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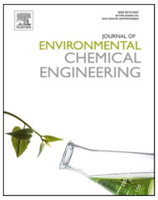

The effect of chlorinated cyanurates on the formation of disinfection byproducts in the production of reuse water from secondary sanitary effluent

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ABSTRACT

Chlorination is an effective and proven method for disinfecting reclaimed water, but side reactions between chlorine and organic matter in the effluent can produce a variety of toxic disinfection byproducts (DBPs). While inorganic chlorine is commonly used in wastewater treatment facilities, little attention has been paid to the use of chlorinated cyanurates such as sodium dichloroisocyanurate (NaDCC) and trichloroisocyanuric acid (TCCA), which have long been used to disinfect drinking water for human consumption and recreation. In this work, the performances of NaDCC and TCCA were compared with sodium hypochlorite (NaClO), either in solution or onsite generated by electrolysis (NaClO-e), to disinfect the secondary effluent (SE) from a municipal wastewater treatment plant (WWTP) aiming for nonpotable reuse applications. The chlorinated product dosages were determined using breakpoint demand tests at 25°C, pH 7.0, and contact times of 0.5 and 24 h. DBPs from trihalomethanes, haloaldehydes, halopicrins, haloacetonitriles, and haloketones were measured. To achieve the breakpoint with a free residual chlorine of 1 mg Cl_2 L^{-1} and promote complete SE disinfection, dosages of 50 mg Cl_2 L^{-1} were required. NaDCC and TCCA produced significantly more chloroform (635.2 μg L^{-1} and 440.1 μg L^{-1}), bromodichloromethane (53.6 μg L^{-1} and 33.9 μg L^{-1}), chloral hydrate (363.4 μg L^{-1} and 308.2 μg L^{-1}), and 1,1,1-trichloropropanone (89.0 μg L^{-1} and 142.2 μg L^{-1}), listed as possible or probable carcinogens. The municipal WWTP's cost assessment for chlorinating 18000 m^3 d^{-1} of SE revealed the benefits of using NaClO-e, including low production of DBPs and no increase in organic carbon in the medium.

NOMENCLATURE

1,1,1-TCP	1,1,1-trichloropropanone
1,1-DCP	1,1-Dichloropropanone
ANOVA	Analysis of Variance
BCAN	Bromochloroacetonitrile
BDCM	Bromodichloromethane
BF	Bromoform
BM	Breakpoint Chlorination Method
BOD_5	5-day Biochemical Oxygen Demand at 20°C
CF	Chloroform
CFU	Colony-forming Unit
CH	Chloral hydrate
CP	Chloropicrin
DBAN	Dibromoacetonitrile
DBCM	Dibromochloromethane
DBP	Disinfection Byproducts
DCAN	Dichloroacetonitrile
NaDCC	Sodium Dichloroisocyanurate
DOC	Dissolved Organic Carbon
DPD	N,N-Diethyl-p-Phenylenediamine
FRC	Free Residual Chlorine
GC-ECD	Gas Chromatography with Electron Capture Detector

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HAA5	Haloacetic Acids Five
HAN	Haloacetonitriles
HAD	Haloaldehydes
HK	Haloketones
HP	Halopicrins
IS	Internal Standard
LLE	Liquid-Liquid Extraction
LoQ	Limit of Quantification
MTBE	Methyl Tert-Butyl Ether
NTU	Nephelometric Turbidity Unit
SE	Secondary Effluent
STP	Sanitary Sewage Treatment Plant
TC	Thermotolerant Coliforms
TCAN	Trichloroacetonitrile
TCCA	Trichloroisocyanuric Acid
TDS	Total Dissolved Solids
THM	Trihalomethanes
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
WWTP	Wastewater Treatment Plant

1. Introduction

The endemic scenario of water scarcity is currently being observed in countries with different levels of development, even in those where there is expected abundant water availability, such as Brazil [21,44]. Water reuse is an effective strategy that contributes to reducing the demand on water resources and, when in compliance with sanitary standards, guarantees safety for the intended uses. The U.S. Environmental Protection Agency [47] categorizes reuse and recommends water quality requirements for each type of application, as well as the treatment required. Applications include: i) urban; ii) industrial; iii) agricultural; iv) environmental and recreational; and v) aquifer recharge. Industrial and domestic effluents are potential sources for obtaining reuse water. Estimates indicate the global production of 359.4×10^9 m^3 yr^{-1} of effluents, of which only 11 % (40.7×10^9 m^3 yr^{-1}) are used for direct and planned reuse [18]. Data also shows that the production of reclaimed water in underdeveloped or developing countries is still not widespread, including Latin American countries such as Brazil [18,21].

Several studies have shown that tertiary-level treatment of sanitary sewage is a promising source of reuse water [1,14,4,56]. Aside from the costs, the primary challenge in producing reuse water is determining the appropriate technology and microbiological parameters for the intended applications [20,33].

To produce reuse water, sewage treatment plants must disinfect their secondary effluent (SE) and chlorine is the most widely used disinfectant. Inorganic chlorine is mostly used, as chlorine gas (Cl_2), chlorine dioxide (ClO_2), sodium hypochlorite (NaClO), hypochlorous acid (HClO) and calcium hypochlorite ($Ca(ClO)_2$) [19,35].

The search for cheaper and ready-to-use disinfectants has led to the use of onsite sodium hypochlorite generators, in which NaCl is converted into NaClO by electrochemical reactions. When dissolved in water, sodium hypochlorite (NaClO) dissociates into sodium ions (Na^+) and hypochlorite ions (OCl^-), which react with water to form hypochlorous acid (HOCl), the main disinfectant agent. NaClO and NaClO-e share the same mechanism of action. Commercial NaClO solutions are produced industrially by reacting chlorine gas with NaOH, and they frequently contain additives such as NaOH for stability, as well as impurities such as chlorates and perchlorates. It is useful for centralized large-scale applications where bulk supply is feasible. However, it necessitates controlled bulk transport and storage, which may be impractical in remote or poor areas. On the other hand, NaClO-e is produced on-site through brine electrolysis and is typically purer, with no stabilizer, because it is used on-demand, reducing storage requirements and time degradation. One disadvantage is the need for electricity, which may be problematic in remote areas but can be overcome with photovoltaic stations. Both hypochlorites are equally effective, but commercial solutions may lose action due to light, heat or metal degradation if stored for an extended period of time [22,32].

Parra et al. [28] successfully studied a prototype with local generation of a sodium hypochlorite disinfectant solution, through NaCl electrolysis, with the aim of serving inhabitants of rural regions that are difficult to access. Studies have emerged evaluating the use of alternative oxidants and disinfectants, such as potassium permanganate, ozone, peroxone and ultraviolet radiation [29,46].

Chlorinated cyanurates, commonly referred to as dichlor (anhydrous sodium dichloroisocyanurate or sodium dichloroisocyanurate dihydrate, NaDCC) and trichlor (trichloroisocyanuric acid, TCCA) have emerged as organic-based alternatives for water disinfection [50]. NaDCC contains 45–65 % chlorine, is highly soluble in water (24–28 g/100 mL), and has a pH of 6 – 7 (1 % aqueous solution at 25°C). TCCA has a higher chlorine content (90 %), is slightly soluble in water (1.2 g/100 mL), and a pH of 2.7 – 2.9.

TCCA and NaDCC are recommended by the National Health Surveillance Agency [Brazil, 1999] for use as an active ingredient in products intended for disinfecting water for human consumption and swimming pools, as well as in the food industry in the processes of disinfecting cooling water, surfaces, pipes, equipment, floors and walls [31]. They have been used by governmental and non-governmental organizations in various underdeveloped and developing countries as an emergency sanitary action for disinfecting water intended for human consumption, especially in communities with a proliferation of waterborne diseases affected by environmental disasters, wars and situations of scarcity [51,6]. The advantages of using TCCA and NaDCC include their lower cost, long-lasting effectiveness in inactivating microorganisms, possibility of use in powder, sticks and tablets and greater stability in the storage process. Patil et al. [30] reported that low-cost portable point-of-use systems with TCCA have been successfully used to decontaminate drinking water, achieving a reduction in coliform bacteria of 2–4 log10.

Whatever disinfectant is chosen, it must be guaranteed that it is effective in inactivating bacteria, viruses and protozoa, among other pathogenic organisms, and that it does not produce any secondary compounds that cause a risk to human health. Chlorine can react with naturally occurring materials in water, resulting in over 700 types of disinfection byproducts (DBP), which are particularly harmful and linked to toxicity and carcinogenicity [11,17,25,38]. DBP in drinking water can enter the human body via ingestion, inhalation, or dermal contact, raising serious public health concerns [38,51].

The formation of DBP in water is influenced by the type of precursor, typically natural organic matter, algae or sanitary excrement, the type and dosage of disinfectant used, contact time, pH, temperature and the presence of bromides [40,39,52,9]. Therefore, when treated sewage is subjected to the chlorine disinfection, the concentration of organic matter present will act as a precursor for the DBP formation, which will be harmful to the health of those who handle it in a future direct non-potable reuse [27].

NaDCC and TCCA are well-known for treating drinking water, but their interaction with organic matter in SE that could yield DBPs in prohibitive levels for reuse is still unclear. Oliveira et al. [26] reported that NaDCC and TCCA are approved by the U.S. Environmental Protection Agency for drinking water disinfection, but they are not being used as routine water treatment, and in Europe, the European Chemicals Agency (ECHA) is reviewing their use for disinfection due to a lack of information on their mode of action.

In this context, the current project supports the UN 2030 Agenda's Sustainable Development Goal (SDG) 6.3, which aims to improve water quality by reducing untreated wastewater and promoting safe reuse. Brazil aims to increase reclaimed water for nonpotable applications from nearly 2 m^3 s^{-1} in 2017–13 m^3 s^{-1} by 2030 [5]. Brazil would then lead the world in water reuse with 4 %. The potential for reusing sanitary effluent in Brazil is estimated at 10–15 $m^3 s^{-1}$ in the next 5–10 years, based on current installed capacity (3419 active sewage treatment plants in 1893 municipalities) [41]. Over time, it is projected to reach 175 $m^3 s^{-1}$, a crucial figure for boosting the country's supply sources. To achieve that, it is crucial to determine how chlorinated cyanurates NaDCC and TCCA affect secondary effluent disinfection compared to conventional products, such as sodium hypochlorite.

2. Material and methods

The flowchart in Fig. 1 summarizes the experimental design and key steps in the present study.

2.1. Wastewater sampling and characterization

The study was carried out at a wastewater treatment plant (WWTP) located in the municipality of Ribeirão Preto, in the state of São Paulo – Brazil (Fig. 2). The plant treats 18,000 $m^3 d^{-1}$ of domestic sewage from about 15 % (120,000 people) of the city's population. The WWTP receives domestic sewage which is sent for pre-treatment, consisting of grids to remove coarse solids, a sand removal box and an oil and grease separator. Subsequently, the pre-treated effluent is sent to secondary treatment, consisting of an activated sludge biological reactor of the prolonged aeration type, which degrades around 95 % of the organic load, and on to the secondary decanter, where part of the biological sludge returns to the reactor and part is dewatered, densified, digested and sent for appropriate disposal. The clarified stream from the decanter (known as secondary effluent, or SE) is discharged directly into the Pardo River near the WWTP. As a precaution, an emergency chlorination chamber is available in case the SE needs to be disinfected before being discharged into the river. The primary goal of this project is to develop viable solutions for producing safe reuse water using the SE available at the plant. The chosen SE for the study is the actual effluent discharged, and the chlorine-based disinfectant used in this case is of great concern, both in terms of economic feasibility and the quality of the resulting parameters.

Samples of secondary effluent were collected every month for a period of one year in the WWTP, immediately after the secondary decanter (Fig. 2), in order to determine its characteristics. The samples were stored and analyzed according to the Standard Methods for the Examination of Water and Wastewater [7]. The analytical parameters evaluated were: UV-254 nm absorbance, ammonium, dissolved organic carbon (DOC), total organic carbon (TOC), thermotolerant coliforms (TC), 5-day biochemical oxygen demand at 20°C (BOD_5), pH, solids series and turbidity. UV absorbance at 254 nm was determined using a Cary 1E UV–vis spectrophotometer (*Varian, Australia*) and the specific absorbance coefficient $SUVA_{254}$ was calculated as the quotient of absorbance measured at a wavelength of 254 nm, and the product of

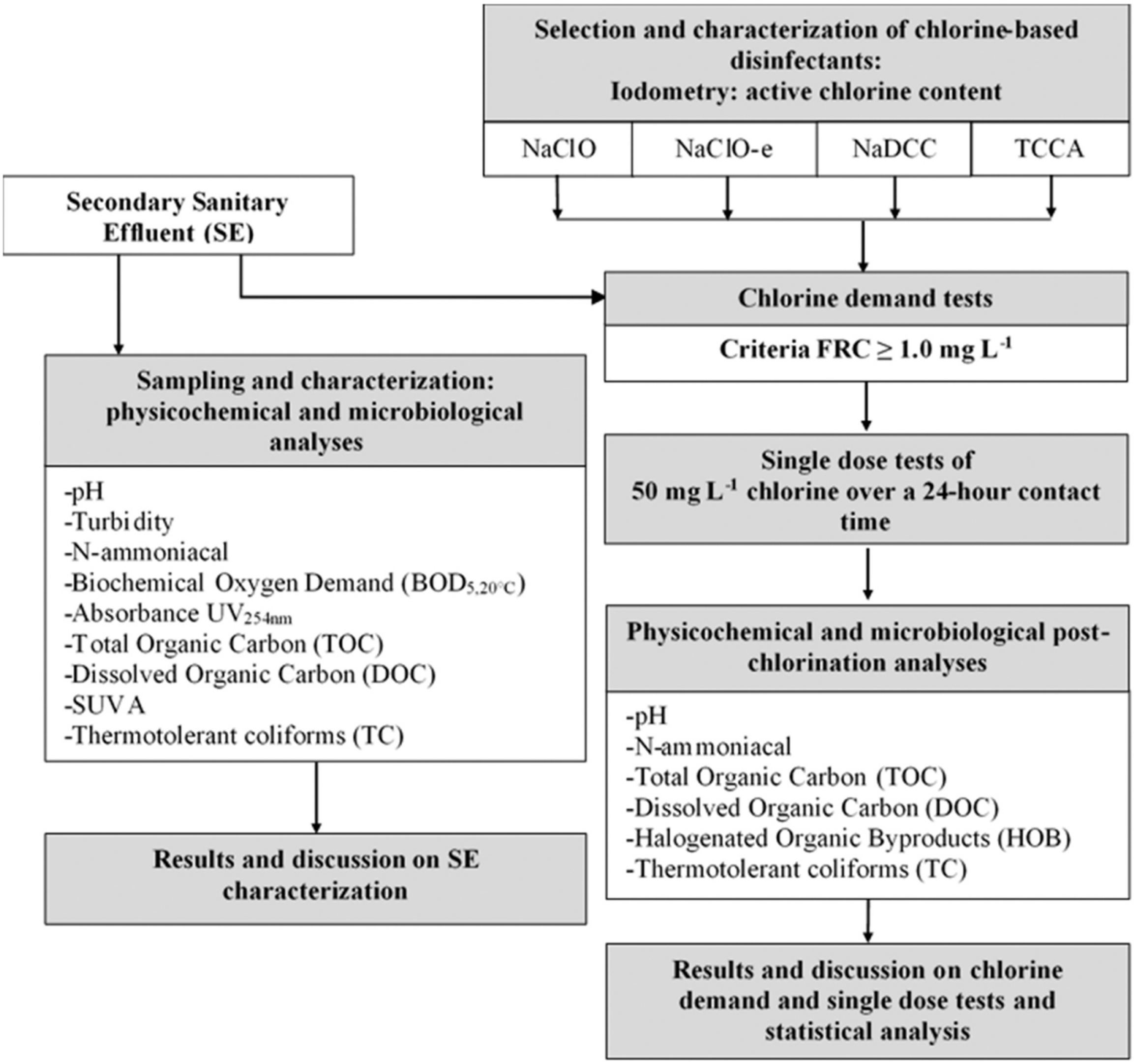

Fig. 1. Flowchart of the research using secondary effluent from the WWTP intended for direct, uncontaminated use.

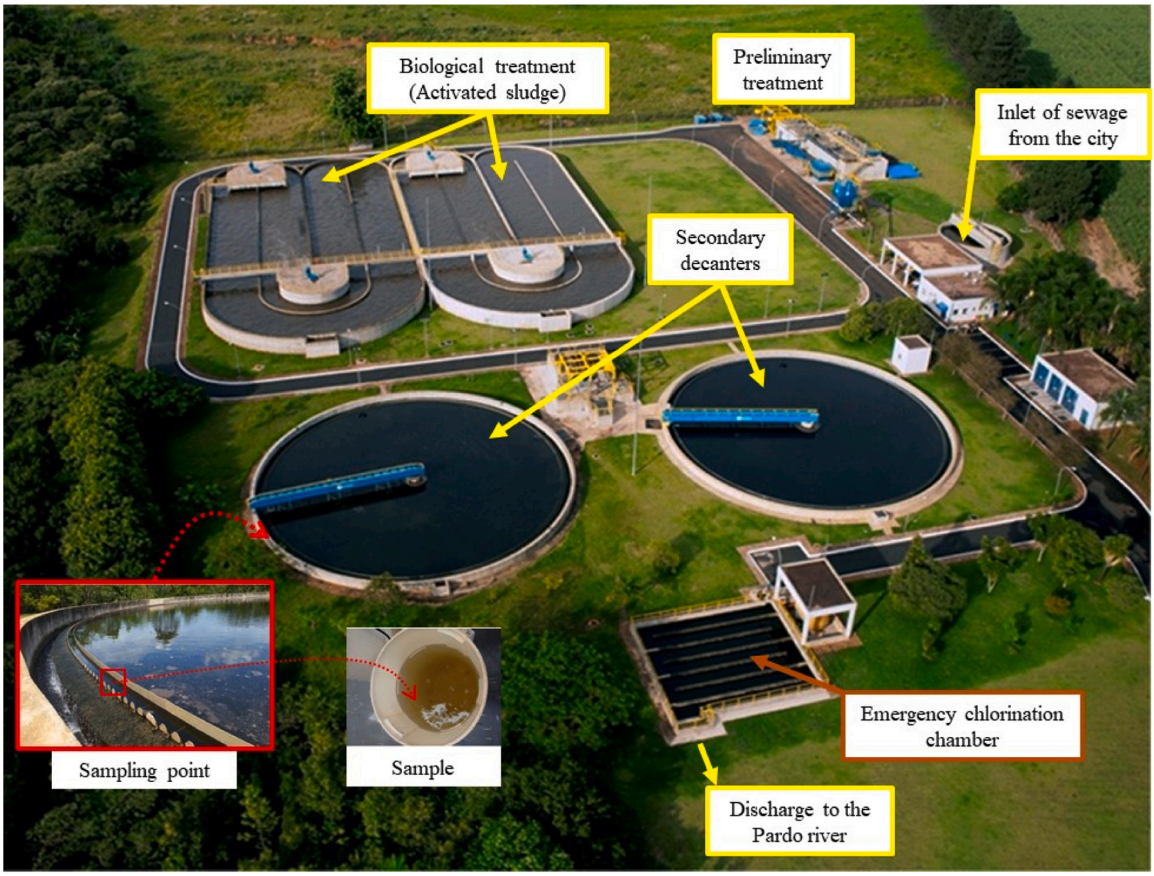

Fig. 2. Municipal Sewage Treatment Plant (STP) and location of the sampling point of secondary effluent for the disinfection tests.

TOC concentration and the optical path of the quartz cuvette [24]. Both DOC and TOC were measured by non-dispersive infrared combustion on a TOC-L Total Carbon Analyzer (*Shimadzu Corporation, Kyoto, Japan*) (LoQ 0.5 mg L^{-1}). Total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) were measured by gravimetric method on an analytical balance (*Sartorius model DL 210 S, Goettingen, Germany*). Turbidity was measured using a 2100 P turbidimeter (*Hach Corporation, Ames, IW, USA*) (LoQ = 0.1 NTU). To quantify DOC and TDS, it was necessary to eliminate interference from suspended solids by filtering through filter paper with a pore size of 0.45 µm. Ammonia was measured using distillation and Nessler's reagent and read using a DR 3900 HACH spectrophotometer (Loveland, USA). Thermotolerant coliforms (TC) were quantified using the filter membrane technique (LoQ = 1 CFU 100 mL^{-1}). BOD_5 was determined using the potentiometric method in a Digimed DM4 oximeter (*Digimed, São Paulo, SP, Brazil*) and 347-G incubator (*FANEM, Guarulhos, SP, Brazil*) at 20 °C (LoQ = 1 mg O_2 L^{-1}). A bench pH meter (*Orion model 230, Beverly, USA*) (LoQ = 0.01) was used to determine pH.

2.2. Tested disinfectants

In this work, inorganic and organic chlorinated disinfectants were tested. The features are described in Table 1.

The commercial sodium hypochlorite solution (NaClO) was acquired in the local market with a concentration of 2.0 % w/v. An onsite electrochlorination system (*HG 1000 model, Hidrogeron, Brazil*) was used to generate the sodium hypochlorite solution by electrolysis (NaClO-e) with a concentration of 4 %w/v from a 0.75 % brine solution. The NaDCC (*Clim 45, Hidrodomi, Brazil*) and TCCA (*Clim 90, Hidrodomi, Brazil*) were acquired as powder tablets in the local market with nominal active chlorine contents of 45 and 90 %w/w, respectively.

Table 1
Chlorinated disinfectants evaluated in this work and their features.

Disinfectant	Formula	CAS	Molar mass (g mol^{-1})	Nominal active chlorine content*
Sodium hypochlorite – solution (NaClO)	NaClO	7681–52–9	74.44	2 %w/v
Sodium hypochlorite - electrolysis generated (NaClO-e)	NaClO	7681–52–9	74.44	4 %w/v
Sodium dichloroisocyanurate (NaDCC)	$C_3N_3O_3Cl_2Na$	2893–78–9	219.95	45 %w/w
Trichloroisocyanuric acid (TCCA)	$C_3Cl_3N_3O_3$	87–90–1	232.41	90 %w/w

[*] Compared to chlorine gas (Cl_2), considered 100 % active. One mole of Cl_2 is equivalent to 71 g of active chlorine.

The expected reactions of NaClO, NaDCC and TCCA in water to release free available chlorine in the form of hypochlorous acid (HOCl) are [10]:

$$NaClO + H_2O \rightarrow HClO + NaOH \tag{1}$$

$$NaCl_2(NCO)_3 + 2H_2O \leftrightarrow 2HClO + NaH_2(NCO)_3 \tag{2}$$

$$C_3Cl_3N_3O_3 + 3H_2O \leftrightarrow 3HClO + C_3H_3N_3O_3 \tag{3}$$

Aqueous solutions of the four disinfectants were prepared to quantify the active chlorine content using the iodometry methodology [49]. 20 mL of the diluted solution was reacted with approximately 2 g of potassium iodide (KI), which acted as a reducing agent, and 3 mL of acetic acid (CH_3COOH). The reaction was maintained for 6 min in the absence of light, and then 5 mL of starch indicator solution (1 %w/v) was added. The resulting solution was titrated with a standardized solution of 0.1 N sodium thiosulfate purity ($Na_2S_2O_3$) until the solution was colorless. Eq. (4) was used to calculate the active chlorine content.

$$\text{Active chlorine}(\%\text{w/v}) = \left[\left(\frac{\text{V}}{1000}\right) \quad \frac{\text{N f MM}}{\text{V}_{\text{sample}}}\right] \times 1000 \qquad (4)$$

where: V is the volume spent in the titration with sodium thiosulfate (mL); N is the normality of sodium thiosulfate (0.1 N); f is the correction factor for 0.1 N sodium thiosulfate; MM is the molar mass of chlorine (35.45 g mol^{-1}); V_{sample} is the volume of sample used (mL).

2.3. Chlorine demand

There are various methods of chlorination in water and wastewater treatment plants, which in practice must be examined in order to adopt the most advantageous solution from a technical and economic point of view. The quality of the water and the safety that must be ensured are predominant factors in this selection. Other factors are smell and taste problems and the time available for contact with the disinfectant. Depending on the method used, more or less chlorine can be used and a longer or shorter contact time should be required, as well as avoiding the formation of undesirable chlorine compounds. The most common methods according to the increasing order of quantity and safety required are: simple or plain chlorination (the most common process), pre- and post-chlorination, chlorination to the breaking point, super-chlorination, ammonium-chlorination, chlorination with chlorine dioxide [43].

The breakpoint chlorination is a safer process, applicable to very polluted waters and therefore requiring much higher doses of chlorine. Free and more stable residuals are produced after total oxidation of ammonia, chloramines and other compounds. The determination of chlorine demand was based on the breakpoint chlorination method (BM), used in effluents that contain ammoniacal nitrogen and form combined chlorine, when the concentration of residual chlorine reaches its threshold (breakpoint), the ammoniacal nitrogen is eliminated and the necessary dosage is established [55].

In this work, the chlorine demand tests were carried out for each disinfectant in amber bottles with a capacity of 1 L, filled with secondary effluent and 2 mL of phosphate buffer solution, to obtain and maintain a pH of 7.0. Fifteen bottles were used with increasing dosages of equivalent chlorine, ranging from 0 to 80 mg Cl_2 L^{-1}. After the initial moment of contact between the disinfectant and the effluent, the bottles were closed, homogenized for 60 s and left to stand at a temperature of 25 ± 2°C for 30 min. The bottles were then opened and the samples filtered through qualitative paper to eliminate the interference of suspended particles. The filtered solution was quantified for free residual chlorine (FRC) using a DR 3900 HACH spectrophotometer (*Loveland, USA*) with the addition of the reagent N,N-Diethyl-p-Phenylenediamine (*DPD, Cat. 2105528-BR, HACH, USA*) and the demand was calculated by the difference between the chlorine dosage (mg Cl_2 L^{-1}) and the measured FRC (mg Cl_2 L^{-1}), with a FRC of 1 mg Cl_2 L^{-1} being required for reuse water [47].

2.4. Tests to evaluate the formation of disinfection byproducts

Once the chlorine dosage had been selected from the previous stage, the tests were carried out in triplicate using amber glass bottles with a capacity of 1 L for each chlorinated disinfectant. The bottles were filled with the secondary effluent from the municipal WWTP, applied at the pre-determined dosage in the demand tests, and 2 mL of phosphate buffer solution. The bottles were then closed, shaken for a few seconds to homogenize and left to stand at 25 ± 2°C for 24 h. This contact time between the effluent and the chlorinated disinfectants was adapted from the recommendations of Baird et al. [7] for testing the potential DBP formation in water intended for public supply. It represents the average time between treatment and effluent use. Following this, the dissolved and total organic carbon, free residual chlorine (FRC), pH, and DBPs were determined.

2.5. Quantification of disinfection byproducts

An aliquot of 100 mL of each sample was dechlorinated with ascorbic acid (*CAS 134–03-02, Sigma-Aldrich*) for liquid-liquid extraction and quantification of DBPs by gas chromatography with electron capture detector (*GC-ECD, Varian, 3600CX, USA*). For the liquid-liquid extraction, 10 mL of the dechlorinated sample and 10 mL of methyl tert-butyl ether (*MTBE, CAS 1634–04-4, J.T. Baker, USA*) were added to a flask and homogenized for 60 min at 100 rpm. After this period, the phases were separated at −4°C for 30 min, 1 μL of which was injected into the GC-ECD for the quantification of DBPs.

GC-ECD was used to quantify the disinfection byproducts. The analytical technique was adapted from method 551.1 [29,45]. The operating conditions were: J&W-DB-1 column, 30 m x 0.32 mm ID and 5 μm film; nitrogen 5.0 ECD with a flow rate of 3.6 mL min^{-1}, 74 cm s^{-1} and a pressure of 15 psi (1.071 atm); injector temperature at 160°C and detector temperature at 290°C; initial temperature of 40°C for 1 min, heating to 125°C at a rate of 5°C min^{-1} and remaining at 125°C for 2 min, heating to 180°C at a rate of 20°C min^{-1} and remaining at 180°C for 10 min; sample split flow of 2 mL min^{-1} and sensitivity of 10; total time of 15 min; volume of 1 μL of extract injected into the GC-ECD. Twelve DBP compounds divided in 5 classes were determined using this method as described in Table 2.

To obtain the calibration curve, chromatographic grade dichloromethane (*J.T. Baker, USA*) was used as the Internal Standard (IS), and the following standards were used for calibration: trihalomethanes mix (*Supelco, 48140-U*); pure chloral hydrate standard (*Supelco, 47335-U*), halogenated volatiles mix 551B (*Supelco, EPA 551 B*), haloacetonitriles, chloropicrin and haloacetones (*Supelco, 48046*).

Preliminarily, a dilution was prepared with a mixture of the standards in acetone medium (*99.9 %, J.T. Baker, USA*) and then a further dilution was made in aqueous medium (purified water, Milli-Q) in 10 mL volumetric flasks, fortified with 10 μL of internal standard. The concentration range of the mixed standard solutions was calculated to result in concentrations in the range of 10–140 μg L^{-1}. Next, a liquid-liquid extraction (LLE) step was carried out, starting with the fortification of 10 μL of internal standard, dichloromethane 1 %v/v dissolved in acetone, over the 10 mL of mixed standard solution for each concentration range. Subsequently, a volume of 10 mL of 99.99 % pure methyl-tert-butyl-ether (MTBE) solvent, HPLC grade (*J.T. Baker, USA*) at 4°C was added for extraction, followed by stirring at 100 rpm for 60 min and settling at −4°C for 30 min to separate the phases. The retention time of the analytes, the concentration range for GC-DCE calibration, the linear regression coefficient (r^2) and the limits of quantification (LoQ) of the analytes are shown in Table S1.

A typical chromatogram obtained after analyzing a mixture of standards for a calibration point is shown in Figure S1. It reveals the stability in the baseline, correct separation and identification of the internal standard and the analytes of interest with clearly defined areas.

2.6. Statistical analyses

For the statistical data analysis, the Shapiro-Wilk test was first used to assess whether the data sets followed a normal distribution. Values greater than 5 % significance ($p > 0.05$) indicate normal distribution and values of $p < 0.05$ indicate non-normal distribution. Boxplots were used to visualize the distribution of the data and verify the results. The Analysis of Variance (ANOVA) test was used to obtain significant differences ($p < 0.05$) in normally distributed samples. The statistical analyses were carried out using the Origin 8.5® software.

Table 2
DBP classes and compounds investigated in this work.

Classes	Compound	Symbol	Formula	CAS
Trihalomethane (THM)	Chloroform	CF	CH_3Cl	67–66–3
	Bromodichloromethane	BDCM	$CHBrCl_2$	75–27–4
	Dibromochloromethane	DBCM	$CHBr_2Cl$	124–48–1
	Bromoform	BF	CH_3Br	75–25–2
Haloaldehyde (HAD)	Chloral hydrate	CH	$C_2H_3Cl_3O_2$	302–17–0
Halopicrins (HP)	Chloropicrin	CP	CCl_3NO_2	76–06–2
Haloacetonitriles (HAN)	Dichloroacetonitrile	DCAN	C_2HCl_2N	3018–12–0
	Trichloroacetonitrile	TCAN	C_2Cl_3N	545–06–2
	Dibromoacetonitrile	DBAN	C_2HBr_2N	3252–43–5
	Bromochloroacetonitrile	BCAN	$C_2HBrClN$	83463–62–1
Haloketones (HK)	1,1-Dichloro−2-propanone	1,1-DCP	$C_3H_4Cl_2O$	513–88–2
	1,1,1-Trichloropropanone	1,1,1-TCP	$C_3H_3Cl_3O$	918–00–3

3. Results and discussion

3.1. Determination of the active chlorine content in the commercial disinfectants

The manufacturers of the disinfectants under study provided information on the active chlorine content on the product's label. In the case of NaClO-e, the manufacturer indicates the active chlorine content that can be achieved if the solution is prepared according to the recommendations. Nonetheless, the active chlorine content of each solution was experimentally determined to ensure accuracy when calculating the experimental dosages. Table 3 shows the results for the four disinfectants tested. The solutions' active chlorine contents were close to the nominal values, with the organic products (NaDCC and TCCA) showing greater deviation, possibly due to the inhomogeneous solid granular form. The subsequent tests were based on the experimental results.

3.2. Determination of chlorine demand for secondary effluent disinfection

The chlorine dosage required to obtain a FRC of 1 mg Cl_2 L^{-1} in the secondary effluent was experimentally investigated for the four chlorinated disinfectants. Fig. 3 shows the chlorination curves, with the FRC as a function of the chlorine dosage. Due to the presence of reducing substances (such as aromatic compounds, molecules with carbon and/or nitrogen, iron, manganese and hydrogen sulfide), there is competition for the consumption of chlorine added by secondary reactions without the exclusive purpose of disinfection, implying the formation of combined chlorine. The breakpoint is the chlorine dosage for which ammonia and other oxidizable compounds present in the SE are fully oxidized. The breakpoint dosages are graphically highlighted in Fig. 3 for each tested disinfectant. It is worth noting that the reported chlorine dosage applied for disinfecting secondary activated sludge effluent is between 1.5 and 8 mg Cl_2 L^{-1} and contact times from 15 to 60 min [19].

In order to meet reuse standards, the dosage selection criterion adopted in this work was to carry out a breakpoint demand test to eliminate combined chlorine and obtain a minimum free residual chlorine (FRC) of 1.0 mg Cl_2 L^{-1} [47]. The breakpoint values observed in Fig. 3 for the NaClO, NaClO-e, NaDCC and TCCA in a contact time of 30 min were, respectively, 47.9, 53.8, 55.8 and 53.0 mg Cl_2 L^{-1}. Based on these results, a fixed dosage of 50 mg Cl_2 L^{-1} was adopted in subsequent tests to assess the formation of DBPs. Fig. 3 also reveals that a false residual chlorine of 1 mg L^{-1} was reached with active chlorine dosages of 10 – 12 mg Cl_2 L^{-1}, which is within the reported range [19], but not sufficient for complete oxidation of combined chlorine.

Table 3
Nominal and experimental active chlorine content of the tested disinfectants.

Active chlorine content	NaClO (% w/v)	NaClO-e (% w/v)	NaDCC (% w/w)	TCCA (% w/w)
Manufacturer's label	2.0–2.5	4.0	45	90
Experimental	2.41 ± 0.33	4.32 ± 0.52	44.35 ± 2.42	89.15 ± 8.8

3.3. Characterization of the secondary effluent

The characterization of the secondary effluent is critical for determining the quality of reuse water, especially when using complementary disinfection treatments. Table 4 displays the results of the parameters analyzed, as well as the reference value (RV) for reuse water, in accordance with the United States Environmental Protection Agency's Guidelines for Water Reuse [47]. It is worth noting that the most restrictive values from the guide's recommended conditions were used for comparison.

The $SUVA_{254}$ coefficient is recognized as a good indicator of the abundance and nature of humic substances since it represents electron-rich sites (e.g. aromatic moieties) and double-bonded carbon groups in humic macromolecules [24]. $SUVA_{254} < 2$ L mg^{-1} m^{-1} indicates high hydrophilic non-humic matter, low chlorine demand, and THM formation potential. Values of 2 – 4 L mg^{-1} m^{-1} indicate hydrophobic humic and hydrophilic non-humic matter, higher chlorine demand, and THM formation potential. $SUVA_{254}$ above 4.0 indicates highly aromatic hydrophobic humic matter with high UV absorbance, chlorine demand, and THM formation potential. In general $SUVA_{254}$ monitoring results for treated water prior to disinfection should generally not exceed 2.0 L mg^{-1} m^{-1} [16,48]. The SUVA values in the raw effluent in this work were 2.19 ± 0.16 L mg^{-1} m^{-1}, which strengthens its potential to act as a precursor of disinfection byproducts. The high coliform values in SE (on average 1000 CFU 100 mL^{-1}) highlight the need for a complementary inactivation technology that allows for non-potable reuses. The average BOD_5 value obtained was 11 mg L^{-1}, which is higher than the United States Environmental Protection Agency USEPA [47] limit for reclaimed water for the most restrictive uses. The average turbidity value was 4.55 NTU, which is less than the predetermined limit of 2 NTU, indicating that it is unsuitable for direct reuse. The SE values for pH (7.67) and TSS (2 mg L^{-1}) are within the ranges of pH 6.0–9.0 and TSS < 30 mg L^{-1} [47]. During the sampling period (1 year), the WWTP's biological treatment technology was deemed satisfactory for discharge into the receiving body of water; however, the quality of the SE did not meet the more stringent reuse standards. The thermotolerant coliform (TC) is the primary parameter that highlights the need for a disinfection stage and/or complementary treatment to ensure that the secondary effluent from the WWTP is safe and sanitary for direct non-potable reuse [12,34]. Sharafi et al. [37] reported that NaDCC and NaOCl were both effective disinfectants for killing gram-negative bacteria at concentrations ranging from 0.01 to 0.4 mg L^{-1} and contact times ranging from 5 to 15 min. NaDCC had a slightly higher removal efficiency at lower concentrations, which was attributed to the slower release of free chlorine over time. The performance was statistically comparable, with 100 % removal at higher concentrations and contact times. In the current study, the chlorine content was higher, and all four disinfection agents met the United States Environmental Protection

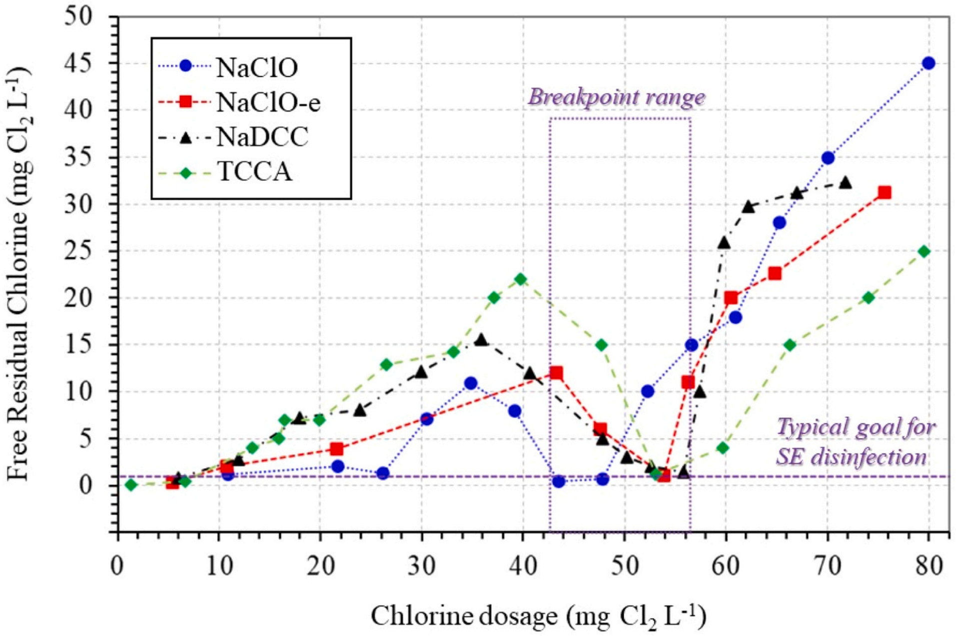

Fig. 3. Breakpoint curves for the four tested disinfectants using the WWTP's secondary effluent.

Table 4

Characterization of the (*raw*) secondary effluent (SE) from the WWTP and after disinfection tests with 50 mg Cl_2 L^{-1} of each disinfectant to achieve FRC of 1.0 mg Cl_2 L^{-1}.

Parameter	SE *raw*	SE + NaClO	SE + NaClO-e	SE + NaDCC	SE + TCCA	RV
pH	7.67 ± 0.11	7.49 ± 0.01	7.58 ± 0.02	7.11 ± 0.10	6.65 ± 0.04	6–9
NH_4^+ (mg N L^{-1})	2.21 ± 2	< 0.1	< 0.1	< 0.1	< 0.1	NE
BOD_5 (mg O_2 L^{-1})	11 ± 6	NA	NA	NA	NA	< 10
$SUVA_{254}$ (L mg^{-1} m^{-1})	2.19 ± 0.16	NA	NA	NA	NA	NA
TDS (mg L^{-1})	255 ± 2	NA	NA	NA	NA	NE
TSS (mg L^{-1})	2 ± 1	NA	NA	NA	NA	< 30
Turbidity (NTU)	4.55 ± 0.15	NA	NA	NA	NA	< 2
TC (UFC 100 mL^{-1})	1000 ± 100	none	none	none	none	none

RV: Reference values for reuse [47]. NE: Not established. NA: not applicable

Agency USEPA [47] minimum values for free residual chlorine (FRC) and thermotolerant coliforms (TC) for reuse, with FRC less than 1 mg Cl_2 L^{-1} and no coliforms in 100 mL of sample.

It is worth noting that a volume of phosphate buffer solution was added to the secondary effluent to reduce the impact of pH on DBP formation. NaClO and NaClO-e showed a slight increase in pH. NaDCC maintained the pH value at around 7.0, while TCCA reduced the pH of the medium to 6.65, indicating that the volume of buffer solution was insufficient, but the pH value variation was not significant in terms of reuse parameters (6.0–9.0).

Fig. 4 displays the DOC and TOC levels in the secondary effluent before and after disinfection. Although not explicitly stated in legislation for reuse, these parameters are critical for quantifying organic matter in water as a precursor to the formation of DBPs [2]. TOC is a commonly used indicator for assessing water quality, representing the total carbon content of organic substances in solution [3], while DOC represents the fraction of dissolved carbon after filtration through a 0.45 μm mesh [53].

The secondary effluent had average DOC (4.32 mg C L^{-1}) and TOC (4.58 mg C L^{-1}) values that were consistent with those reported in the literature [13,36]. The NaClO and NaClO-e showed a slight increase in carbon concentration after single dosage tests. Statistical analysis ($p < 0.05$) revealed minor changes in TOC (6.66 and 7.36 mg C L^{-1}). Although NaClO molecules do not contain carbon, commercial sodium hypochlorite solutions may contain impurities such as carbonates. Nonetheless, the most likely reason for the increase in TOC and DOC in NaClO-treated samples is bacterial cell lysis or partial solubilization of organic compounds present in the TSS, resulting in the release of humic acid-like and protein-like substances, as consistently reported by Cai et al. [8].

NaDCC and TCCA showed significant changes ($p < 0.00001$) in TOC levels (20.29 and 18.17 mg C L^{-1}, respectively). This is due to the chemical compositions of NaDCC and TCCA, which contain 16.36 and 15.48 % carbon by mass, respectively.

3.4. Formation of disinfection byproducts (DBPs)

Table 5 shows the results obtained for the formation of DBPs for each disinfectant under study.

In the THM class, chloroform (CF) was formed with the use of all disinfectants, with a greater predominance in organic disinfectants (635.22 μg L^{-1} for NaDCC and 440.05 μg L^{-1} for TCCA). Only NaDCC and TCCA produced bromodichloromethane (BDCM) (53.60 μg L^{-1} and 33.89 μg L^{-1}, respectively). It is important to note that the presence of brominated byproducts must be linked to the presence of bromine in the SE, which was not directly measured during effluent characterization in this work due to methodological constraints. However, studies have widely reported the presence of bromide and bromine species in wastewater in ranges from μg L^{-1} to mg L^{-1}, which is mostly related to industrial contamination [42,54,57].

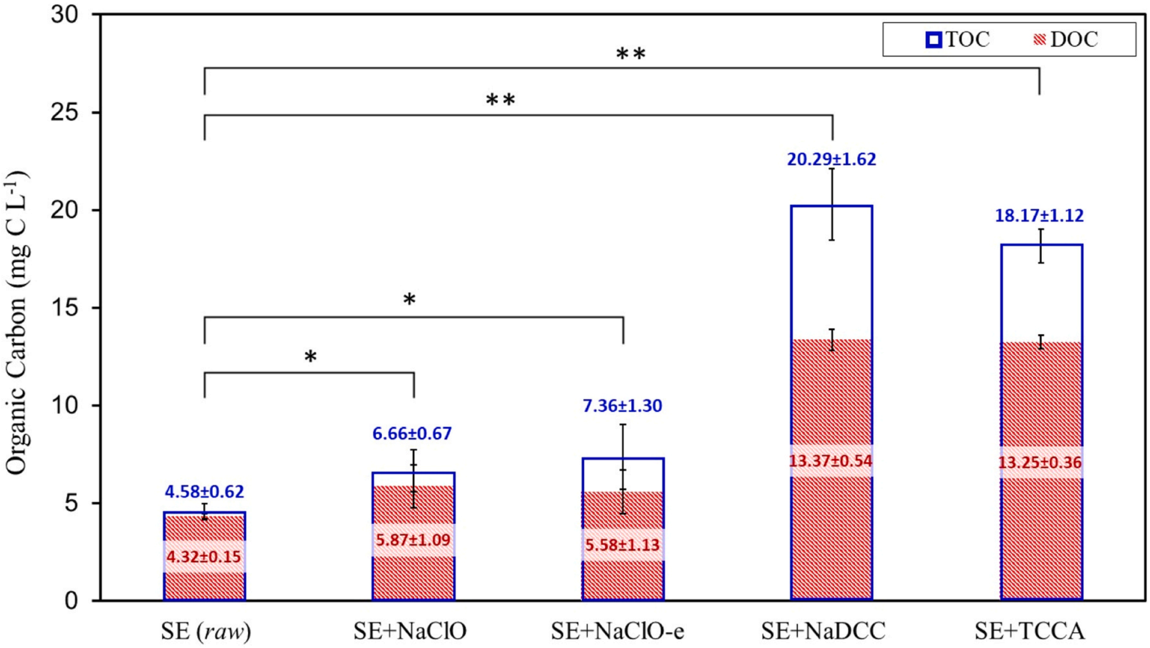

Fig. 4. Concentration of TOC and DOC before and after the secondary effluent disinfection process with 50 mg Cl$_2$ L^{-1}. The total organic carbon dosage refers to the sum of dissolved organic carbon and suspended (non-dissolved) organic carbon. Asterisk represents statistically significant difference (* $p < 0.05$; ** $p < 0.001$).

Table 5
Formation of DBPs (n = 3) after dosing with 50 mg Cl$_2$ L^{-1} for the four disinfectants analyzed over a contact time of 24 h and pH = 7.0.

Class	DBP	EPA groups*	NaClO (µg L^{-1})	NaClO-e	NaDCC	TCCA
THM	CF	B2	102.63	126.93	635.22	440.05
	BDCM	B2	< 0.1	< 0.1	53.60	33.89
	DBCM	C	< 0.1	< 0.1	< 0.1	< 0.1
	BF	B2	< 0.1	< 0.1	< 0.1	< 0.1
HAD	CH	C	34.23	38.68	363.41	308.20
HP	CP	-	< 0.1	< 0.1	< 0.1	6.80
HAN	DCAN	C	24.89	33.15	161.75	189.21
	TCAN	-	1.64	1.14	< 0.1	< 0.1
	DBAN	C	< 0.1	< 0.1	< 0.1	< 0.1
	BCAN	-	< 0.1	< 0.1	< 0.1	< 0.1
HK	1,1-DCP	-	10.25	10.20	< 0.1	< 0.1
	1,1,1-TCP	-	2.66	2.53	89.02	142.22
Total DBPs			*175.41*	*212.63*	*1303.00*	*1120.37*

[*] Based on the U.S. EPA. 1986. Guidelines for Carcinogen Risk Assessment. Group B1: "Probable Human Carcinogen". There is limited evidence that it can cause cancer in humans, but at present it is not conclusive. Group B2: "Probable Human Carcinogen". There is inadequate evidence that it can cause cancer in humans but at present it is far from conclusive. Group C: "Possible Human Carcinogen". There is limited evidence that it can cause cancer in animals in the absence of human data, but at present it is not conclusive.

All four disinfectants produced chloral hydrate (CH), a compound from the haloaldehyde class (HAD). The occurrence was predominant with NaDCC (363.41 µg L^{-1}) and TCCA (308.20 µg L^{-1}). CH has been identified as a major DBP with the highest formation rate in drinking water, second only to THMs [29]. Chloropicrin (CP) was only formed when TCCA came into contact with the secondary effluent, with a result of 6.80 µg L^{-1}. CP is a strong irritant that is toxic to all biological systems, interfering with respiratory function and cellular oxygen transport. It is a broad-spectrum fumigant used to control weeds, nematodes, insects, rodents, and soil-borne pathogens.

Dichloroacetonitrile (DCAN) was produced by all disinfectants, with NaDCC (161.75 µg L^{-1}) and TCCA (189.21 µg L^{-1}) forming the majority. Trichloroacetonitrile (TCAN) was formed in small quantities using sodium hypochlorite (NaClO). In the haloketone (HK) class, 1,1-dichloropropanone was found in small amounts and only with NaClO (10.25 µg L^{-1}) and NaClO-e (10.20 µg L^{-1}). In contrast, 1,1,1-trichloropropanone was detected with all four disinfectants, with NaDCC (89.02 µg L^{-1}) and TCCA (142.22 µg L^{-1}) yielding the highest levels.

The most abundant DBPs identified in disinfected SE were CF, CH, BDCM, and DCAN, all of which are on the EPA's list of potential or likely carcinogen. Ingestion is their primary exposure route, however CF and BDCM are more volatile and can be absorbed through inhalation, as well as skin absorption. The short-term side effects include dizziness, headache, fatigue, liver and kidney inflammation, sedation, sleepiness, stomach trouble, eye, skin, and respiratory irritation. Long-term exposure to these DBPs can cause liver and kidney damage, as well as mutagenic and carcinogenic effects.

Du et al. [15] published a review of the levels of 29 DBPs discovered in reclaimed water during chlorination. It is remarkable that Du et al. [15] reported much lower average levels for CF (64 mg L^{-1}, n = 93), BDCM (14.98 mg L^{-1}, n = 78), DCAN (8.89 mg L^{-1}, n = 95), and 1,1,1-TCP (9.86 mg L^{-1}, n = 85) than what was observed here. To our knowledge, no referred work in the review included NaDCC or TCCA as chlorinated agents for wastewater disinfection. Moreover, the author's review did not mention chloral hydrate, which was found here in concentrations as high as 363 mg L^{-1}.

Fig. 5 shows the results of the statistical analysis of the concentration of the DBPs grouped in the five classes for each disinfectant.

NaDCC and TCCA produced significantly higher levels of byproducts than all five DBP classes evaluated. It can be attributed to the slower chlorine release from these cyanuric agents, which allows for longer contact with dissolved organic matter, increasing halogenation reactions. On the contrary, NaOCl releases chlorine immediately and contains no stabilizing agents, resulting in faster consumption but shorter exposure times for organic matter, lowering the potential for DBP formation. Furthermore, the organic carbon in the NaDCC ($C_3N_3O_3Cl_2Na$) and TCCA ($C_3Cl_3N_3O_3$) molecules contributes to higher DOC and TOC values detected in the treated samples [50]. Peng et al. [31] reported an opposite effect of TCCA during the disinfection of swimming pool water, where the resulting DBP species were more concentrated when using conventional NaClO disinfectant when

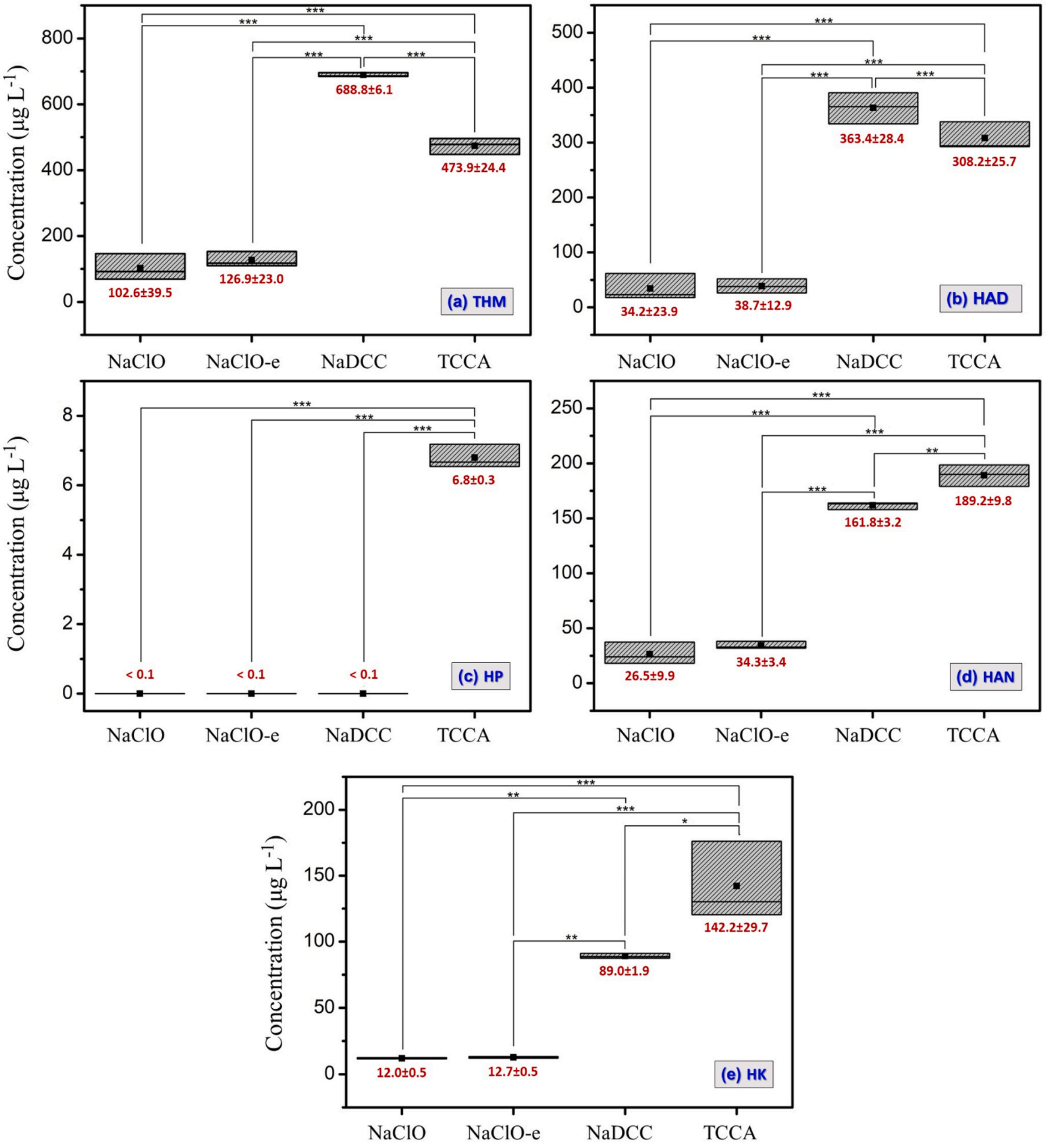

Fig. 5. Statistical representation of the concentration of DBPs classes formed with the contact with chlorinated disinfectants: (a) Trihalomethanes (THM); (b) Haloaldehydes (HAD; (c) Halopicrins; (d) Haloacetonitriles; (e) Haloketones. Asterisks represent a statistical significantly difference: *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

compared to TCCA. These authors, however, revealed that temperature exhibited the most significant impact on TCM formation, while pH played a major role in HAD formation. Moreover, chlorine dosage and contact time exhibited greater influence than precursor concentration on total DBPs. Fig. 5 shows that NaClO and NaClO-e performed similarly as expected given their similar action mechanisms.

3.5. Cost estimate for SE chlorine disinfection in the WWTP

The present study found that NaDCC and TCCA may produce toxic byproducts in higher levels than NaClO and NaClO-e when treating SE from a municipal WWTP. Given the primary goal of this project, which is to provide viable solutions for producing safe reuse water, it is instructive to compare the costs of the four chlorinated disinfectants based on the WWTP's actual scale. Currently, the plant produces 18,000 $m^3\,d^{-1}$ (750 $m^3\,h^{-1}$) of SE, which is fully discharged into the river. The municipal facility already has an emergency chlorination chamber, as shown in Fig. 2, which could be used on a regular basis to produce reclaimed water for landscape irrigation, dust and fire control, soil compaction, and street cleaning, among other nonpotable applications. Based on the findings, a fixed dosage of 50 mg $Cl_2\,L^{-1}$ was chosen. The commercial sodium hypochlorite solution was chosen with an active chlorine concentration of 120 g L^{-1} (12 %w/v) and costs US$1.00 per liter or US$8.33 per kg of NaClO. The estimated cost of producing sodium hypochlorite onsite (NaClO-e) included electricity consumption, salt cost, system efficiency, and operational costs, resulting in a total cost of US$1.00 per kg of NaClO, based on a 1 %w/v solution concentration. The costs for the organic disinfectants were estimated in the local market to be US$2.50 per kg of NaDCC 45 % and US$3.00 per kg of TCCA 90 % respectively. Table 6 displays the results.

Table 6 shows that the most cost-effective method for chlorinating SE in the municipal WWTP is onsite-generated hypochlorite (NaClO-e),

Table 6
Cost estimate for chlorine disinfection of 18,000 m^3 day^{-1} of secondary effluent from the WWTP.

Disinfectant	Unitary price	Dosage	Unitary cost	Daily costs
	(US$ kg^{-1})	(g Cl_2 m^{-3} effluent)	(US$ m^{-3})	(US$ day^{-1})
NaClO	8.33	50	0.42	7497.00
NaClO-e	1.00	50	0.05	900.00
NaDCC	2.50	50	0.28	5000.00
TCCA	3.00	50	0.17	3000.00

which costs US$0.05 per m^3. Onsite sodium hypochlorite has an advantage over NaDCC and TCCA as it does not add organic carbon to the effluent and does not produce high levels of CF, BDCM, CH, DCAN, and 1,1,1-TCP. The use of photovoltaic (PV) stations can help to meet the demand for electricity, which can be difficult in remote or off-grid locations [23]. While the initial investment in PV infrastructure and electrolytic equipment may be higher, utilizing free, renewable solar energy significantly reduces long-term operating costs. Furthermore, energy independence strengthens the resilience of NaClO generation, particularly in remote or off-grid areas where chlorinated cyanurates are still widely used for economic and logistical reasons. On the other hand, commercial NaClO solutions are still a viable option for centralized large-scale applications where bulk supply is feasible. However, they frequently contain additives for stability, as well as impurities such as chlorates and perchlorates. It also necessitates controlled bulk transport and storage, and light or heat degradation may occur if stored for an extended period of time.

A promising strategy that must be investigated is the combination of NaClO-e, UV and ozonation (O_3), as it may improve cost-efficiency, reduce harmful byproducts, and minimize environmental impact compared to traditional chlorine- or chloramine-based methods. The use of UV and ozonation has the obvious advantage of reducing the amount of chemicals used to treat wastewater, which is beneficial for logistics of transport and storage. Pretreatment with UV/O_3 breaks down organic matter, reducing chlorine demand and NaClO-e production costs. Lower chlorine levels also help to reduce pipe corrosion and halogenated byproducts. Another advantage is that the three techniques may rely on photovoltaic electricity rather than chemicals, expanding their viability for use in remote areas.

4. Conclusions

Chlorinated cyanurates NaDCC and TCCA have been widely used to disinfect drinking water for human consumption and recreation, but information on their use and effects on secondary effluent disinfection for nonpotable reuse applications is still limited. This study found that using NaDCC and TCCA to chlorinate to the breakpoint resulted in high concentrations of DPBs, including chloroform (635.2 μg L^{-1} and 440.1 μg L^{-1}), bromodichloromethane (53.6 μg L^{-1} and 33.9 μg L^{-1}), chloral hydrate (363.4 μg L^{-1} and 308.2 μg L^{-1}), and 1,1,1-trichloropropanone (89.0 μg L^{-1} and 142.2 μg L^{-1}). The majority of these compounds are on the EPA's list of possible or probable carcinogens. The values are significantly higher than those produced by NaClO in solution or electrolysis, as well as the average values reported in the literature. As a result, the use of these cyanurates is not recommended for the treatment of secondary effluents with high organic matter levels, such as those from the municipal WWTP being studied. Our findings indicate that NaClO-e is beneficial for disinfecting secondary effluent and producing reclaimed water. NaClO-e, a simple and safe disinfectant produced at the treatment site, does not add organic carbon content in the medium or produce high levels of DBPs, unlike chlorinated cyanurates. If the chlorinated cyanurates NaDCC and TCCA are used for economic and logistical reasons, DBP formation should be monitored and controlled more closely. Reuse strategies involving these agents must raise safety concerns about long-term exposure risks to humans, crops, and ecosystems, as well as propose a balance between disinfection and chemical risk reduction. Further research is needed to determine the formation of DBP in reclamation water as a result of using NaDCC and TCCA in secondary effluents with varying organic loads.

CRediT authorship contribution statement

Cristina Filomêna Pereira Rosa Paschoalato: Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Angela Di Bernardo Dantas:** Validation, Conceptualization. **Murilo Daniel de Mello Innocentini:** Writing – review & editing, Project administration, Funding acquisition. **Marília Vanconcellos Agnesini:** Writing – original draft, Validation. **Guilherme Sgobbi Zagui:** Writing – review & editing, Formal analysis, Data curation. **Talita Rafaella da Silva Boldrin Dias:** Visualization, Investigation, Formal analysis, Data curation. **Márcia Maísa de Freitas Afonso:** Investigation, Formal analysis.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.117165.

Data availability

Data will be made available on request.

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