OCCURRENCE OF TRIHALOMETHANES AND MULTIPLE PATHWAY HEALTH RISK EVALUATION IN DRINKING WATER IN MOROCCO

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Abstract. The objective of this study was to determine the concentrations of trihalomethane species in Morocco's drinking water and to assess their carcinogenic risk and non-cancer hazard index for human health via oral ingestion, dermal absorption, and inhalation. Two water sources were studied, surface water and groundwater. Sampling sites were selected along the water source to the consumer tap, via the treatment plant and the drinking water storage reservoir. Surface water has a higher trihalomethane formation potential than groundwater. Trihalomethane-total concentrations were 0 µg/L (Raw water), 24.11 µg/L (Filtered water), 24.82 µg/L (Disinfected water), 29.98 µg/L (Reservoir), 31.69 µg/L (Tap water). The average percentage contribution of each THM species chloroform, bromodichloromethane, dibromochloromethane, and bromoform were 42%, 34%, 24%, 0%, respectively. The found concentrations were well below the maximum allowable value in WHO guideline. The lifetime risk of non-cancer diseases studied was lower than the (USEPA) guideline of 1. The lifetime cancer risk linked to trihalomethanes in drinking water sourced from surface supplies exceeded the 'negligible risk' threshold established by USEPA. According to the cancer risk study, inhalation presented the highest risk (90%), with chloroform having a significant impact. Furthermore, both the oral and dermal routes of exposure to bromodichloromethane and dibromochloromethane present an increased cancer risk.

Keywords: *disinfection by-products, cancer risk, Hazard index, exposure route*

Introduction

Drinking water carries viruses, bacteria, parasites, plant and animal microorganisms that can cause serious waterborne diseases such as cholera, typhoid, amoebiases, gastroenteritis (Masschelein, 1996; WHO, 2017). Fortunately, through a combination of natural water resource protection measures and appropriate disinfection, these risks have been controlled. Chlorination is still the most widely used method worldwide to disinfect drinking water and ensure food safety by inhibiting undesirable microorganisms. Due to its bactericidal effect, it destroys all undesirable germs and is suggested to be used instead by altering the cell walls, changing the permeability and enzymatic activity of microorganisms, and also due to its persistence it remains in the drinking water distribution network (Duan et al., 2020; Mishaqa et al., 2022). However, the formation of disinfection by-products (DBP) is an unintended consequence of disinfection. These disinfection by-products are formed primarily by reaction between chlorine and natural organic materials found in water (WHO, 1986; Health Canada, 2006), which contains compounds such as humic acids- fulvene acids – hydrophobic acids – hydrophobic neutral substances – transfilic acids – transfilic neutral substances – hydrophilic acids –

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hydrophilic neutral substances proven to be precursors of DBPs (Wang et al., 2013; Dong et al., 2021).

Many disinfection by-products are formed, most of which are chlorinated DBPs, including trihalomethanes (THMs), aloacetic acids (AHAs), haloacetones (HKs), halonitromethanes (HNMs), haloacetonitriles (HANs), haloacetamides (HAMs), and nitrosamines (NAs), but THMs trihalomethanes are the most common disinfection by-products (WHO, 2017; Dong et al., 2021; Mishaqa et al., 2022). Trihalomethanes THMs are mono-carbon compounds bound to substituted halogens, of the general formula CHX3 where X may be chlorine (Cl), fluorine (F), bromine (Br) or iodine (I) or a combination thereof. The THMs found in chlorinated water are chloroform CHCl3, bromodichloromethane CHBrCl2, dibromochloromethane CHClBr2, and bromoform CHBr3. Numerous studies have been carried out to investigate the formation potential of THMs during chlorination of water from different sources, namely surface water, seawater and groundwater. The four trihalomethanes species that originate from various sources have varied creation tendencies. Surface water has a larger THM formation potential than groundwater (Mujathel et al., 2022). Several studies have estimated the correlation between THMs and non-cancerous diseases and cancer linked to multiple routes of exposure, namely oral ingestion, inhalation through breathing and skin contact, during regular indoor activities such as showering, bathing, washing up, cooking. This studies have demonstrated the toxicity, teratogenicity and carcinogenicity of DBPs, they caused metabolic genetic mutations, cancers of digestive and urogenital systems, liver damage and may also have reproductive and developmental effects, and hypertension (Richardson et al., 2007; Wang et al., 2013; Dong et al., 2021; Mishaqa et al., 2022; Zhang et al., 2023). It has been shown that the risk of cancer is higher by inhalation than by oral ingestion and skin absorption (Tafesse et al., 2023).

Given the potential health risks, the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have regulated DBPs in drinking water. They established maximum permissible values based on the carcinogenic potency of its substances in animals, to mitigate health risks, including trihalomethanes THMs (WHO, 2005; The European Parliament and The Council of the European Union, 2020). The WHO guidelines and Moroccan Standard NM03.7.001 set maximum allowable values (MAV) for chloroform (MTC), bromoform (TBM), dibromochloromethane (DBCM), bromodichloromethane (BDCM) are 200 μg/L, 100 μg/L, 100 μg/L, and 60 μg/L, respectively (WHO, 2005; Direction de Contrôle des Produits Alimentaires, 2018). Total THMs are limited to a maximum permissible yearly average level of 80 μg/L by USEPA (2006). The USEPA has created rules for evaluating each THM's carcinogenic and non-carcinogenic diseases risk through multiple routes and has categorized each one using carcinogenic groups and classes. Cancer risk is defined in four classes: negligible risk ($CR < 10^{-06}$), acceptable low risk ($1 \times 10^{-06} \leq CR < 5.1 \times 10^{-05}$), acceptable high risk ($5.1 \times 10^{-05} \leq CR < 10^{-04}$), and unacceptable risk ($CR \geq 10^{-04}$) (USEPA, 1991a). The Hazard index for non-cancer risk associated with THMs in drinking water is limited of one (USEPA, 1991a). Although having done many studies, the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have defined the various ways of exposure to THMs, namely ingestion, as well as inhalation and dermal absorption (WHO, 2005).The USEPA has established a total exposure estimate for trihalomethanes. The estimates are presented in Tables 1,2,3 below. Very few researchers have monitored the formation of THMs and assessed the associated health risks via the multiple pathways in the drinking water treatment circuit,

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from the water source to the consumer's tap, whether in an old or new neighborhood, and under different types of sources (surface water and groundwater).

The goals of this study are to determine the THMs formation potential of chlorinated surface and groundwater at eight different sites from the point of origin of water to the tap for the end user. As well as evaluating the risk of cancer and non-cancerous diseases linked to lifetime exposure to THMs through multiple routes of exposure, including oral ingestion, skin absorption and inhalation. As no study of this type has yet been carried out in Morocco (Scopus, 2023).

Materials and methods

Water source analysis

Eight different samples sites were selected for this study in Marrakech city of Morocco, namely raw water – surface water, groundwater from a borehole, filtered water from a treatment plant, potable water from a treatment plant outlet, reservoir water, tap water from an old neighborhood, and tap water from a new neighborhood. *Figure 1* explains the sampling sites.

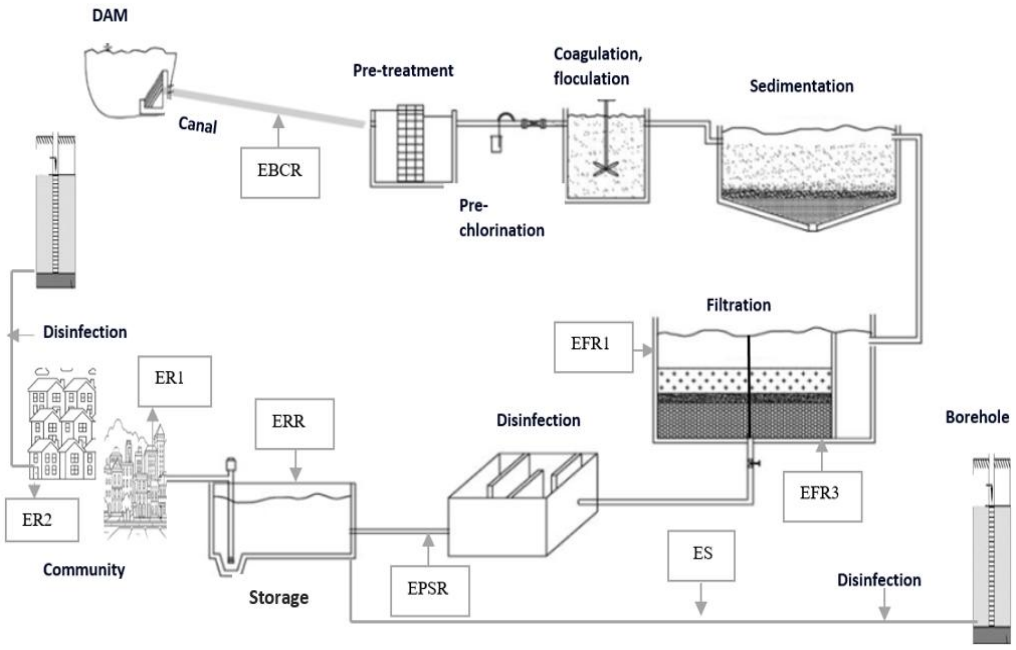

Figure 1. *Description of water samples*

-A raw surface water sample **(EBCR)** was collected on the canal carrying water from a dam - Water not intended for human consumption.

-A groundwater freshwater sample from a borehole **(ES)** - Drinking water to supply the population.

-Two samples of treated and filtered water from the different treatment wires at the station (**EFR1** and **EFR3**); EFR1 is the filtered water from the old production unit, and EFR3 is the filtered water from the new unit - Water not intended for human consumption.

-A drinking water sample disinfected– end of treatment process (**EPSR**) - Drinking water to supply the population.

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-A drinking water sample stored in reservoir (**ERR**) - Drinking water to supply the population.

-Two samples of tap water from two neighborhoods, one from the old neighborhood **(ER1)** and the other from a new neighborhood (**ER2**) - Drinking water to supply the population.

DBPs-THMs analysis method

Gas chromatography (GC) combined with an electron capture detector (ECD) and a headspace sampler was used for the determination of four THMs including Chloroform (MTC), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM). Samples were collected in May 2023. Three replicates were performed for each site to obtain mean THM concentrations. All samples were collected from taps, except for EBCR samples collected from root canals. Samples were usually collected after flushing the system until the water temperature stabilized (approximately 5 minutes). Samples are stored at approximately 4°C.The sample storage area must not contain vapors of organic solvents and direct or intense light. The retention period between sampling and analysis must not exceed 14 days (USEPA, 1995; Québec, 2008).

For THMs analysis, the water sample collected was placed in a glass bottle (40 mL) rinsed with methanol and incubated at 70 °C for 2 hours. Sodium thiosulfate (3 drops) was added to 5 mL of the representative sample, he is recommended to reduce the residual chlorine. 25 µL 1,1-Dichloroethane Standard (2 mg/L in MeOH) were added as solution of similar extraction standards «surrogate», then sealed with caps silicone septa. All chemicals used in this study were provided by Sigma-Aldrich. THMs were analyzed by gas chromatography (Thermo-Scientifique) coupled to an automatic headspace sampler (HS-Herd Space) (Thermo-Scientifique). Capillary column GC (30 m*0.25 mm, inside diameter, 0.25 µm - film thickness) was used. The temperature program maintained was 70 °C at the Autosampler level (Head Space), then 250 °C in injector and 40 °C in column. The detector associated with gas chromatography is an ECD (Electron Capture Detector), allowing detection THMs molecules carried by the vector gas with a flow rate of 98.5 mL/min, by the attachment of electrons by ionization by electron capture. For Chloroform (MTC), the limits of quantification are 0.47 (µg/L), Bromodichloromethane (BDCM) is 0.46 (µg/L), Dibromochloromethane (DBCM) is 0.46 (µg/L), and Bromoform (TBM) is 0.53 (µg/L).

Risk evaluation for exposure to THMs

Carcinogenic or non-carcinogenic risks may be the focus of the assessment of human health concerns. According to USEPA guideline, exposure a possible carcinogen like trihalomethanes increases a person's lifetime risk of developing cancer (USEPA, 2005). Based on the concentration of THMs, the cancer risk assessment for THMs in drinking water was calculated for the multiple exposures routes like oral ingestion, dermal absorption, and inhalation.

Non-cancer risk assessment

Utilizing the Hazard index (HI) of the various exposure routes, the non-carcinogenic risk of THMs was calculated. The United States Environmental Protection Agency declares that there may be adverse effects on human health when the HI is more than 1.

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Equations (1), (2) and (3) are used to calculate hazard index (HI) for the determination of non-cancer risks of THMs via oral ingestion, dermal absorption and inhalation exposure.

$$\text{HI oral} = \frac{\text{CDI oral}}{\text{RfD oral}} \quad \text{(Eq.1)}$$

where,
CDI is the chronic daily intake (mg/kg/day),
RfD oral is the reference dose for non-carcinogen risk (mg/kg/day).
The references values are shown in *Table 1*.

$$\text{HI dermal} = \frac{\text{DAD}}{\text{RfD ABS}} \quad \text{(Eq.2)}$$

where,
DAD is dermal absorbed dose (mg/kg/day),
SF_{ABS} is absorbed reference dose (mg/kg/day).
The references values are shown in *Table 2*.

$$HI\ inhalation = \frac{EC}{RfC\ inhalation * 1000} \quad \text{(Eq.3)}$$

where,
EC is exposure concentration (μg/m^3),
RfC inhalation is Inhalation Chronic Reference Concentration (mg/m^3).
The references values are shown in *Table 3*.

Table 1. *Parameters of cancer and non-cancer risks assessment of oral route*

Ingestion Oral				
Parameter	**Symbol**	**unit**	**Value**	**Reference**
Concentration trihalomethanes	CW	mg/L	Found concentrations	This study
Ingestion rate of water	IR	L/day	2,5	(USEPA, 2014)
Exposure frequency	EF	day/year	350	(USEPA, 2014)
Exposure duration	ED	years	26	(USEPA, 2014)
Body weight	BW	kg	80	(USEPA, 2014)
Average exposure time	AT	days	70*365	(USEPA, 2014)
Slope factor – oral	SF	mg/kg/day	MTC:0,0031 BDCM:0,062 DBCM:0,084 TBM: 0,0079	(RAIS, 2023)
Reference dose	RfDf	mg/kg/day	MTC:0,01 BDCM:0,008 DBCM:0,02 TBM:0,02	(RAIS, 2023)

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Table 2. *Parameters of cancer and non-cancer risks assessment of dermal absorption*

Dermal absorption				
Parameter	**Symbol**	**unit**	**Value**	**Reference**
Skin surface area available for contact	SA	cm^2	20900	(USEPA, 2014)
Event frequency	EV	events/day	1	(USEPA, 2014)
Exposure frequency	EF	days/year	350	(USEPA, 2014)
Exposure duration	ED	years	26	(USEPA, 2014)
Body weight	BW	kg	80	(USEPA, 2014)
Average exposure time	AT	days	Non carcinogenic effects AT = 26 (ED) x 365 carcinogenic effects AT = 70 x 365	(USEPA, 2014)
Fraction-absorbed water	FA	dimensionless	1	(USEPA, 2014)
Dermal permeability coefficient	Kp	cm/hr	MTC: 0,0068 BDCM: 0,0046 DBCM: 0,0032 TBM: 0,0022	(USEPA, 2014)
Concentration trihalomethanes	CW	mg/cm^3	Found concentrations	This study
Lag time per event	ƒevent	hr/event	MTC:0,5 BDCM:0,88 DBCM:1,57 TBM: 2,79	(USEPA, 2014)
Event duration	tevent	hr/event	0,71	(USEPA, 2014)
Time to reach steady-state	t*	hr	MTC:1,19 BDCM:2,12 DBCM:3,77 TBM: 6,70	(USEPA, 2014)
Slope factor - Dermal	SF	mg/kg/day	MTC:0,0031 BDCM: 0,062 DBCM: 0,084 TBM: 0,0079	(RAIS, 2023)
Fraction of THMs absorbed in gastrointestinal	ABSGI	dimensionless	1	(USEPA, 2014)
Absorbed cancer slope factor	SF ABS	mg/kg/day	MTC:0,0031 BDCM: 0,062 DBCM: 0,084 TBM: 0,0079	(USEPA, 2014),(RAIS, 2023)
Reference dose	RfD	mg/kg/day	MTC:0,01 BDCM: 0,008 DBCM: 0,02 TBM: 0,02	(USEPA, 2014), (RAIS, 2023)

Cancer risk assessment

The health risk assessment was completed in accordance with USEPA recommendations (USEPA, 1991b, 2004, 2009) and a methodology that has recently been employed by several research (Wang et al., 2007; Basu et al., 2010; Salih and Al-Azzawi, 2016; Kujlu et al., 2020; Costa et al., 2022; Dėdelė et al., 2022).The following are the estimated cancer risks from oral ingestion, dermal absorption, and inhalation exposure (*Equations 4, 5 and 6*).

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Table 3. *Parameters of cancer and non-cancer risks assessment of inhalation*

Inhalation exposure				
Parameter	**Symbol**	**unit**	**Value**	**Reference**
Exposure time	ET	hr/day	14	This study (ET=24h/day (USEPA, 2014))
Exposure frequency	EF	days/year	350	(USEPA, 2009, 2014)
Exposure duration	ED	years	26	(USEPA, 2009, 2014)
Averaging time	AT	h	70*365*24	(USEPA, 2009, 2014)
Volumetric water flow rate	QL	L/min	5	(Little, 1992)
Henry's law constant	m	dimensionless	MTC:0,15 BDCM:0,0876 DBCM:0,032 TBM:0,0219	(RAIS, 2023)
Overall mass-transfer coefficient	KolA	L/min	MTC:7,4 BDCM:5,9 DBCM:4,6 TBM: 3,7	(Little, 1992)for TCM (Téllez Tovar and Rodríguez Susa, 2021)
Volumetric air flow rate in shower	Q_{Gs}	L/min	50	(Little, 1992)
Volume of air in shower	Vs	L	5000	(Dėdelė, Nikiforov and Miškinytė, 2022)
Time	t	min	10	(Little, 1992)
Concentration of contaminant in inlet water	Cin	mg/L	Found concentrations	This study
Inhalation unit risk	IUR	$\mu g/m^3$	MTC: 0,000023 BDCM: 0,000037 DBCM: 0,0000177 TBM: 0,0000011 Chloroform:0.0977	(RAIS, 2023) (DEQ, 2015)for DBC
Inhalation Chronic Reference Concentration	RfC	mg/m^3	(RfC from DCB and DBC are not available in RAIS).	(RAIS, 2023)

Cancer risk for THMs of oral route:

$$CR\ oral: CDI\ oral * SF\ oral \quad \text{(Eq.4)}$$

where,
CDI is the chronic daily intake (mg/kg/day),
SF oral is the slope factor for carcinogen (mg/kg/day).

The CDI was calculated for each of the oral ingestion according to the following equation:

$$CDI\ oral = \frac{(CW \times IR \times EF \times ED)}{(BW \times AT)} \quad \text{(Eq.4-1)}$$

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where,
CW is the concentration of trihalomethanes in the drinking water samples (mg/l),
IR is the ingestion rate of water (L/day),
EF is the exposure frequency (day/year),
ED is the exposure duration (years),
BW is the body weight (kg),
AT is the average exposure time (days).

The references values are shown in *Table 1*.

Cancer risk for THMs of dermal absorption:

$$CR\ Dermal = D * SF(ABS) \quad \text{(Eq.5)}$$

where,
DAD is dermal absorbed dose (mg/kg/day),
SF_{ABS} is absorbed cancer slope factor (mg/kg/day).

The DAD was calculated for each of the dermal absorption according to the following equations:

$$DAD = \frac{DAevent*EV*ED*EF*SA}{BW*AT} \quad \text{(Eq.5-1)}$$

where,
DAevent is absorbed dose per event (mg/cm^2 -event),
SA is skin surface area available for contact (cm^2),
EV is event frequency (events/day),
EF is exposure frequency (days/year),
ED is exposure duration (years),
BW is body weight (kg),
AT is averaging time (days).

DAevent (mg/cm^2-event) is calculated for organic compounds as follows:

$$If\ tevent \leq t*, then: DAevent = 2FA * Kp * Cw \sqrt{\frac{6\tau event * tevent}{\pi}} \quad \text{(Eq.5-2)}$$

where,
FA is fraction-absorbed water,
Kp is dermal permeability coefficient of compound in water (cm/hr),
Cw is the concentration of trihalomethanes in the drinking water samples (mg/cm^3),
τevent is lag time per event (hr/event),
tevent is event duration (hr/event),
t * is time to reach steady-state (hr).

The SF_{ABS} was calculated for each of the dermal absorption according to the following equation:

$$SF\ ABS = \frac{SF0}{ABS\ (GI)} \quad \text{(Eq.5-3)}$$

where,
SF_0 is slope factor oral ingestion (mg/kg/day),

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ABS_{GI} is fraction of contaminant absorbed in gastrointestinal tract in the critical toxicity study. Absorption fraction in GI tract = 1.0 (assuming 100% GI absorption).

The references values are shown in *Table 2*.

Cancer risk for THMs of inhalation exposure:

$$CR\ inhalation = IUR * EC \quad \text{(Eq.6)}$$

where:
IUR is inhalation unit risk (μg/m^3),
EC is exposure concentration (μg/m^3).

The following equation was used to calculate the EC for each inhalation exposure:

$$EC = \frac{Cair*ET*EF*ED}{AT} \quad \text{(Eq.6-1)}$$

where,
Cair is THMs concentration in air (μg/m^3),
ET is exposure time (hours/day),
EF is exposure frequency (days/year),
ED is exposure duration (years),
AT is averaging time (h).

The THMs volatilized from the drinking water into the shower room were calculated in this investigation using the inhalation exposure model, which Little (1992) developed based on the two-resistance theory. C air is determined for inhalation exposure by Little (1992):

$$Cair = \frac{(Ys(t)+ Ysi)}{2} \quad \text{(Eq.6-2)}$$

where,
Ysi is the initial THM concentration in the shower room (mg/l) (assumed as 0 mg/l),
Ys (t) is the THM concentration in the shower room at time t (min) (mg/l) (assumed 10 min in this study).

Ys (t) is determined by:

$$Ys\ (t) = (1 - e^{(-bt)}) * \frac{a}{b} \quad \text{(Eq.6-3)}$$

$$b = \frac{\frac{QL}{m}*(1-e^{(-N)})+Q\ GS}{Vs} \quad \text{(Eq.6-4)}$$

$$a = \frac{QL*Cin*(1-e^{(-N)})}{Vs} \quad \text{(Eq.6-5)}$$

$$N = \frac{Kol\ A}{QL} \quad \text{(Eq.6-6)}$$

where,
Q_L is volumetric water flow rate (L/min),
m is Henry's law constant (dimensionless),
N is overall mass-transfer coefficient (dimensionless),

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KolA is overall mass-transfer coefficient (L/min),
Q_{Gs} volumetric air flow rate in shower (L/min),
Vs is volume of air in shower (L),
t is time (min),
Cin concentration of contaminant in inlet water (mg/L).

The references values are shown in *Table 3*.

Results and discussions

Levels of THMs samples

Figure 2 displays the total average amounts of trihalomethanes (THMs) in water from two distinct sources: groundwater from a borehole and surface water from a canal. *Figure 2* data demonstrates how THMs-T concentrations can change based on the source. While THMs-T concentrations in fresh borehole water are negligible or almost nonexistent (ES=1.3 µg/L), the highest THMs concentrations are found in treated surface water (EPSR=24.82 µg/L, ERR=29.98 µg/L, ER1=31.69 µg/L). The primary factor causing THM formation in the presence of chlorine (CRF=1mg/L) is high concentrations of organic matter, which is the reason for the high concentration of THMs-T in surface water. This is consistent with other research (Health Canada, 2006; Padhi et al., 2019).

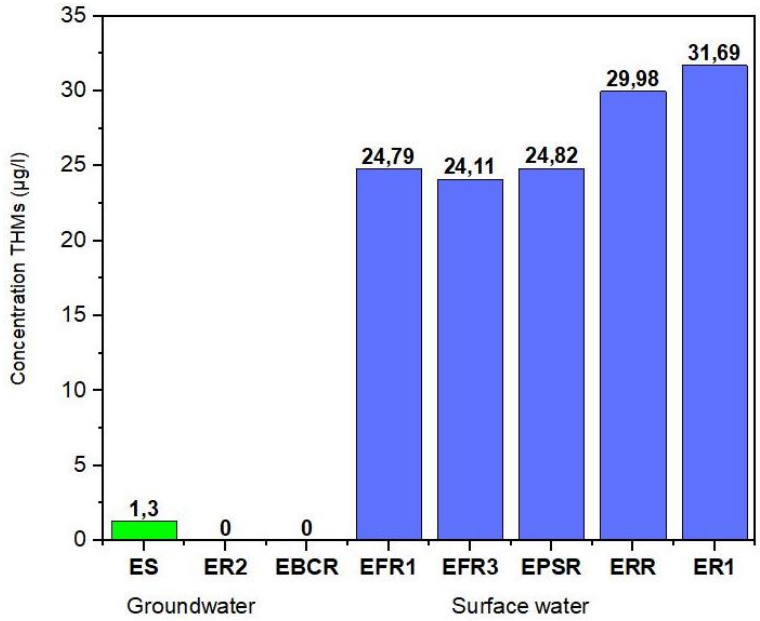

Figure 2. *Total average concentrations of THMs in eight samples. EBCR: raw surface water; ES: groundwater; EFR1: filtered water – old unit; EFR3: filtered water- new unit; EPSR: disinfected water; ERR: reservoir water; ER1: tap water-old neighborhood; ER2: tap water-new neighborhood*

THMs-T concentrations in the raw water of the Canal (EBCR) were not detected related to the absence of chlorination. This explains why chlorine is the main agent that induces the formation of trihalomethanes in drinking water even though organic matter is normally present. Two sites have been chosen at the treatment plant: EFR1 and EFR3. The potential for THM-T formation at these two sites is different. The concentration of

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THMs-T was 24.79 µg/L (EFR1) and 24.11 µg/L (EFR3). Because of the organic deposit known as biofilm, the hydromechanics equipment's in the older filter unit (ERF1) became contaminated, resulting in the concentration difference between the two units.

The highest THMs-T concentration (31.69 µg/L) was observed in tap water in old neighborhood (ER1) from the surface water. These high concentrations are due to the reaction of free residual chlorine with the organic materials that may be found in the drinking water distribution system, in particular the biofilm attached to the pipe walls; which was also observed in subsequent studies (WHO, 2005; Health Canada, 2006). In this study, the rate of formation of THMs increases as water moves away from the treatment plant in the distribution system due to the continued presence of residual chlorine (WHO, 2005; Health Canada, 2006; Mishaqa et al., 2022). However, a concentration lower than the quantification limit of the instrument GC-ECD (~0 µg/L) was observed in the tap water of the new neighborhood. This is because of the newly installed pipeline and the high quality of the water from the underground source. The absence of organic matter and the modest amount of chlorine added for disinfection are the reasons why THMs do not form in ER2.

Figure 3 shows the concentrations of the different trihalomethanes species in the samples. There are three types of trihalomethanes formed during the chlorination of surface water samples: Chloroform (MTC), bromodichloromethane (BDCM), dibromochloromethane (DBCM). Bromoform was the undetected compound in all water types tested. Chloroform MTC was the predominant trihalomethanes compound.

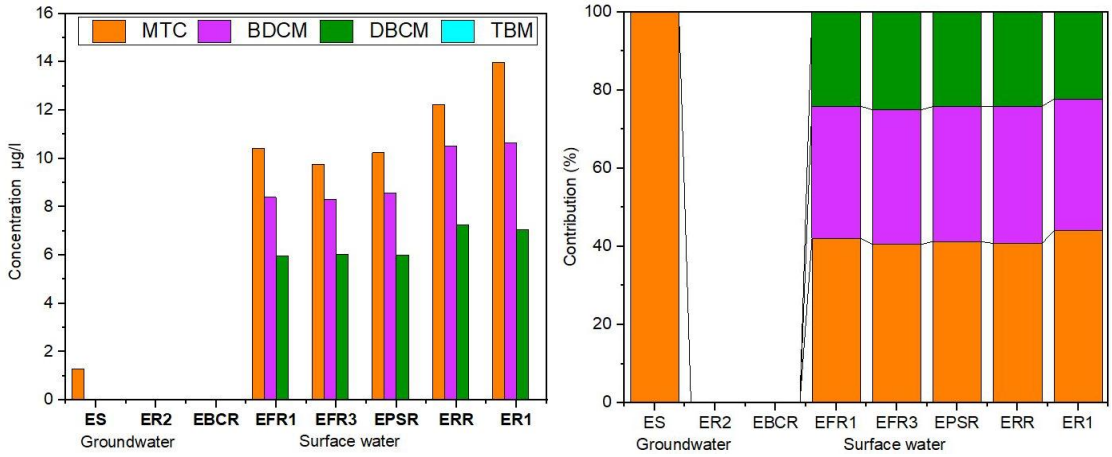

Figure 3. *(a)Distribution of THM species in sample, and (b) percentage of contribution of each THMs species to TTHMs. EBCR: raw surface water; ES: groundwater; EFR1: filtered water – old unit; EFR3: filtered water- new unit; EPSR: disinfected water; ERR: reservoir water; ER1: tap water-old neighborhood; ER2: tap water- new neighborhood. MTC: Chloroform, BDCM: Bromodichloromethane, DBCM: Dibromochloromethane, TBM: bromoform*

The THM-MTC concentrations formed in original surface water samples were: 13.97 µg/L (ER1), 12.22 µg/L (ERR), 10.24 µg/L (EPSR), 10.43 µg/L (EFR1), 9.77 µg/L (EFR3). Concentrations of species followed the following order: chloroform (MTC) > bromodichloromethane (BDCM) > dibromochloromethane (DBCM). These results are consistent with previous studies (Wang et al., 2013; Duan et al., 2020; Tafesse et al., 2023). The only species formed during the disinfection of fresh borehole water is

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chloroform (ES = 1.3 µg/L). There are no brominated species found. The chloroform concentration in sample ER2 is negligible. From a sanitary point of view, the samples meet the requirements of the World Health Organization (WHO) regarding the maximum permissible values for THMs. Concentrations of THMs were below the guidelines of WHO and Moroccan standards. Can regular water use cause long-term negative effects even if THM concentrations are lower? As a result, both cancerous and non-cancerous disease indices must be monitored.

Non-cancer risk assessment

Utilizing the Hazard index (HI) of the various exposure routes, the non-carcinogenic risk of THM was calculated (*Equations 1, 2 and 3*). The United States Environmental Protection Agency declares that there may be adverse effects on human health when the HI is more than 1. In this study, the calculated IH for all routes was less than 1.

The graph (*Figure 4*) show the values of the hazard index (HI) for THMs compounds after ingestion, absorption dermal and inhalation exposure. Each trihalomethanes species poses a non-cancerous risk to human health, hazard index was calculated using the reference dose for each species and exposure route. The inhalation hazard index only represents the adverse effects of chloroform; no references dose for other species are available. The findings show that oral ingestion has higher values than absorption dermal and inhalation exposure. The overall hazard index for the oral route for samples is non identical. THMs compound hazard index (HI) values in surface water samples for the three exposure routes (0.0573 (EFR1), 0.0547 (EFR3), 0.0569 (EPSR), 0.0684 (ERR), 0.0751 (ER1)) are higher than those in groundwater (0.0048 (ES)). The hazard index for trihalomethanes species for oral ingestion for all samples except ER1 is in the following order: BDCM > MTC > DBCM. While the hazard index of trihalomethanes species for the dermal route is ordered as follows: MTC > BDCM > DBCM.

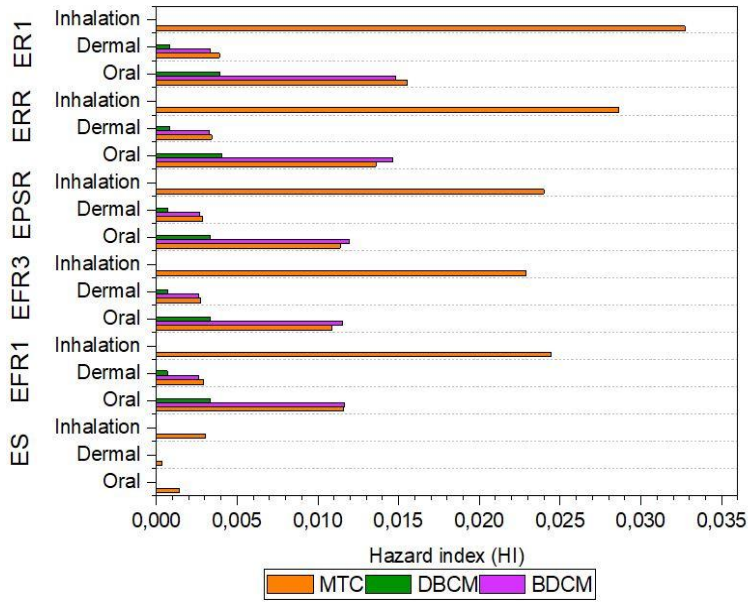

Figure 4. *Hazard index of THMs through multiples exposures routes. ES: groundwater; EFR1: filtered water – old unit; EFR3: filtered water- new unit; EPSR: disinfected water; ERR: reservoir water; ER1: tap water-old neighborhood. MTC: Chloroform, BDCM: Bromodichloromethane, DBCM: Dibromochloromethane*

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Cancer risk assessment analysis of THMs through multiple routes exposure

The cancer risk related to THMs exposure was calculated using *Equations 3, 4, and 5* and based on the THMs concentrations detected in samples. *Figure 5* depicts the overall cancer risk graphically.

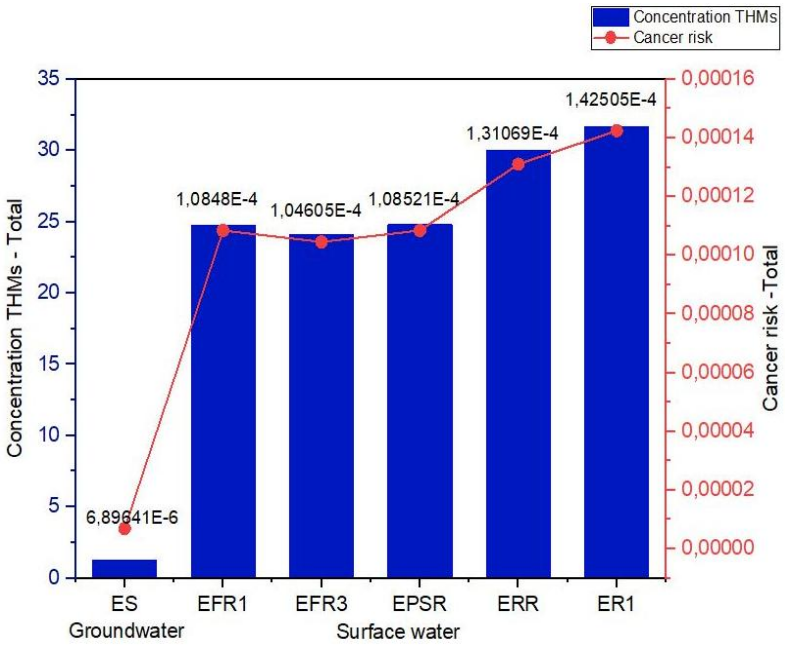

Figure 5. *Lifetime cancer risk of THMs-T in samples. ES: groundwater; EFR1: filtered water – old unit; EFR3: filtered water- new unit; EPSR: disinfected water; ERR: reservoir water; ER1: tap water-old neighborhood*

Tap water (ER1) from surface water was found to have the highest cancer risk at a value of 1.42505E-4, which corresponds to the highest THM levels; while the groundwater had the lowest cancer risk at 6.9E-6. The lifetime cancer risk for THMs throughout the various exposure pathways in the drinking water samples (EPSR, ERR, ER1) was within the range of an unacceptable risk (CR ≥ 10E-4), with the exception of the groundwater sample (ES), which had a negligible risk.

Cancer risk from ingestion route

The lifetime risk of developing cancer as a result of oral chloroform consumption was in the range of negligible risk, whereas the BDCM and DBCM belonged to the low risk category. The risk of cancer associated with oral THM was in the following order: BDCM > DBCM > Chloroform. Among the THMs species, the BDCM posed the highest cancer risk (0 (ES), 5.7897E-6 (EFR1), 5.7276E-6 (EFR3), 5.9208E-6 (EPSR), 7.2526E-6 (ERR), 7.3492E-6 (ER1)). However, chloroform had a cancer risk of less than 10E-6 (4.49E-8 (ES), 3.5987E-7 (EFR1), 3.371E-7 (EFR3), 3.5332E-7 (EPSR), 4.2163E-7 (ERR), 4.8201E-7 (ER1)). The most significant impact on lifetime average cancer risk was related to BDCM (42%), then DBCM (39%), and finally MTC (19%). *Figure 6* displays the cancer risk linked to each THM species.

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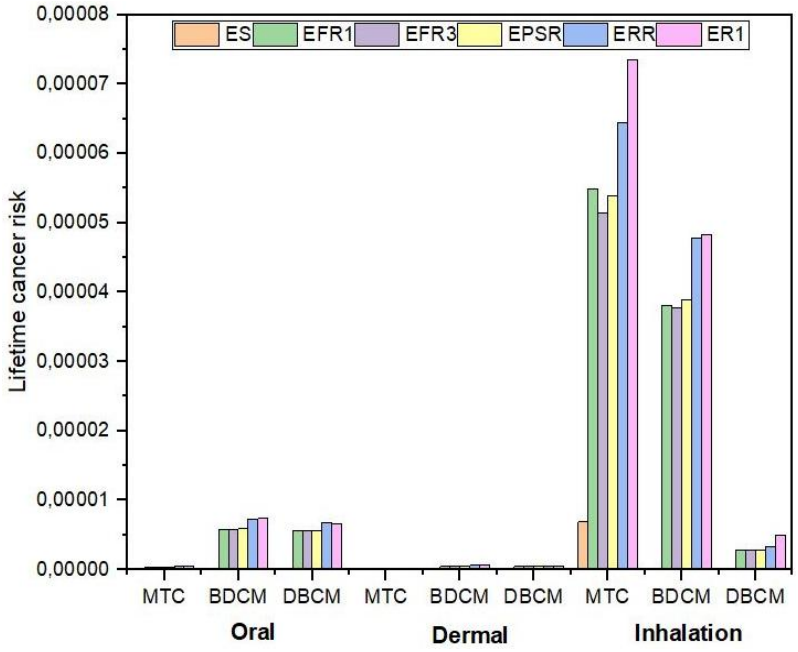

Figure 6. *lifetime cancer risk of THMs through multiple routes exposure. ES: groundwater; EFR1: filtered water – old unit; EFR3: filtered water- new unit; EPSR: disinfected water; ERR: reservoir water; ER1: tap water-old neighborhood. MTC: Chloroform, BDCM: Bromodichloromethane, DBCM: Dibromochloromethane*

Cancer risk from dermal absorption

The risk of cancer from THMs through dermal absorption in samples is lower than the USEPA-recommended level of negligible risk. In this study, THMs have cancer risk levels that are often less than 10E-6. As a result, there will be no risk associated with dermal absorption. *Figure 6* displays the species of THMs cancer risk by dermal absorption. Like oral ingestion, Le BDCM is the main contributor and carries the highest risk of cancer (0 (ES), 4.8643E-7 (EFR1), 4.8121E-7 (EFR3), 4.9744E-7 (EPSR), 6.0934E-7 (ERR), 6.1746E-7 (ER1)). In the calculated total risk, MTC is the least significant factor (4.20E-9 (ES), 3.369E-8 (EFR1), 3.1559E-8 (EFR3), 3.3077E-8 (EPSR), 3.9472E-8 (ERR), 4.5125E-8 (ER1)). The percentage of risks of cancer due to dermal absorption showed that the BDCM contributed the most (43%) to overall risks, followed by the DBCM (38%) and chloroform (20%).The risk of cancer via absorption cutaneous was not particularly high compared to the oral route.

Cancer risk from inhalation exposure

As shown in *Figure 6*, the risk of cancer for THMs due to inhalation exposure exceeds the level of risk of cancer accepted by USEPA, mostly due to MTC, which has the highest risk of cancer (6.85E-6 (ES), 5.49369E-5 (EFR1), 5.14605E-5 (EFR3), 5.39361E-5 (EPSR), 6.43651E-5 (ERR), 7.35827E-5 (ER1)). As a result of its volatility, the majority of chloroform that is present in water eventually escapes into the air. Months of residence time in the atmosphere are occupied by chloroform before it is chemically changed and eliminated (WHO, 2004). The percentage of inhalation-related cancer risks showed that chloroform contributed the most (64%) to overall risks, followed by BDCM (33%) and DBCM (3%).

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Inhalation exposure accounted for 90,1 percent of the overall cancer risk associated with THMs exposure. *Figure 7* illustrate that the primary cancer risk from exposure to THMs is inhalation, followed by oral intake (9.1%) and skin absorption (0.8%).

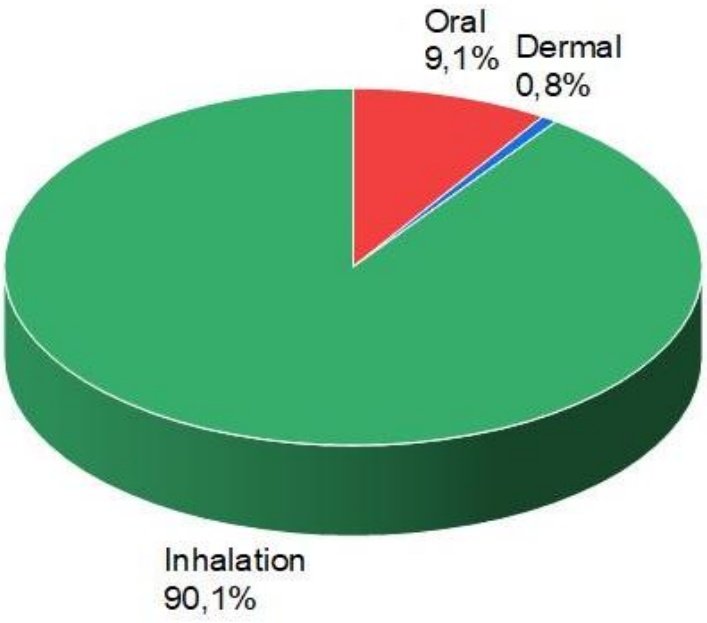

Figure 7. *Contribution of each route of exposure to THMs to lifetime cancer risk*

The present one is the first study to show Morocco's drinking water quality with regard to disinfection byproducts. From the water's source to the end user's tap, it assessed the possibility of THM formation in chlorinated surface and ground water at eight distinct locations. Additionally, it evaluates the risk of cancer and non-cancerous diseases linked to lifetime exposure to THMs through a variety of exposure routes, such as inhalation, skin absorption, and oral ingestion. The results showed that even though the concentrations of THMs in the samples from surface water met the standards set by the USEPA and WHO, there is still a high risk of cancer from it. This means that one in every 10 000 residents may develop cancer as a result of regularly consuming potable water throughout their lives, in addition to other potential illnesses. The lifetime cancer risk associated with BDCM and DBCM represents the highest percentages for the oral and dermal routes compared to MTC. This indicates that even at low concentrations, BDCM and DBCM have a potency factor that is eight times greater than that of chloroform. however, inhalation was the most important route of exposure, as represented by the high risk of chloroform cancer. The risk of cancer from trihalomethanes can be integrated into a broader public health risk assessment of drinking water, particularly in areas where water is contaminated with both trihalomethanes and waterborne pathogens, as these can also increase the risk of cancer.

Conclusion

The potential of trihalomethanes formation in drinking water of Marrakech has been studied. The risks of exposure to the reported concentration of THMs by ingestion, dermal absorption, and inhalation exposure of drinking water were then evaluated for both cancer

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and non-cancer risks. The THMs content was far lower than the Moroccan and WHO guideline's maximum acceptable MAV. While the lifetime cancer risk was greater than the USEPA's "negligible risk" standard.

The following findings are drawn from this study:

- The potential of THMs formation during the treatment of raw surface water was very high compared to the groundwater.
- Chloroform was observed to be the predominant species of THMs; where as bromoform was not detected.
- Concentrations of species followed the following order: chloroform (MTC) > bromodichloromethane (BDCM) > dibromochloromethane (DBCM).
- The total THMs concentrations in samples from the surface water to the consumer tap followed the following order: Raw water < Filtered water- new unit < Filtered water- old unit < disinfected water < Storage water < Tap water.
- THMs formation rates increase as water moves away from the treatment plant in the distribution system.
- The Hazard index for all routes was less than 1.
- Oral ingestion has a higher hazard index value than absorption, dermal, and inhalation exposure.
- The lifetime cancer risk for THMs in drinking water samples was within the range of an unacceptable risk, except for groundwater samples, which had a negligible risk.
- The main exposure route was through inhalation, which was followed by ingestion oral and dermal absorption.
- MTC, which carries the highest risk of cancer, is mostly to blame for the fact that THM's inhalation exposure cancer risk surpasses the amount of risk approved by USEPA.
- The risk of cancer associated with inhalation THM was in the following order: Chloroform (64%) > BDCM (33%) > DBCM (3%).
- Oral chloroform consumption carried a negligible lifetime risk of getting cancer, however the BDCM and DBCM were considered to carry a low lifetime risk.
- The risk of cancer associated with oral THMs was in the following order: BDCM > DBCM > Chloroform.
- BDCM is the main contributor to dermal absorption and has the highest risk of cancer, however the risk assessment's least significant factor is the MTC.
- According to the percentage of cancer risks due to dermal absorption, the BDCM contributed the most (43%) to overall risks, followed by the DBCM (38%), and chloroform (20%).

THMs levels in drinking water are consistent with Moroccan and WHO drinking water guidelines, but given these negative effects on human health, the term "Disinfection by-Products" prompts us to consider effective alternative techniques with zero by-products as a way of ensuring complete food security for both the ecological system and the general public.

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