

Assessment of health safety related to inhalation of volatile organic compounds present in fumes of water delivered through the public distribution system

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ABSTRACT

The following paper assesses the health safety related to contact with toxic or carcinogenic volatile organic compounds (VOC) inhaled from water delivered through the public distribution system. The study involves the calculations of hazard indexes related to everyday use of water from the water distribution system by children and for adults. The materials comprise the results of analyses of processed water conducted in the years 2012–2019. The analyses involved determining the contents of benzo(a)pyrene, benzene, acrylamide, epichlorohydrin, vinyl chloride and the chlorinated volatile compound – 1,2-dichloroethane (for a total of 98 determinations). The study was conducted on a water supply system operating in accordance with the regulations in force at the time of the study. The obtained results of determinations for all VOCs were significantly lower than the permissible concentrations in water, close to the limit of quantitation (LOQ = from 10⁻⁴ to 10⁻⁶). The results obtained allowed for calculating the maximum non-carcinogenic hazard index for the inhalation exposure (HI_{inhal}) to the xenobiotics studied which amounted to 3.03E-03 in children and 2.86E-02 in adults which is equal to 0.3% and 2.9% of the permissible exposure level respectively (HI_{perm}). The carcinogenic risk index for the inhalation exposure (CR_{inhal}) to benzo(a)pyrene and benzene through contact with tap water amounted to 1.57E-09 which is equal to 0.16% of the permissible value (CR_{perm}). It was found that adults are at a greater risk of being affected by VOCs than children because of greater inhalation rate and longer exposure duration. The research demonstrated that under the conditions analysed, potable water containing the VOCs studied did not pose any risk to humans.

Keywords: Inhalation; Organic compounds; Potable water; Risk index (carcinogenic and non-carcinogenic); Safety of water intake and distribution systems

1. Introduction

Potable water contains dissolved organic and inorganic substances. The majority of those substances are natural and have a positive impact on water quality. However, some of them are unwanted and their presence is often the result of anthropogenic activity and the release of pollutants to the environment. The xenobiotic substances studied known as volatile organic compounds (VOC) include: benzo(a) pyrene, benzene, acrylamide, epichlorohydrin, vinyl chloride and the chlorinated volatile compound: 1,2-dichloroethane [1–3]. The selected VOCs have potentially toxic, mutagenic and carcinogenic effects. In accordance with the US EPA [4] classification, benzene and vinyl chloride belong to H group – carcinogenic to humans; benzo(a) pyrene, 1,2-dichloroethane and epichlorohydrin belong to B2 group – probable human carcinogens (with sufficient

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evidence in animals and inadequate or no evidence in humans) and acrylamide is considered likely to be carcinogenic to humans (L group). In accordance with IARC [5] classification, benzene belongs to group 1 – substances carcinogenic to humans. Additionally, all of the xenobiotics analysed are found in US EPA [4] and WHO [6] classifications and are considered substances that have a considerable impact on human health due to the consumption of potable water.

The VOCs analysed can originate from various anthropogenic sources, for example, the burning of fuels used for cooking or household heating [7], propellants used in the production and consumption of some food products, cleaning agents and cosmetics, production of glues, cleaning solvents, fabrics, floor linings, dyes or pesticides [8], sewage [9], spills or fires of oil and oil-based products, for example, gasoline spills or leaks from vehicle fuel tanks [10,11], and from the emission of vehicle exhaust gases into the atmosphere. These compounds can accumulate in aquatic organisms, which results in an increased environmental risk in water ecosystems and other ecosystems [12,13]. The substances contained in water can enter living organisms via two routes: by ingestion and by inhalation [14,15].

Taking into consideration the importance of health safety related to the presence of toxic or carcinogenic volatile organic compounds (VOC) in water supplied through the water distribution system, the aim of the following study is to:

- calculate the hazard indexes (carcinogenic and non-carcinogenic) caused by inhalation of selected VOCs for water consumers (children and adults);
- estimate the cumulative health risk for selected organic xenobiotics in the case of ingestion and inhalation.

2. Materials and methods

Two water treatment plants (WTP) were selected for this study: (1) Stary Sacz water treatment plant (WTPss) and (2) Świniarsko water treatment plant (WTPs). Both facilities are located in southern Poland (Małopolska Province, EU) and supply about 100 thousand inhabitants with household water [16]. The water treatment plants use the following treatment processes: coagulation combined with sedimentation in vertical sedimentation tanks, filtration in high-rate anthracite-quartz filters with contact coagulation, aeration using ozone and final disinfection using UV light and chlorine gas. WTPss also uses filtration with activated carbon bed filters. The treatment process used at WTPss and WTPs allows for effective removal of physical and chemical pollutants, including organic compounds, from water [16].

The materials comprise the results of analyses of processed water supplied directly to the public water distribution system from both water treatment plants, for which the contents of benzo(a)pyrene, benzene, acrylamide, epichlorohydrin, vinyl chloride and the chlorinated volatile compound – 1,2-dichloroethane were determined. Water samples (n = 18) were collected in the years 2012–2019 in an annual cycle, but in 2019 samples were collected twice. There was a total of 98 determinations including:

- 18 determinations of benzo(a)pyrene,
- 16 determinations each of benzene, acrylamide, epichlorohydrin, vinyl chloride and 1,2-dichloroethane.

The determinations of the substances analysed were performed at an accredited laboratory in Pszczyna (Poland, EU, accreditation no. AB 1232).

Table 1 presents the standards and methods used in laboratory analyses.

Water quality assessment based on the content of the listed substances as well as their chemical and metabolic properties were presented in a previous study [23] and will not be repeated in the study herein. The results of all VOC determinations were very low, close to the method's limit of quantitation (LOQ = from 10^{-4} to 10^{-6}), and did not exceed permissible values. To clarify the results, a figure listing the concentrations of VOCs and their permissible values, as published earlier in Wysowska and Kicińska, 2021 [23], is provided below (Fig. 1). The aforementioned study assessed the exposure of water consumers to the substances studied through ingestion by direct consumption of water, the preparation of hot and cold drinks and the preparation of meals. The following article focuses on exposure through inhalation in which the dose of substance enters the body by inhaling the fumes of substances released from water. The inhalation risk was estimated based on a residential scenario, taking into consideration potential chronic exposure.

When calculating exposure to substances delivered with water to households through inhalation the authors used the methodology recommended by US EPA [24] for chronic exposure to hazards (the so called residential scenario). The detailed assessment of health risk related to the ingestion of substances in water for this scenario has been provided in Kicińska and Wysowska [25]. However, it is worth noting that the selected approach is recommended mostly to the assessment of ground water polluted with petroleum products. Hydrogeological structure is particularly important for forming a natural barrier for infiltration of pollutants from the vadose zone to aquiferous strata [26,27]. The facilities studied (WTPss and WTPs) are supplied with water mostly from surface intakes on the Dunajec River (46%), while ground water supplied from wells has infiltration water properties [28]. Surface water from the river supplies the aquifer through natural or forced circulation in a system of basins and a watering ditch.

Non-carcinogenic hazard index related to the inhalation of VOC in water (HI_{inhal}) was calculated using Eqs. (1) and (2) [24]:

$$HI_{inhal} = HQ_{inhal_1} + HQ_{inhal_2} + HQ_{inhal_m}$$
(1)

where HI_{inhal} – total hazard index for exposure through inhalation (–); $HQ_{inhal_{1,2,...,n}}$ – hazard quotient for each chemical substance, for exposure through inhalation (–).

$$HQ = \frac{PI}{RfD} \left[- \right]$$
 (2)



Fig. 1. Average concentrations (av.) in water: (a) benzo(a)pyrene, (b) polycyclic aromatic hydrocarbons, (c) benzene, (d) acrylamide, (e) epichlorohydrin, (f) vinyl chloride, and (g) 1,2-dichloroethane in 2012–2019. Maximum allowable concentrations (MAC) according to: *Minister of Health (Regulation 2017); **US EPA Guidelines (2012); ***US EPA Guidelines (2018); ****WHO (2017); CW – concentration in water. *Source*: [23].

Table 1 Research standards for analysed VOC

VOC	Research standard
Benzo(a)pyrene	KJ-I-5.4-97 method based on the PN-EN ISO 17993:2005 [17] standard and following the KJ-/I-5.4-13C research procedure
Benzene	KJ-I-5.4-155 method based on the standards PN-EN ISO 15680:2008 [18] and PN-EN ISO 11423-1:2002 [19]
Acrylamide	KJ-I.5.4-94 method based on the EPA Method 8032A 1996 and in accordance with KJ-I.5.4-14C [20]
Epichlorohydrin	PN-EN 14207:2005 standard [21]
Vinyl chloride	KJ-I-5.4-155 method based on the standards PN-EN ISO 15680:2008 [18] and PN-EN ISO 11423-1:2002 [19]
1,2-Dichloroethane	KJ-I-5.4-155 method based on the standards PN-EN ISO 15680:2008 and PN-EN ISO 10301:2002 [22]

where HQ_{inhal} – hazard quotient for each chemical substance, for exposure through inhalation (–); PI – pulmonary intake of volatile substance inhaled in the form of fumes released from water (mg/kg/d); RfD – reference dose of a chemical substance taken in through inhalation (mg/kg/d).

The pulmonary intake (PI) of substances taken in through the inhalation of fumes released from water was calculated using Eq. (3) [29]:

$$PI = \frac{CW \times EF \times ED \times CF_2 \times IR_1 \times K}{AT \times BW} \left[mg/kg/day \right]$$
(3)

where PI – pulmonary intake of volatile substance inhaled in the form of fumes released from water (mg/kg/d); CW – concentration of contaminant in water (mg/dm³); EF – exposure frequency (d/y) ([30]; modified).

The inhalation exposure to fumes released from water in residential conditions is incidental (during a shower, a hot bath, morning or evening hygiene routine) throughout the day, not chronic as in the case of ingestion. For this reason the authors selected the following average exposure duration:

- adults: 30 min during the day (hygiene routine: 10 min in the morning (shower), 20 min in the evening) for a total of: EF in adults: 1/24 × 365 = 15.21 (d/y),
- children: 30 min during the day (30 min bath in the evening), for a total of: EF in children: 0.5/24 × 365 = 7.60 (d/y);

ED – exposure duration (y) – a residential scenario was used in the analysis with the exposure duration of: ED = 26 in the case of adults and ED = 6 in the case of children [31]; CF_2 – conversion factor (1,000 dm³/m³); IR_1 – inhalation rate (m³/d), 10 in children [32] and 20 in adults [30]; K – volatilization factor (–), K = 0.0005, based on the average volume of water used in a household amounting to 720 dm³/d, house volume of 150 m³, air exchange rate of 0.25 m³/h, and the volatilization of 50% of the volatile substance contained in water [33,29]; AT – averaging time (d), AT = 25 550 for children and adults in the case of carcinogenic substances [5]. The substances studied are classified either as carcinogenic or as possibly carcinogenic; BW – body weight (kg), BW = 80 kg in the case of adults and 15 kg in the case of children [31].

The use of Eq. (3) for the calculation of non-carcinogenic hazard index is the implication of the Andelman model [33]. It assumes that all volatile substances are subject to equal volatilization. Also, the model does not assume the changes in concentrations during the exposure, for example, during a shower or a hot bath (diffusivity of water vapour) or the use of cold water, for example, a cold shower. However, it was chosen by the authors in an attempt to estimate the maximum hazard index (HI_{max}). The authors are fully aware that considering the semi-volatile characteristics of some xenobiotics the assumptions used in calculations can cause a tendency for overestimation of risk. The analyses ware conducted for operational water treatment plants supplying a public water distribution system with a total length of about 900 km and providing water to over 100,000 consumers. The applied inhalation exposure model can also be used to estimate the dose of substance taken in from the air as a result of using water for household purposes. Even though the more complex models of exposure suggested by other researchers use complicated algorithms to calculate the change of substance concentration over time [34,35], they in fact also use average values of concentrations for calculating exposure.

Eq. (4) was used to calculate reference doses (RfD) for inhalation exposure using reference concentrations (RfC) of substances [36]:

$$RfD = \frac{RfC \times IR_1}{BW} [mg/kg/day]$$
(4)

where RfC – reference concentration of substance (mg/m³), the total chronic inhalation exposure which should not result in any detrimental health effects as adopted by US DoE: RAIS [37]; IR₁ and BW – as in Eq. (3).

Eq. (4) that is usually used to establish RfD for petroleum products [36] was applied by the authors to also calculate RfD for other organic xenobiotics. It is worth noting that the available databases containing information on toxicity [37,38] for the inhalation exposure route are based on RfC values, while RfD values for the inhalation of fumes released from water containing the hazardous substances are required to assess the risk level. The authors' observations indicate that the model applied to calculations generates very restrictive RfD values, which may result in overestimating the HI_{inhal} value.

The carcinogenic hazard index (CR_{inhal}) related to the inhalation of VOCs studied was calculated using Eq. (5) [24]:

$$CR_{inhal} = PI \times SF(-)$$
(5)

where CR_{inhal} - carcinogenic hazard index related to the exposure to a given carcinogen (-); PI - pulmonary intake of a given carcinogenic substance through inhalation, average value for 70 y of life of an aggregate resident (a person potentially at risk of experiencing the carcinogenic effects of a given substance in their childhood and adult life) (mg/kg/d); SF - slope factor for inhalation exposure (so called carcinogenic substance strength coefficient) denoting an upper-bound probability of an individual developing cancer as a result of exposure to a particular substance [24] (mg/kg/d)⁻¹, SF values were taken from US EPA: IRIS Chemicals [38].

The carcinogenic hazard index was calculated for benzo(a)pyrene and benzene only. In the case of other xenobiotics carcinogenicity and toxicity data do not refer to the slope factor (SF) value for inhalation.

The cumulative total risk index (HI and CR) calculated for the analysed xenobiotics found in water was estimated for two exposure scenarios: ingestion (I) and inhalation (II) following the risk additivity principle [using Eqs. (6) and (7)]:

$$\text{Total HI} = \sum_{i=1}^{n} \text{HI}_{1}$$
(6)

$$Total CR = \sum_{i=1}^{n} CR_{1}$$
(7)

where: HI_1/CR_1 – non-carcinogenic (HI_{inhal} and HI_{oral})/carcinogenic (CR_{inhal} and CR_{oral}) risk index for one of the exposure routes; n – quantity of substances taken into consideration during risk evaluation.

An assumption was made that the xenobiotics analysed enter the human body unintentionally throughout the entire period of normal functioning within a household, both through ingestion (I) and inhalation (II).

Based on the results of the study herein and the studies published previously [23] the cumulative total hazard index for consumers of water from the public distribution system was calculated for 2 exposure scenarios - ingestion and inhalation. The worst-case scenario was used for calculations [Eqs. (1)-(7)] and analyses. It was assumed that the concentrations of the xenobiotics analysed were only an order of magnitude lower than the limit of quantitation.

The results obtained were compared with acceptable non-carcinogenic risk index $(\mathrm{HI}_{\mathrm{perm}})$ and acceptable carcinogenic risk index (CR_{perm}) of $HI_{perm} = 1$ and $CR_{perm} = E^{-6}$.

3. Results

3.1. Non-carcinogenic risk index – inhalation exposure route

The non-carcinogenic risk index (HI) calculated for adults exposed to organic xenobiotics contained in water through inhalation was 2.47E-02 (for average calculated concentration n = 18) and 2.86E-02 (for maximum values). This amounts to 2.47% and 2.86% of the permitted HI value respectively (HI_{perm}) (Table 2). The results of HI calculations for children are 2.86E-03 (for average CW values) and 3.30E-03 (for maximum concentration of substances



- (1) Benzo (a) pyrene
- (2) Benzene
- (3) Acrylamide
- (4) Epichlorohvdrin
- (5) Vinyl chloride
- (6) 1.2-Dichloroethane

Fig. 2. Share of the calculated HQ of a given xenobiotic in the total risk level (HI_{inbal}) for the inhalation route of exposure of children and adults.

Table 2

Reference doses and risk quotients for the exposure of adults to selected volatile xenobiotics (VOC) contained in water through inhalation

VOC	RfC ^a	RfD^b	MAX value			Average value		
	(mg/m³)	(mg/kg/d)	CW (mg/dm ³)	PI (mg/kg/d)	HQ _{inhal} (–)	CW (mg/dm ³)	PI (mg/kg/d)	HQ _{inhal} (–)
Benzo(a)pyrene	2.00E-06	5.00E-07	6.90E-06	1.33E-08	2.67E-02	5.96E-06	1.15E-08	2.31E-02
Benzene	3.00E-02	7.50E-03	4.99E-04	9.65E-07	1.29E-04	4.99E-04	9.65E-07	1.29E-04
Acrylamide	6.00E-03	1.50E-03	7.49E-05	1.45E-07	9.66E-05	7.49E-05	1.45E-07	9.66E-05
Epichlorohydrin	1.00E-03	2.50E-04	7.49E-05	1.45E-07	5.80E-04	6.55E-05	1.27E-07	5.07E-04
Vinyl chloride	8.00E-02	2.00E-02	1.99E-04	3.85E-07	1.92E-05	1.93E-04	3.73E-07	1.87E-05
1,2-Dichloroethane	7.00E-03	1.75E-03	9.99E-04	1.93E-06	1.10E-03	8.49E-04	1.64E-06	9.39E-04
HI _{inhal}					2.86E-02			2.47E-02

^aAccording to US DoE, RAIS: Risk Assessment Information System, http://rais.ornl.gov [37];

^bCalculated using formula no. 4;

CW - concentration of substance in water.

analysed). This amounts to 0.29% and 0.33% of the HI level considered safe respectively (Table 3). The comparison of calculated HI values demonstrates that the hazard index in adults exposed to VOC released from water is 88.46% higher than in the case of children (Table 2). The considerably higher HI value in adults stems mostly from longer potential exposure duration (ED) in the residential scenario and the daily inhalation rate (IR₁) being twice as high in adults.

When analysing the percentage share of individual xenobiotics in the total HI it was found that benzo(a) pyrene has the biggest share in the maximum inhalation exposure in the case of adults and children alike, amounting to 93.26% respectively (Fig. 2). The toxicity of this substance is further confirmed by the most restrictive RfC and RfD values of 2.00E-06 mg/m³ and 5.00E-07 mg/kg/d respectively (Table 2 and 4). The non-carcinogenic risk index for inhalation exposure (HI_{inhal}) to any of the xenobiotics studied, as well as the total non-carcinogenic hazard index, did not exceed the permissible value (HI_{perm} = 1) in children and in adults, which is a satisfactory result.

3.2. *Carcinogenic risk index – inhalation exposure route*

The calculated carcinogenic risk index (CR) related to the inhalation of fumes of benzo(a)pyrene and benzene released from water amounted to 1.74E-10 and 1.40E-09 respectively (Table 5). The total CR value for the xenobiotics analysed was 1.57E-09 which is equal to 0.16% of the permissible exposure level at 10E-06. Benzene had a considerable share in the total CR (89%), but it amounted only to 0.14% of CR_{perm} for an aggregate resident.

3.3. Cumulative total non-carcinogenic risk index – inhalation and ingestion exposure routes

The substances studied are classified as carcinogenic (benzene, vinyl chloride) and possibly carcinogenic (benzo(a)pyrene, 1,2-dichloroethane, acrylamide, epichlorohydrin) [4,5]. As mentioned before, the main routes of exposure to xenobiotics are ingestion and inhalation (through breathing atmospheric air into the lungs). Therefore, following the rule of additivity, the next step involved the estimation of the cumulative total risk index (HI) for each of the substances studied for both exposure routes – ingestion and inhalation (Table 6). When considering the two potential scenarios of exposure to the xenobiotics analysed it was demonstrated that the cumulative total HI was 5.14E-03 for children and 3.34E-02 for adults which amounts to 0.51% and 3.34% of HI_{perm}.

The non-carcinogenic risk index for inhalation exposure did not exceed the permissible value. However,

Table 3

Reference doses and risk quotients for the exposure of children to selected volatile xenobiotics contained in water through inhalation

VOC	RfC ¹⁾	RfD ²⁾	MAX value			A	verage value	
	(mg/m³)	(mg/kg/d)	CW (mg/dm ³)	Pl (mg/kg/d)	HQ _{inhal} (–)	CW (mg/dm ³)	Pl (mg/kg/d)	HQ _{inhal} (–)
Benzo(a)pyrene	2.00E-06	1.33E-06	6.90E-06	4.11E-09	3.08E-03	5.96E-06	3.55E-09	2.66E-03
Benzene	3.00E-02	2.00E-02	4.99E-04	2.97E-07	1.49E-05	4.99E-04	2.97E-07	1.49E-05
Acrylamide	6.00E-03	4.00E-03	7.49E-05	4.46E-08	1.11E-05	7.49E-05	4.46E-08	1.11E-05
Epichlorohydrin	1.00E-03	6.67E-04	7.49E-05	4.46E-08	6.69E-05	6.55E-05	3.90E-08	5.85E-05
Vinyl chloride	8.00E-02	5.33E-02	1.99E-04	1.18E-07	2.22E-06	1.93E-04	1.15E-07	2.15E-06
1,2-Dichloroethane	7.00E-03	4.67E-03	9.99E-04	5.95E-07	1.27E-04	8.49E-04	5.05E-07	1.08E-04
$\mathrm{HI}_{_{\mathrm{inhal}}}$					3.30E-03			2.86E-03

Key: See Table 2.



Fig. 3. Share of the calculated HQ_{oral} and HQ_{inhal} of a given xenobiotic in the total risk level (HI) of children (a) and adults (b).

when comparing the obtained HI to exposure values calculated for ingestion [23] it was found that there are differences between the inhalation and ingestion route. The highest share of hazard index (calculated for maximum VOC concentrations) in the case of ingestion exposure amounted to 36% and 14% (in children and in adults respectively), while in the case of inhalation exposure the share amounted to 64% and 86% respectively. These values amounted to several percent of the permissible level (HI_{perm}). The main factor responsible for the differences is the permissible dose applicable to a given exposure route which affects the HI value (Table 4).

The cumulative total risk index was influenced by the inhalation exposure risk index, especially the risk index related to the inhalation of benzo(a)pyrene (81%). When it comes to other xenobiotics (benzene, vinyl chloride, 1,2-dichloroethane, acrylamide), with the exception of epichlorohydrin, a reverse tendency was found. The risk index was lower in the case of inhalation than in the case of ingestion both in children and in adults (Fig. 3).

When comparing HI values for the selected exposure scenarios a similar relation between the age groups studied was found. The non-carcinogenic risk index was considerably lower in the case of children for both exposure routes (HI_{oral} in children amounted to about 38% of HI_{oral} in adults and HI_{inhal} in children amounted to about 12% of HI_{inhal} in adults). The main factors that influence this relation are exposure duration, that is, the age of the group analysed,

Table 4
Reference doses of selected volatile xenobiotics contained in wa-
ter taken in through inhalation (RfD _{inhal}) and ingestion (RfD _{oral})

VOC	$\mathrm{RfD}_{\mathrm{inhal}}^{a}$		$\mathrm{RfD}_{\mathrm{oral}}^{b}$
		(mg/kg/d)	
	Adults	Children	Adults and children
Benzo(a)pyrene	5.00E-07	1.33E-06	3.00E-04*
Benzene	7.50E-03	2.00E-02	4.00E-03*
Acrylamide	1.50E-03	4.00E-03	2.00E-03*
Epichlorohydrin	2.50E-04	6.67E-04	6.00E-03**
Vinyl chloride	2.00E-02	5.33E-02	3.00E-03*
1,2-Dichloroethane	1.75E-03	4.67E-03	6.00E-03**

^aRfD_{inhal} – references dose taken by inhalation;

^bRfD_{oral} – references dose taken by ingestion [23].

Data sources:

*US EPA: IRIS Chemicals, https://comptox.epa.gov [38];

**US DoE: RAIS: Risk Assessment Information System, http://rais. ornl.gov [37].

body weight and quantity of substance absorbed (related to water intake and inhalation rate), which are higher in adults than in children. Another observation made by the authors is that in the case of ingestion exposure, 1,2-dichloroethane has the highest share in the risk index in adults and in children, while benzo(a)pyrene has the highest share in the case of inhalation exposure. This confirms the impact of using different (more or less restrictive) permissible doses of substances on the risk index calculated for different substances. Although the RfD value for 1,2-dichloroethane is identical to that of epichlorohydrin (for the ingestion exposure route), the concentration of the former in water was higher. This resulted in its greater share in HI_{oral} (Table 6; [23]).

3.4. Cumulative total carcinogenic risk index – inhalation and ingestion exposure routes

The cumulative total carcinogenic risk index for the inhalation and ingestion route is presented in Table 7. The total CR_{max} was 3.08E-07 and amounted to 30.8% of the permissible value (10E-06). When comparing exposure routes, ingestion (CR_{oral}) had a greater influence on CR_{max} as it amounted to 3.07E-07. However, it is worth noting that in the case of inhalation, only benzo(a)pyrene and benzene were taken into consideration, while in the case of ingestion all the xenobiotics studied were analysed.

The substances that contributed the greatest amount of the cumulative total CR were the ingested 1,2-dichloroethane (32% of CR_{max}) and the total of the ingested and

inhaled benzene (10% of CR_{max}). CR_{oral} calculated for benzene had the biggest share (96%) in the CR_{max} value calculated for benzene. The share of benzo(a)pyrene in the carcinogenic risk index was only 2.5%, while in the case of non-carcinogenic risk index the share of this substance was 62% in children and 81% in adults. The values of both risk indexes obtained (CR, HI) amounted to just a few percent of the permissible values. This is a satisfactory result that confirms the safety of using water with the specified VOC.

4. Conclusions

Prudency requires having a complete knowledge of maximum potential risk levels that may affect water consumers even if the risk is overestimated.

- The value of estimated non-carcinogenic risk index (HI_{inhal}) related to the inhalation of fumes released from water by children amounted to 0.3% of the permissible HI value (HI_{perm}), while in adults this value was higher and amounted to 2.9% of the permissible HI value.
- Adults are at a greater risk related to VOCs. In the case of inhalation, the higher value in adults stems mostly from longer exposure duration (ED) and the daily inhalation rate (IR₁) being twice as high in adults than in children.

Table 5

Carcinogenic hazard index (CR) for inhalation of selected volatile xenobiotics contained in water

VOC	SF		MAX value			
	(mg/kg/d)	CW (mg/dm ³)	Pl (mg/kg/d)	CR (-)		
Benzo(a)pyrene	1.30E-02*	6.90E-06	1.33E-08	1.74E-10		
Benzene	1.45E-03*	4.99E-04	9.65E-07	1.40E-09		
Acrylamide	_	7.49E-05	1.45E-07	_		
Epichlorohydrin	-	7.49E-05	1.45E-07	_		
Vinyl chloride	_	1.99E-04	3.85E-07	_		
1,2-Dichloroethane	_	9.99E-04	1.93E-06	_		
Total CR				1.57E-09		

*According to: US EPA IRIS Chemicals, https://comptox.epa.gov [38];

- Not calculated.

Table 6

Total non-carcinogenic hazard index (HI) for the exposure of adults and children to selected volatile xenobiotics contained in water through inhalation (HQ_{inhal}) and ingestion (HQ_{oral})

VOC	MAX H	IQ _{oral}	MAX HQ	Q _{inhal}	MAX HI for VOC	
	Adults	Children	Adults	Children	Adults	Children
Benzo(a)pyrene	2.56E-04	9.83E-05	2.67E-02	3.08E-03	2.70E-02	3.18E-03
Benzene	1.39E-03	5.33E-04	1.29E-04	1.49E-05	1.52E-03	5.48E-04
Acrylamide	4.17E-04	1.60E-04	9.66E-05	1.11E-05	5.14E-04	1.71E-04
Epichlorohydrin	1.39E-04	5.34E-05	5.80E-04	6.69E-05	7.19E-04	1.20E-04
Vinyl chloride	7.38E-04	2.84E-04	1.92E-05	2.22E-06	7.57E-04	2.86E-04
1,2-Dichloroethane	1.85E-03	7.12E-04	1.10E-03	1.27E-04	2.95E-03	8.39E-04
HI for exposure route	4.79E-03	1.84E-03	2.86E-02	3.30E-03	3.34E-02	5.14E-03

Table 7

Total carcinogenic hazard index (CR) for the exposure to selected volatile xenobiotics contained in water through inhalation (CR_{inhal}) and ingestion (CR_{oral})

VOC	MAX CR _{oral}	MAX CR _{inhal}	MAX CR for VOC
Benzo(a)pyrene	7.68E-09	1.74E-10	7.85E-09
Benzene	3.05E-08	1.40E-09	3.19E-08
Acrylamide	4.17E-10	_	4.17E-10
Epichlorohydrin	8.25E-09	_	8.25E-09
Vinyl chloride	1.59E-07	_	1.59E-07
1,2-Dichloroethane	1.01E-07	_	1.01E-07
CR for exposure route	3.07E-07	1.57E-09	3.08E-07

- Benzo(a)pyrene (93%) in adults and in children had the highest percentage share in inhalation exposure (HI_{inhal}).
- By comparing the cumulative total non-carcinogenic risk index (HI) for ingestion (HI_{oral}) and for inhalation (HI_{inhal}) it was demonstrated that the risk for inhalation was higher than for ingestion in the case of benzo(a)pyrene and epichlorohydrin, while in the case of benzene, vinyl chloride, 1,2-dichloroethane and acrylamide the hazard index for ingestion was higher than for inhalation.
- The cumulative total risk index (HI) was influenced mostly by the inhalation exposure hazard index (64%–86%), especially that related to the inhalation of benzo(a) pyrene (81% for adults and 62% for children).
- The carcinogenic risk index for inhalation exposure (CR_{inhal}) to benzo(a)pyrene and benzene amounted to 1.57E-09 which is 0.16% of the permissible level (CR_{perm}).
- The substances that contributed the greatest amount of the total CR were 1,2-dichloroethane taken in through ingestion (32% CR_{max}) and benzene taken in through ingestion and inhalation (10% CR_{max}).
- In the case of both carcinogenic (CR) and non-carcinogenic (HI) risk indexes, the obtained values amounted to only a few percent of the permissible values applicable to potable water. This is a very satisfactory result, confirming the safety of using water supplied by water providers operating advanced treatment processes.

Abbreviations

AT	—	Averaging time, d
BW	—	Body weight, kg
CF ₂	—	Conversion factor, 1,000 dm ³ /m ³
CR	—	Carcinogenic risk index, –
CR _{perm}	—	Acceptable value for carcinogenic risk
penn		index, –
CR	—	Carcinogenic risk index for exposure
niitai		through inhalation, –
CR	—	Carcinogenic risk index for exposure
onui		through ingestion, –
CW	—	Concentration of contaminant in water,
		mg/dm ³
ED	—	Exposure duration, y
EF	—	Exposure frequency, d/y
HI	—	Non-carcinogenic hazard index, –

HI_{perm} – Acceptable value for non-carcinogenic risk index, –

$\mathrm{HI}_{\mathrm{inhal}}$	—	Total risk index for exposure through inhalation, –
HQ _{inhal 1,2,,n}	—	Risk quotient for each chemical substance, for exposure through inhalation. –
HQ_{inhal}	_	Risk quotient for each chemical substance, for exposure through inhalation –
$\mathrm{HI}_{\mathrm{oral}}$	_	Total risk index for exposure through ingestion –
$HQ_{oral 1,2,,n}$	-	Risk quotient for each chemical substance,
HQ _{oral}	_	Risk quotient for each chemical substance,
IR	_	Inhalation rate, m^3/d
K	_	Volatilization factor. –
LOO	_	Limit of quantitation, mg/dm ³
PI	_	Pulmonary intake of volatile substance
		inhaled in the form of fumes released from
		water, mg/kg/d
RfC	-	Reference concentration of substance, mg/ m ³
RfD	_	Reference dose of a chemical substance
		taken in through inhalation, mg/kg/d
US EPA	—	United States Environmental Protection
		Agency
WTP	_	Water treatment plant
WTPs	—	Water treatment plant in Świniarsko
		(Poland)
WTPss	—	Water treatment plant in Stary Sącz
		(Poland)
VOC	_	Volatile organic compound

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Conceptualization, A.K. and E.W.; Methodology, A.K. and E.W.; Formal Analysis, A.K. and E.W.; Data Curation, E.W.; Writing-Original Draft Preparation E.W., A.K.; Writing-Review & Editing, A.K. and E.W.; Visualization, E.W.; All authors have read and agreed to the published version of the manuscript. EW – 60%, A.K – 40%.

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Conflict of interest

The authors declare no conflict of interest.

References

- P. Ofman, I. Skoczko, M. Włodarczyk-Makuła, Biosorption of LMW PAHs on activated sludge aerobic granules under varying BOD loading rate conditions, J. Hazard. Mater., 418 (2021) 126332, doi: 10.1016/j.jhazmat.2021.126332.
- [2] J. Kozak, M. Włodarczyk-Makuła, Photo-oxidation of PAHs with Calcium Peroxide as a Source of the Hydroxyl Radicals, E3S Web Conf., The First Conference of the International Water Association IWA for Young Scientist in Poland "Water, Wastewater and Energy in Smart Cities", 30 (2018) 02009, doi: 10.1051/e3sconf/20183002009.
- [3] A. Kicińska, A. Gruszecka-Kosowska, Long-term changes of metal contents in two metallophyte species (Olkusz area of Zn-Pb ores, Poland), Environ. Monit. Assess., 188 (2018) 339, doi: 10.1007/s10661-016-5330-3.
- [4] US EPA, Edition of the Drinking Water Standards and Health Advisories Tables, US Environmental Protection Agency, EPA 822-F-18-00, Washington D.C., USA, 2018. Available at: https://www.epa.gov/system/files/documents/2022-01/ dwtable2018.pdf.
- [5] IARC, List of Classifications by Cancer Site, International Agency for Research on Cancer. Available at: https://monographs.iarc. fr/agents-classified-by-the-iarc and at: https://monographs. iarc.who.int/list-of-classifications
- [6] WHO, Guidelines for Drinking-Water Quality, 4th ed., Incorporating the 1st Addendum, World Health Organization, 2017. Available at: https://apo.who.int/publications/i/item/ 9789241549950
- [7] A. Kicińska, G. Caba, H. Serwatka, Ecological risk assessment related to the presence and toxicity of potentially toxic elements in ashes from household furnaces, Int. J. Environ. Res. Public Health, 19 (2021) 1770, doi: 10.3390/ijerph19031770.
- [8] Y. Tepe, A. Çebi, Acrylamide in environmental water: a review on sources, exposure, and public health risks, Exposure Health, 11 (2019) 3–12.
- [9] J. Kozak, M. Włodarczyk-Makuła, A. Popenda, Impact of aerobic stabilization of sewage sludge on PAHs concentration in reject waters, J. Ecol. Eng., 22 (2021) 27–35.
- [10] W.M. Draper, N. Li, G.M. Solomon, Y.C. Heaney, R.B. Crenshaw, R.L. Hinrichs, R.E.P. Chandrasena, Organic chemical contaminants in water system infrastructure following wildfire, ACS EST Water, 2 (2022) 357–366.
- [11] G.M. Solomon, S. Hurley, C. Carpenter, T.M. Young, P. English, P. Reynolds, Fire and water: assessing drinking water contamination after a major wildfire, ACS EST Water, 1 (2021) 1878–1886.
- [12] M. Włodarczyk-Makuła, Threat exchanged by conditions with petroleum compounds, LAB Lab. Apparatus Res., 21 (2016) 12–16 (in Polish).
- [13] E. Wiśniowska, M. Włodarczyk-Makuła, J.R. Rak, B. Tchórzewska-Cieślak, Estimation of potential health and environmental risk associated with the presence of micropollutants in water intakes located in rural areas, Desal. Water Treat., 199 (2020) 339–351.
- [14] A. Kicińska, P. Glichowska, M. Mamak, Micro- and macroelement contents in the liver of farm and wild animals and the health risks involved in liver consumption, Environ. Monit. Assess., 191 (2019) 132, doi: 10.1007/s10661-019-7274-x.
- [15] A. Kicińska, Risk Assessment of Children's Exposure to Potentially Harmful Elements (PHE) in Selected Urban Parks of the Silesian Agglomeration, E3S Web Conf., 1st International Conference on the Sustainable Energy and Environment Development (SEED 2016), 10 (2016) 00035, doi: 10.1051/ e3sconf/20161000035.
- [16] E. Wysowska, I. Wiewiórska, A. Kicińska, The impact of different stages of water treatment process on the number of selected bacteria, Water Resour. Ind., 26 (2021) 100167, doi: 10.1016/j.wri.2021.100167.

- [17] PN-EN ISO 17993: Standard Water Quality Determination of 15 Polycyclic Aromatic Hydrocarbons (PAHs) in Water by HPLC With Fluorescence Detection after Liquid–Liquid Extraction, 2005.
- [18] PN-EN ISO 15680: Water Quality Determination of Selected Monocyclic Aromatic Hydrocarbons, Naphthalene and Some Chlorinated Compounds by Gas Chromatography Using the Rinsing and Catching Technique and Thermal Desorption, 2008.
- [19] PN-EN ISO 11423-1: Standard Water quality. Determination of Benzene and Some Derivatives. Part 1: Gas Chromatography Method for Headspace Analysis, 2002.
- [20] EPA Method 8032A, 1996. Available at: https://www.epa. gov/hw-sw846/sw-846-test-method-8032a-acrylamide-gaschromatography
- [21] PN-EN 14207: Standard Water Quality. Determination of Epichlorohydrin, 2005.
- [22] PN-EN ISO 10301: Standard Water quality. Determination of Readily Volatile Halogenated Hydrocarbons. Methods Using Gas Chromatography, 2002.
- [23] E. Wysowska, A. Kicińska, Assessment of health risks with water consumption in terms of content of selected organic xenobiotics, Desal. Water Treat., 234 (2021) 1–14.
- [24] US EPA, Risk Assessment Guidance for Superfund, Vol. 1: Human Health Evaluation Manual, Part A. Interim, Final, EPA/540/1-89/002, Office of Emergency and Remedial Response, US EPA, United States Environmental Protection Agency, Washington, D.C., USA, 1989. Available at: https://www.epa. gov
- [25] A. Kicińska, E. Wysowska, Health risk related to the presence of metals in drinking water from different types of sources, Water Environ. J., 35 (2021) 27–40.
- [26] J. Ciuła, A. Generowicz, K. Gaska, A. Gronba-Chyła, Efficiency analysis of the generation of energy in a biogas CHP system and its management in a waste landfill – case study, J. Ecol. Eng., 23 (2022) 143–156.
- [27] J. Ciuła, K. Gaska, Ł. Iljuczonek, A. Generowicz, V. Koval, Energy efficiency economics of conversion of biogas from the fermentation of sewage sludge to biomethane as a fuel for automotive vehicles, Archit. Civ. Eng. Environ., 12 (2019) 131–140.
- [28] E. Wysowska, A. Kicińska, G. Nikiel, Analysis of natural vulnerability of groundwater intakes to migration of surface pollutants based on a selected part of the Dunajec River basin, Pol. J. Environ. Stud., 29 (2020) 2925–2934.
- [29] US EPA, Risk Assessment Guidance for Superfund, Vol. 1. Human Health Evaluation Manual. Part B. Development of Risk-based Preliminary Remediation Goals. Interim EPA/540R-92/003. Publication 9285.7-01B, Office of Emergency and Remedial Response, Washington, D.C., USA, 1991.
- [30] US EPA, Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, OSWER 9355, 4–24, Office of Solid Waste and Emergency Response, US EPA, Washington, D.C., USA, 2002. Available at: https://nepis.epa.gov
- [31] US EPA, Exposure Factors Handbook: 2011Edition.EPA/600/ R-090/052F, Sep. 2011. Available at: https://cfpub.epa.gov/ncea/ risk/recordisplay.cfm
- [32] L.E. Tonner-Navarro, J.L. Phelps, S.M. Roberts, C.M. Teaf, Current risk assessment approaches to address petroleum hydrocarbon mixtures in soils, Hum. Ecol. Risk Assess.: An Int. J., 4 (1998) 721–736.
- [33] J.B. Andelman, Total Exposure to Volatile Organic Compounds in Potable Water, Significance and Treatment of Volatile Organic Compounds in Water Supplies, Levis Publishers, Inc., Chelsea, Michigan, 1990, pp. 485–504.
- [34] J.C. Little, Applying the two-resistance theory to contaminant volatilization in showers, Environ. Sci. Technol., 26 (1992) 1341–1349.
- [35] T.E. McKone, J.P. Knezovich, The transfer of trichloroethylene (TCE) from a shower to indoor air: experimental measurements and their implications, J. Air Waste Manage. Assoc., 41 (1991) 282–286.
- [36] TPHCWG, Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total

Petroleum Hydrocarbons (TPH), Total Petroleum Hydrocarbon Criteria Working Group Series, Prepared by: Exxon Biomedical Chieria Working Group Series, Prepared by: Exxon Biomedical Sciences, Inc.,: D.A. Edwards, Ph.D., M.D. Andriot, Ph.D., M.A. Amoruso, Ph.D., A.C. Tummey, C.-J. Bevam, Ph.D., A. Tveit, Ph.D., L.A. Hayes, M.S., MLS, EA Engineering, Science, and Technology, Inc., S.H. Yungren, Ph.D., Remediation Technologies, Inc.,: D.V. Nakles, Ph.D. Amherst, Amherst Scientific Publishers, Massachusetss, USA, 1997.

- [37] US DoE (U.S. Department of Energy), RAIS: Risk Assessment
- [38] US EPA, IRIS Chemicals, US Environmental Protection Agency. Available at: http://rais.ornl.gov
 [38] US EPA, IRIS Chemicals, US Environmental Protection Agency. Available at: www.comptox.epa.gov/dashboard/ chemical_lists/ris
- [39] US EPA, Supplemental Guidance to RAGS: Region 4: Human Health Risk Assessment, Originally Published November 1995, 2018. Available at: https://www.epa.gov