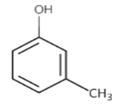
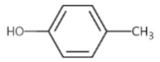
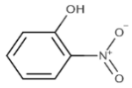
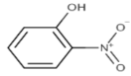
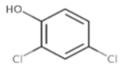
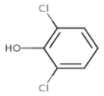
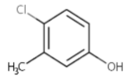
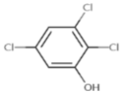
Chapter III provided a monitoring of phenolic compounds in a river and in a treated water by a conventional water treatment plant (WTP) around a year in Brazil. Furthermore, the environmental risk (hazard quotient (HQ)) and the human health risk (margin of exposure (MOE)) were calculated for the compounds. The results indicated that sixteen phenolic compounds were detected at some point in the samplings between the seventeen investigated compounds. The most detected compounds in the studied raw water were 234TCP, 24DMP, and 4NP, and in the treated water were 4NP and BPA. Concerning to the concentration variation of the phenolic compounds in the surface water during the monitoring year, the highest values of total concentration were related to the months in which there was less precipitation, demonstrating that the presence of this micropollutants are subject to seasonality. From the treat water results were observed that the efficiency of the conventional treatment process of the WTP to eliminate the phenols did not show a logic in the removal or increase of the compounds, since in some samples the phenolic compounds were totally removed and in others their increase or formation occurred. Regarding to the risk assessments, most of the evaluated compounds were highly toxic to any trophic level and posed a significant human health risk. Subsequently the risk reduction of phenolics using conventional WTP was low.

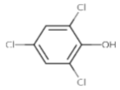
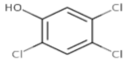
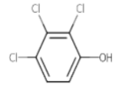
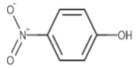
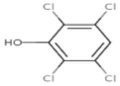
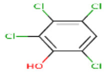
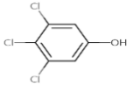
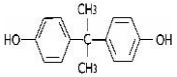
Finally, in Chapter IV, the performance of DCMD as an alternative technology for the removal of phenolic compounds in water was pre evaluated. Being demonstrated that still are many challenges to better understand the use of this technology in the retention of volatile and semi volatile compounds in trace concentrations. The permeate flux over time in the MD test showed a dropped of flow, with the ratio between the initial and final flows of approximately 0.7. It was recommended work with RR<63% to avoid problems with fouling. But the conductivity remained constant indicating the absence of ionic impurities in the permeate. Despite this decrease in permeate flux, the retention rates of the phenolic compounds in the raw water (2-nitrophenol, 2,3,4-trichlorophenol, and BPA) was more than 80%. The reduction of risk was also assessed proving that the technology is efficient.

Based on this work, it was possible to confirm that is important to establish sensitive and reliable analytical method that allow the determination of a wide range of phenolic compounds in water at the low levels of concentration, since this micropollutants are a reality in surface waters and conventional water treatments have not been able to remove them, thus raising in drinking water. The identification methods associated with risk analysis are essential tools for the management and the establishment of standards for these pollutants that are still often neglected. It is also necessary to think critically about the complexity of the water which is arriving at the water treatment plants and the importance of alternative technologies, as MD, researches for a future water treatment scenario.

ANNEX

ANNEX I: Compounds analyzed in the process of identification and quantification

Compounds	Retention Time (minutes)	Abbreviation	CAS	Molar mass	Vapor pressure at 25 ° C (mmHg)^{ab}	Solubility in Water at 25 °C (mg L^{-1})^{ab}	pKa^{c}	Log K_{ow}^{a}	Log D^{c} at pH 7	Molecular formula	Molecular structure
2-chlorophenol	8.253	2CP	95-57-8	128.56	2.53	28500	8.49	2.15	2.21	C_6H_5ClO	
2-methylphenol	10.098	2MP	95-48-7	108.05	0.29	22200	10.29	2.09	2.09	C_7H_8O	
3-methylphenol	10.899	3MP	108-39-4	108.05	0.2	21500	10.1	2.09	2.09	C_7H_8O	
2-nitrophenol	13.417	2NP	88-75-5	139.02	0.113	2503.98	7.23	1.36	1.36	$C_6H_5NO_3$	
2,4-dimethylphenol	14.241	24DMP	105-67-9	122.07	0.102	7867.55	10.6	2.36	2.36	$C_8H_{10}O$	
2,4-dichlorophenol	15.519	24DCP	120-83-2	161.96	0.09	4498.72	7.89	3.05	3.05	$C_6H_4Cl_2O$	
2,6-dichlorophenol	18.583	26DCP	87-65-0	161.96	0.0889	1900	6.79	2.33	2.33	$C_6H_4C_{l2}O$	
4-chloro-3-metylphenol	20.055	4C3MP	59-50-7	142.01	0.05	3835.46	9.55	2.83	2.83	C_7H_7ClO	
2,3,5-trichlorophenol	20.735	235TCP	933-78-8	195.92	0.022	90.09	6.45	2.84	2.84	$C_6H_3Cl_3O$	

Compounds	Retention Time (minutes)	Abbreviation	CAS	Molar mass	Vapor pressure at 25 ° C (mmHg)^{ab}	Solubility in Water at 25 °C (mg L^{-1})^{ab}	pKa^{c}	Log K_{ow}^{a}	Log D^{c} at pH 7	Molecular formula	Molecular structure
2,4,6- trichlorophenol	20.991	246TCP	88-06-2	195.92	0.008	799.63	6.23	2.78	2.78	$C_6H_3Cl_3O$	
2,4,5- trichlorophenol	21.288	245TCP	95-95-4	195.92	0.0075	114.1	7.43	3.24	3.24	$C_6H_3Cl_3O$	
2,3,4- trichlorophenol	21.914	234TCP	15950-99-0	195.92	0.00156	97.46	7.1	3.26	3.26	$C_6H_3Cl_3O$	
4-nitrophenol	26.709	4NP	100-02-7	139.02	0.0000979	11601.77	7.15	1.31	1.31	$C_6H_5NO_3$	
2,3,5,6-tetrachlorophenol	27.152	2356TCP	935-95-5	229.88	0.000168	54.9	5.14	2.01	2.01	$C_6H_2Cl_4O$	
2,3,4,6- tetrachlorophenol	27.417	2346TCP	58-90-2	231.881	0.000666	23	5.22	4.45	2.56	$C_6H_2Cl_4O$	
3,4,5- trichlorophenol	29.331	345TCP	609-19-8	195.92	0.000496	64.49	7.84	3.68	3.68	$C_6H_3Cl_3O$	
4,4’-(propane-2,2-diyl)diphenol (bisphenol A)	43.964	BPA	80-05-7	228.11	0.000000227	120	9.6	3.63	3.63	$C_{15}H_{16}O_2$	

Source: ^{a}Chemspider (2018); ^{b}EPA (2018); ^{c}PubChem (2018).

ANNEX II: EC50, LC50, and NOEC values

Compounds	Trophic level	Specie	EC50	LC50	Value (mg L^{-1})	Reference	Specie	NOEC	Value (mg L^{-1})	Reference
2-chlorophenol	Algae	*Pseudokirchneriella subcapitata*	Growth - 4 d		70	SHIGEOKA et al., 1988	*Pseudokirchneriella subcapitata*	Population/ Physiology - 2 d	4.93	CHEN & LIN, 2006
	Crustacean	*Daphnia carinata*	Intoxication - 1 d		25	SHIGEOKA et al., 1988	*Daphnia magna*	Reproduction - 21 d	0.5	KUHN et al., 1988
	Fish	*Tilapia zillii*	Mortality - 2 d		6.549	YEN et al., 2002	*Pimephales promelas*	Mortality - 30 d post-hatch	4	LEBLANC, 1984
2-methylphenol	Algae	*Selenastrum sp.*	Population - 3 d		100	SLOOFF, 1982	Scenedesmus quadricauda	Growth - 8 d	11	BRINGMANN & KUEHN, 1979
	Crustacean	*Daphnia magna*	Intoxication/Immobile - 1 d		17.9512234	DEVOLLERS, 1988	n.r.	n.r.	n.r.	n.r.
	Fish	*Oncorhynchus mykiss*		Mortality - 2 d	13	SLOOFF, 1983	n.r.	n.r.	n.r.	n.r.
2-nitrophenol	Algae	*Pseudokirchneriella subcapitata*	Population - 2 d		1.08	TSAI & CHEN, 2007	*Chlorella zofingiensis*	Assimilation efficiency - 2d	0.695553	WEBER et al., 1984
	Crustacean	*Daphnia magna*		Mortality - 2 d	13.17	KIM et al., 2006	n.r.	n.r.	n.r.	n.r.
	Fish	*Cyprinus carpio*		Mortality - >2 d	0.565	YEN et al., 2002	n.r.	n.r.	n.r.	n.r.
2,4-dimethylphenol	Algae	*Pseudokirchneriella subcapitata*	Population - 2 d		13.5	TSAI & CHEN, 2007	*Chlorella pyrenoidosa*	Biochemistry/Chlorophyll - 3 d	50	HUANG & GLOYNA, 1968
	Crustacean	*Daphnia magna*	Intoxication/Immobile - 1 d		11.7280128	DEVILLERS, 1988	*Ceriodaphnia dubia*	Mortality - 7 d	3.41	SPEHAR, 1987
	Fish	*Pimephales promelas*		Mortality - 4 d	18.1	BRODERIUS et al., 1995	*Pimephales promelas*	Growth/lenght - 32 d	0.398	RUSSOM, 1993
2,4-dichlorophenol	Algae	*Pseudokirchneriella subcapitata*	Population - 3 d		3586.0704	ANDREOZZI et al., 2011	*Chlorella vulgaris*	Population - 3 d	<0.73	GEIGER et al., 2016

Compounds	Trophic level	Specie	EC50	LC50	Value (mg L^{-1})	Reference	Specie	NOEC	Value (mg L^{-1})	Reference
	Crustacean	*Daphnia magna*	Behavior/swimming - 0.75 d		1.5	BAHRNDORFF et al., 2016	*Macrobrachium superbum*	Mortality - 21 d	0.05	JIN et al., 2011
	Fish	*Danio rerio*	Development - 4 d		2.3	STENGEL et al., 2017	*Danio rerio*	Enzyme(s)/Acetylcholinesterase - 4 d	0.4	STENGEL et al., 2017
2,6-dichlorophenol	Algae	*Chlorella vulgaris*	Growth - 4 d		9.7	SHIGEOKA et al., 1988	*Dunaliella tertiolecta*	Growth - 3d	20	ERTURK & SAÇAN, 2012
	Crustacean	*Daphnia magna*	Intoxication/Immobile - 1 d		6	KUHN et al., 1989	n.r.	n.r.	n.r.	n.r.
	Fish	*Tilapia zillii*		Mortality - >2 d	1.732	YEN et al., 2002	n.r.	n.r.	n.r.	n.r.
4-chloro-3-methylphenol	Algae	*Chlorella pyrenoidosa*	Population - 3 d		15	RAMOS et al., 1999	*Chlorella pyrenoidosa*	Population - 3 d	1.9	RAMOS et al., 1999
	Crustacean	*Daphnia magna*	Intoxication/Immobile - 2 d		1.5	RAMOS et al., 1998	*Daphnia magna*	Reproduction - 21 d	1.3	KUHN et al., 1988
	Fish	*Lepomis macrochirus*	Physiology - 1.1388d		100	BABICH & BORENFREUND, 1987	n.r.	n.r.	n.r.	n.r.
2,3,5-trichlorophenol	Algae	*Pseudokirchneriella subcapitata*	2,26 - 3d			ARUOJA et al., 2011	*Macrophyt*	n.r.	16	NIPHE, 2001
	Crustacean	*Daphnia magna*	Intoxication - 1d		2.28	DEVILLERS & CHAMBON, 1986	n.r.	n.r.	n.r.	n.r.
	Fish	*Tilapia zillii*		Mortality - >2d	1.29	YEN et al., 2002	n.r.	n.r.	n.r.	n.r.
2,4,6-trichlorophenol	Algae	*Pseudokirchneriella subcapitata*	Growth - 4d		3.5	SHIGEOKA et al., 1988	*Pseudokirchneriella subcapitata*	Population - 2d	< 0.5	CHEN & LIN, 2006
	Crustacean	*Ceriodaphnia dubia*	Behavior - 0.0417d		4.2	BITTON et al., 1996	*Daphnia magna*	Behavior - 0.1458d	15	MARTINS et al., 2007
	Fish	*Oryzias latipes*	Mortality - 15d		2.6	SHIGEOKA et al., 1988	*Danio rerio*	Genetic - 1d	5	YIN et al., 2009

Compounds	**Trophic level**	**Specie**	**EC50**	**LC50**	**Value (mg L^{-1})**	**Reference**	**Specie**	**NOEC**	**Value (mg L^{-1})**	**Reference**
2,4,5-trichlorophenol	Algae	*Pseudokirchneriella subcapitata*	Population - 3d		1.57	EPA, 1978	*Chlorella pyrenoidosa*	Biochemistry - 3d	1	HUANG & GLOYNA, 1968
	Crustacean	*Daphnia magna*	Intoxication - 1d		2.08	DEVILLERS & CHAMBON, 1986	*Daphnia magna*	Mortality - 2d	0.78	LEBLANC, 1980
	Fish	*Poeciliopsis lucida*	Cells -1d		43	FENT & HUNN, 1996	*Pimephales promelas*	Mortality - 7d	0.361	NORBERG-KING, 1989
2,3,4-trichlorophenol	Algae	*Selenastrum capricornutum*	Growth - 4d		2	WILKINSON et al., 1999	*Dunaliella tertiolecta*	Growth - 3d	1	ERTURK & SAÇAN, 2012
	Crustacean	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
	Fish	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
4-nitrophenol	Algae	*Scenedesmus abundans*	Growth - 4d		32	GEYER et al., 1985	*Pseudokirchneriella subcapitata*	Population - 4d	0.3	EPA, 1978
	Crustacean	*Daphnia magna*	Intoxication - 2d		6	EPA, 2000	*Daphnia magna*	Mortality - 2d	13	LEBLANC, 1980
	Fish	*Poeciliopsis lucida*	Genetics - 1d		556	FENT & HUNN, 1996	*Cyprinodon variegatus*	Mortality - 7d	10.6	LINTON et al., 1994
2,3,5,6-tetrachlorophenol	Algae	*Pseudokirchneriella subcapitata*	Population - 3d		3.31	EPA, 1978	*Pseudokirchneriella subcapitata*	Population - 4d	0.6	EPA, 1978
	Crustacean	*Daphnia magna*		Mortality - 1d	2.5	LEBLANC, 1980	*Daphnia magna*	Mortality - 2d	0.01	LEBLANC, 1980
	Fish	*Cyprinodon variegatus*		Mortality - 3d	2	HEITMULLER et al., 1981	*Cyprinodon variegatus*	Mortality 4d	1	HEITMULLER, 1981
2,3,4,6-tetrachlorophenol	Algae	*Pseudokirchneriella subcapitata*	Growth - 4 d		1.3	SHIGEOKA et al., 1988	*Pseudokirchneriella subcapitata*	Population - 2d	< 0.1	CHEN & LIN, 2006
	Crustacean	*Daphnia carinata*	Population - 7d		0.5	LIBER et al., 1992	*Daphnia magna*	Mortality - 21d	0.25	LIBER & SOLOMON, 1994

Compounds	Trophic level	Specie	EC50	LC50	Value (mg L^{-1})	Reference	Specie	NOEC	Value (mg L^{-1})	Reference
3,4,5-trichlorophenol	Fish	*Oryzias latipes*		Mortality - 2 d	1.27	SMITH et al., 1991	n.r.	n.r.	n.r.	n.r.
	Algae	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
	Crustacean	*Nitocra spinipes*	Growth - 2d		0.4	NEILSON et al., 1990	n.r.	n.r.	n.r.	n.r.
	Fish	*Platichthys flesus*		Mortality - 4d	2.31	SMITH et al., 1994	n.r.	n.r.	n.r.	n.r.
BPA	Algae	*Chlorella pyrenoidosa*	Population - 2d		46.04	ZHANG et al., 2014	*Chlorolobion braunii*	Cells size - 4d	4	GATTULLO et al., 2012
	Crustacean	*Gammarus fossarum*	Intoxication - 4d		1.9	PLAHUTA et al., 2015	*Gammarus fossarum*	Mortality - 103d	0.5	LADEWIG et al., 2006
	Fish	*Rivulus marmoratus*		Mortality - 4d	3.5	RHEE et al., 2011	*Rivulus marmoratus*	Genetic	0.6	SEO et al., 2006

n.r.: not reported

ANNEX III: NOAEL, LOAEL, and TDI values

Compounds	NOAEL	LOAEL	Value (mg kg^{-1}d^{-1})	Value (ug kg^{-1} bw day^{-1})	Reference	TDI	Value (ug kg^{-1} bw day^{-1})	Reference
2-chlorophenol	Reproductive effects - 10 d			5	EXON & KOLLER, 1985	Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
2-methylphenol	Decreased body weights - 90 d			50	EPA, 1986	n.r.	50	EPA, 2019
2-nitrophenol	Nasal lesions - 28 d			0.005	EPA, 2007	n.r.		
2,4-dimethylphenol	Clinical signs/lethargy - 90 d			50	EPA, 1989	Calculated/effects on the immune system	20	EPA, 2019
2,4-dichlorophenol	Decreased delayed hypersensitivity response - 126 d		0.3		EXON & KOLLER, 1985	Calculated/effects on the immune system	3	EPA, 1986
2,6-dichlorophenol						Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
4-chloro-3-methylphenol	Growth and kidneys - 28 d			30000	JANSSEN et al., 1998	Growth and kidneys - 28d	300	JANSSEN et al., 1998
2,3,5-trichlorophenol						Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001

Compounds	NOAEL	LOAEL	Value (mg $kg^{-1}d^{-1}$)	Value (ug kg^{-1} bw day^{-1})	Reference	TDI	Value (ug kg^{-1} bw day^{-1})	Reference
2,4,6-trichlorophenol	Weight - 3 d			0.3	NATIONAL CANCER INSTITUTE, 1979	Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
2,4,5-trichlorophenol	Behavior, mortality, food consumption, growth, body and organ weights, and histopathology - 98 d		1000		MCCOLLISTER et al., 1961	Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
2,3,4-trichlorophenol						Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
4-nitrophenol	Body weight changes - 18 d			110000	KOIZUMI et al., 2001.			
2,3,5,6-tetrachlorophenol						Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
2,3,4,6-tetrachlorophenol	Increased liver weights and centrilobular hypertrophy - 21d			25	EPA, 1986	Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
3,4,5-trichlorophenol						Calculated/effects on the immune system	3*	MOERMOND & HEUGENS, 2009; EPA, 1986; BAARS et al., 2001
BPA		Rat Chronic	1000		NTP, 1982	Genetics- 3d	50	THARP et al., 2012

Compounds	**NOAEL**	**LOAEL**	**Value (mg kg^{-1}d^{-1})**	**Value (ug kg^{-1} bw day^{-1})**	**Reference**	**TDI**	**Value (ug kg^{-1} bw day^{-1})**	**Reference**
		Oral Bioassay						

* The TDI for 2,4-dichlorophenol of 3 μg kg^{-1} bw day^{-1} (EPA, 1986) was considered to be valid for all mono-, di-, tri-, and tetrachlorophenol compounds (Baars et al., 2001); n.r.: not reported.

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