Assessment of health risks with water consumption in terms of content of selected organic xenobiotics

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\textbf{abstract}

The study assesses the health risk for the recipients of the selected collective water supply system in terms of consuming water containing organic xenobiotics such as: benzo[\textit{a}]pyrene, polycyclic aromatic hydrocarbons, benzene, acrylamide, epichlorohydrin, vinyl chloride and 1,2-dichloroethane, which, due to their toxic, mutagenic and carcinogenic effects, pose a potential threat to human life and health. The results of water quality monitoring studies from 2012–2019 (a total of 116 concentration values were analysed from 18 water samples) conducted on treated water from the Water Treatment Plant (WTP) in southern Poland (EU), supplying water to about 100,000 inhabitants were compared with normative limits stemming from EU regulations and the US EPA and WHO recommendations. Non-carcinogenic health risk (HI) was assessed separately for adults and children under 6 years of age. In addition, carcinogenicity risk (CR) assessments were performed and safe local levels of these substances in water were estimated. The obtained values of the parameters analysed were significantly lower than the maximum allowable concentrations. The calculated HI indexes for adults were higher than those for children. The estimated carcinogenic risk was approximately 27\% of the allowable risk level. It was shown that the determined concentrations of xenobiotics present in the water analysed are safe for the health of recipients who have used the water supply system for many years.

\textbf{Keywords:} Drinking water; Carcinogenic and non-carcinogenic health risk; Benzene; PAH; benzo[\textit{a}]pyrene; Acrylamide; Epichlorohydrin; Vinyl chloride; 1,2-dichloroethane

\textbf{1. Introduction}

Right2Water – a citizens’ initiative states, just like the Water Framework Directive [1], that drinking water is a public good and extensive measures should be taken so that everyone has access to it [2]. Despite the work and actions taken to ensure one of the basic aspects of the safe existence of societies, millions of people in the world (especially in marginalised areas) still struggle with the lack of access to potable water. According to the forecasts of the United Nations and UNESCO, with the current, increasing rate of water consumption, the deficit of drinking water will affect as many as 1/3 of the humanity by 2025. This problem is exacerbated not only by the shrinking groundwater and surface water resources but also, and perhaps above all, by the progressive contamination safety of the existing water resources which can be used for human consumption. Health safety resulting from consuming water that meets quality requirements plays an enormous role in people’s lives. The collective water supply systems give residents much greater certainty in terms of the quality of the food product used, that is water, compared to uncontrolled individual water intakes, such as house wells [3]. This is due to...
the fact that water in water supply networks is subject to constant quality control.

The constantly controlled technological processes of water treatment and distribution undoubtedly contribute to the increase in the level of health safety of water recipients.

Human activity leads to the production of anthropogenic water pollutants, some of which are toxic to the human body [4–6]. Any chemical substance that is not a natural building block of the body is known as a xenobiotic. These can be organic and inorganic substances. Most of the organic xenobiotics are toxic, also carcinogenic, to humans [7]. The main routes of human exposure and absorption of xenobiotics are the oral route, that is absorption through the lungs from the air in the process of breathing (vapours of pollutants, for example paint) and the dermal route (absorption through the skin, for example with cosmetics).

Due to the significant impact of xenobiotics on the human body, a group of seven organic compounds was selected for this study, that is benzo[a]pyrene, polycyclic aromatic hydrocarbons (PAHs), benzene, acrylamide, epichlorohydrin, vinyl chloride and 1,2-dichloroethane. The content of these compounds was determined in samples of water from collective water supply systems. The paper assesses the safety of water in terms of the presence of selected chemical compounds, both in the context of non-carcinogenic and carcinogenic risk, and attempts to estimate the safe local concentration levels for these substances.

Pursuant to the Polish regulations in force, the requirements for the suitability of water for consumption are specified in the Regulation of the Minister of Health [8]. According to this legal act xenobiotics mentioned in the article undergo quality tests in treated water at least once a year (group B) and their parametric values are estimated at concentrations below which there is a low risk to human health. A similar approach in this regard is presented by the US Environmental Protection Agency (US EPA) [9,10]. According to its guidelines, the maximum concentration of chemical (MAC) substances in drinking water is defined as the concentration below which there is a low risk of negative toxic effects on the body, with average daily water consumption (different for adults and children). These levels are determined with regard to carcinogenic and non-carcinogenic effects of substances and are based on the so-called reference doses (RfD). In this study, the risk of negative health effects was assessed using the exposure assessment procedure indicated by US EPA.

1.1. Chemical properties and sources of xenobiotics in domestic water

The xenobiotics selected for the study are regarded as highly toxic, mutagenic, teratogenic, and carcinogenic to human health. In accordance with the US EPA toxicity classification [10,11], benzene and vinyl chloride are classified in group 1 – human carcinogens; benzo[a]pyrene, 1,2-dichloroethane and epichlorohydrin in group 2B – possibly carcinogens (proven carcinogenic effect in animals, but there is insufficient evidence of carcinogenicity in humans), while acrylamide is identified as probably carcinogenic to humans. According to the IRAC [12,13] carcinogenicity classification, benzene belongs to group 1, that is substances carcinogenic to humans. The potential health effects that may occur as a result of exposure to the indicated substances are presented in Table 1.

Benzo[a]pyrene \((C_{20}H_{12})\) belongs to PAHs, which are benzene homologues (Fig. 1a). Benzene \((C_6H_6)\) is an example of monochromatic hydrocarbons (Fig. 1b), whose primary source in the environment is the combustion of organic materials (including automotive fuels), coking processes, as well as tobacco smoke. The main sources of

![Fig. 1. Structural formulas of xenobiotics: (a) benzo(a)pyrene, (b) benzene, (c) acrylamide, (d) epichlorohydrin, (e) vinyl chloride, and (f) 1,2-dichloroethane.](image-url)
benzo[a]pyrene and benzene entering surface and ground-water are the so-called low emissions from the combustion of fossil fuels, especially during the heating season, and air emissions from road transport [14] and from petroleum pollutant infiltration [15–17]. Petroleum-derived compounds show the ability to accumulate in aquatic organisms, and thus pose a threat to humans [18]. Acrylamide (acrylic amide, C₃H₅NO, Fig. 1c) in household conditions is formed mainly as a result of the thermal processing of food, especially potato products [19,20]. This compound is widely used in industry as a polymer, for example, for the production of plastics and dyes. Due to its high mobility and solubility in water, the compound has a high ability to pollute surface and groundwater [21]. According to WHO data [22], the main source of acrylamide contamination of drinking water is the use of polycrylamidic flocculants in technological processes, which may contain monomers of this xenobiotic. Theoretically, a source of epichlorohydrin (C₃H₅ClO, Fig. 1d) in potable water may be the migration of this compound following the use of chemicals containing epichlorohydrin residues in flocculation processes, and its leaching from water distribution pipes (resin, epoxy coatings of pipes) [23]. Vinyl chloride (C₂H₃Cl, Fig. 1e) is relatively rarely detected in surface waters due to its high evaporation capacity (volatility) [24]. The main route of exposure is the inhalation of air containing this compound [25]. As reported by the WHO [26], 1,2-dichloroethane (C₂H₄Cl₂, Fig. 1f), which is the last of the xenobiotics analysed, is mostly present in drinking water in concentrations much lower than the amounts considered hazardous to human health.

All of the xenobiotics studied are included in the US EPA [10] and WHO [26] classifications as substances with a significant impact on human health through the consumption of drinking water. According to the Polish regulations, which reflect EU requirements, the assessment of water suitability for consumption in terms of PAH content includes testing for the content of both benzo[a]pyrene and the sum of four PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzog[h,i]perylene and indeno[1,2,3-cd]pyrene), while both US EPA [9,10] and WHO [26] guidelines provide only the content of benzo[a]pyrene in drinking water as a qualitative criterion, which has already been pointed out by Witkowski and Ślósarczyk [27].

2. Materials and methods

The subject of the analysis was the results of water quality monitoring studies from 2012 to 2019 conducted on treated water from the Water Treatment Plant (WTP) in Świniarsko and WTP in Stary Sącz, located in southern Poland (EU), supplying water to about 100,000 inhabitants.
in six municipalities in Małopolskie Voivodeship. The tests were performed in an accredited laboratory based on the following, respective standards:

- benzo[α]pyrene and PAHs: KJ-I-5.4-97 based on the PN-EN ISO 17993:2005 standard [28] and in accordance with the KJ-I-5.4-13C test procedure,
- benzene: based on the KJ-I-5.4-155 method following the PN-EN ISO 15680:2008 standard [29] and in accordance with the PN-EN ISO 11423-1:2002 standard [30],
- epichlorohydrin: in accordance with PN-EN 14207:2005 [31],
- acrylamide: based on KJ-I-5.4-94 and EPA Method 8032A [32], and in accordance with KJ-I-5.4-14C,
- 1,2-dichloroethane based on the KJ-I-5.4-155 method following the [29] and PN-EN ISO 10301: 2002 [33] standards,
- vinyl chloride: based on the KJ-I-5.4-155 method following the [29] and [32] standards.

In addition, the independent sampling and determination of the parameters analysed were carried out in 2019 in another accredited laboratory for water and wastewater testing in Krakow. For this series of tests, PAH values were determined based on the accredited test procedure WES 496 (ed. 9 of 3 September 2018). According to this method, the concentration of PAHs is the sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[g,h,]perylene, benzo[g,h,]perylene and indeno [1,2,3-c,d]pyrene levels. The method used was the determination of the multi-ring aromatic systems using a gas chromatograph coupled to a mass spectrometer (GS-MS). The sample preparation was a standard phase extraction with n-hexane, the organic fractions are dried with anhydrous sodium sulfate. The remaining sodium sulfate with the addition of 5 mL of hexane is combined into the previously obtained extract and then concentrated at 40°C to a volume of about 1 mL. Then the volume thus obtained is filtered through a column of 2 g of silica gel (previously activated and conditioned). The obtained fractions of aliphatic and monoaromatic hydrocarbons are eluted with 12 mL of n-hexane. The extracted PAHs are then eluted from the bed with 18 mL of dichloromethane. Thus the collected eluate is sequenced and concentrated and analyzed with the standard (PAH InStd) in GC-MS in Rtx-5ms columns (30 m × 0.25 mm × 0.25 µm) using helium as a carrier gas with a constant flow of 1.6581 mL/min at 300°C.

The concentration of chlorobenzenes was determined in accordance with PN-EN ISO 6468:2002 [29]. Due to the fact that the test results pertained to treated water directed to the water supply network by both WTPs, the total number of samples analysed comprised water collected at both WTPs and was treated as one set, that is no separate risk assessments were performed for each of the WTPs. The samples were collected in the years 2012–2019, on an annual basis (samples were taken once a year in April in WTPs after treatment processes (samples of water directed to the water supply network supplying residents with water for residential purposes). In 2019, there were two samplings (in April and June). A total of 18 water samples were taken directly from the WTPs. A total of 116 concentration values were analysed, of which 18 for (1) benzo[α]pyrene and (2) PAH, and 16 for (3) benzene, (4) acrylamide, (5) epichlorohydrin, (6) vinyl chloride and (7) 1,2-dichloroethane each (these parameters were not tested twice in 2019).

As part of the research, the safety of the water supplied in the collective water supply systems was assessed in terms of the presence of selected xenobiotics, taking into account the non-carcinogenic (HI) and carcinogenic (CR) risk. An exposure scenario was adopted in which most of the water entered the body through the ingestion of water, hot and cold drinks, and food. This scenario has the largest share in the level of health risk and served as the basis for further analyses.

The HI health risk associated with contaminated water ingestion was calculated according to Eq. (1) [34,35]:

$$ HI = \frac{CI}{RfD} [-] $$

where HI is the chemical substance exposure index for a given route of exposure (–); CI is the dose of a given chemical substance taken by the oral route (mg/kg d); RfD is the reference dose of a given chemical substance [mg/kg d].

The doses absorbed by the body (CI) as a result of water consumption were determined using Eq. (2) [34,35]:

$$ CI = \frac{CW \times EF \times ED \times IR}{BW \times AT} \left[ \frac{mg}{kg \times d} \right] $$

where CI is the dose of a given chemical substance taken by the oral route (mg/kg/d); CW is the substance concentration in water (mg/dm³); EF is the exposure frequency (d/y); ED is the exposure duration (y); BW is the body weight (kg); AT is the exposure averaging time (d); IR is the daily water intake rate (dm³/d), the adopted IR, was 2.5 dm³ for adults and 0.78 dm³ for children in accordance with US EPA [36]; BW is the body weight (kg), the assumed BW was 80 kg for adults and 15 kg for children [36]; AT is the exposure duration time (d), AT = 25,550 for children and adults, the average exposure time of 70 y was assumed due to the potentially carcinogenic chemicals analysed.

The reference doses (RfD) adopted were obtained from the Integrated Risk Information System (IRIS) base, except for the RfD values for epichlorohydrin and 1,2-dichloroethane, which were taken from the Risk Assessment Information System (RAIS) [37].

The carcinogenic risk index (CR) for the oral route of exposure was calculated using Eq. (3) [34]:

$$ CR = CDI \times SF [-] $$

where CR is the carcinogenic risk resulting from exposure to a given carcinogen through a given exposure route (–); CDI is the dose of carcinogenic substance taken by a given route of exposure, averaged for 70 y of human life (mg/kg d); SF is the slope factor appropriate for a given route of exposure, denoting the upper limit of the probability of neoplastic disease occurrence as a result of exposure to a given factor [34] (mg/kg d), SF values were taken from RAIS.
A safe, local level of substance concentration in water (RBRL) was estimated using Eq. (4) [10]:

$$\text{RBRL} = \frac{\text{CW} \times \text{TR}}{\text{Av.}}$$

where RBRL is the (site-specific risk-based remedial safe) safe, local concentration of a pollutant in water for oral exposure (mg/dm$^3$); CW is the pollutant concentration in water (mg/dm$^3$); TR is the target risk (carcinogenic or non-carcinogenic), HI = 1 and CR = 10$^{-4}$ were assumed; Calculated Risk (HI or CR) is the calculated for a given pollutant.

The adjustment of the local levels of the pollutants was calculated using Eq. (5) [38]:

$$\text{ARBRL} = \frac{\text{RBRL}}{n}$$

where ARBRL is the (adjusted risk-based remedial level) adjusted safe local concentration of a given pollutant in water for oral exposure (mg/dm$^3$); RBRL is the safe local concentration of a given pollutant in water for oral exposure (mg/dm$^3$); n is the number of non-carcinogenic substances causing critical effects in the same target organ/system (−); n=6.

3. Results

3.1. Water quality assessment in terms of the content of selected xenobiotics

The obtained values of the parameters studied were very low, close to the limit of quantification, for both WTPs in all years analysed (Table 2). The worst possible scenario was selected for further considerations and algorithm calculations [Eqs. (1)–(5)], assuming that the concentration of xenobiotics whose levels were below the limit of quantification was an order of magnitude lower than the lowest limit of quantification (LOQ). The laboratory tests carried out have shown that for each of the parameters the obtained concentration values are below the limit of quantification (LOQ). This means that the applied test procedure (device), although very precise, allowed the detection of a given parameter in water, without giving any information about its exact content. Due to the fact that the aim of the research work was to assess the health risk of water recipients, it was decided to adopt the most unfavorable variant, that is, the concentration of the substance by an order of magnitude lower than its lower limit of quantification (e.g., LOQ of <0.007 µg/dm$^3$), the concentration of 0.0069 µg/dm$^3$), thus assuming the measurable concentration value applicable in the calculations.

First, the test results obtained were compared with the values of the maximum allowable concentrations (MAC) for drinking water specified in (a) the Regulation of the Minister of Health [8], (b) US EPA guidelines [10], and (c) WHO recommendations [26,39]. The WHO limits are guideline values for substances that have an impact on health. When comparing the allowable concentrations of the analysed xenobiotics, recommended by the US EPA [10], which are (values in µg/dm$^3$): 0.2 for benzo[a]pyrene, 5.0 for benzene and 1,2-dichloroethane, and 2.0 for vinyl chloride, with the requirements set in the Polish regulation concerning the quality of drinking water, amounting to 0.01, 1.0, 0.5 and 3.0, respectively (values in µg/dm$^3$), it can be noted that the Polish requirements are very strict in relation to the US EPA regulations. The US EPA guidelines [10] define the limit values indicated above as achievable

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>n</th>
<th>LOQ</th>
<th>Max</th>
<th>Av.</th>
<th>MAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(µg/dm$^3$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>RMH</td>
<td>US EPA</td>
<td>WHO</td>
<td></td>
</tr>
<tr>
<td>Bezno(a)pyrene</td>
<td>18</td>
<td>7 × 10$^{-5}$ to 5 × 10$^{-3}$</td>
<td>6.90 × 10$^{-5}$</td>
<td>5.96 × 10$^{-5}$</td>
<td>0.01</td>
</tr>
<tr>
<td>Sum of PAHs</td>
<td>18</td>
<td>4 × 10$^{-2}$ to 3 × 10$^{-2}$</td>
<td>3.90 × 10$^{-2}$</td>
<td>2.62 × 10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>16</td>
<td>4 × 10$^{-1}$ to 5 × 10$^{-1}$</td>
<td>4.99 × 10$^{-1}$</td>
<td>4.99 × 10$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>16</td>
<td>7.5 × 10$^{-2}$</td>
<td>7.50 × 10$^{-2}$</td>
<td>7.49 × 10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>16</td>
<td>6 × 10$^{-2}$ to 7.5 × 10$^{-2}$</td>
<td>7.49 × 10$^{-2}$</td>
<td>6.55 × 10$^{-2}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>16</td>
<td>1.5 × 10$^{-1}$ to 2 × 10$^{-1}$</td>
<td>1.99 × 10$^{-1}$</td>
<td>1.93 × 10$^{-1}$</td>
<td>0.5</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>16</td>
<td>1.0 × 0.8</td>
<td>9.99 × 10$^{-1}$</td>
<td>8.49 × 10$^{-1}$</td>
<td>3</td>
</tr>
</tbody>
</table>

n – A total of water samples collected in the years 2012–2019;
LOQ – Limit of quantification;
Max. – Maximum value measured in the period 2012–2019;
Av. – Average value calculated for the period 2012–2019;
*US EPA (2018) and WHO (2017) guidelines do not refer to limit values for the sum of PAHs;
**according to US EPA (2018) in the case of acrylamide in drinking water, the combination of dose and monomer level must not exceed the equivalent of a polyacrylamide polymer containing 0.05% monomer in 1 mg/dm$^3$;
***according to US EPA (2018) in the case of epichlorohydrin, the combination of dose and monomer level must not exceed the equivalent of an epichlorohydrin-based polymer containing 0.01% monomer at a dose of 20 mg/dm$^3$. 

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using the best available technology (BAT), considering the cost of achieving BAT reductions an enforceable standard as well. In terms of the recommendations indicated for acrylamide and epichlorohydrin, the US EPA [10] specifies them for the dose equivalent of polyacrylamide monomer containing 0.05% monomer dosed at 1 mg/dm³ and epichlorohydrin-based polymer containing 0.01% monomer at 20 mg/dm³, respectively. It should be emphasised that for all parameters studied, the allowable values provided in the US EPA and WHO guidelines are higher than those set in the Polish regulations, except for vinyl chloride. The maximum permissible (according to the Polish regulations [8]) and recommended (according to the US EPA, WHO) levels of contamination are indicated in Table 1. These data indicate that the legal requirements in Poland in this respect are much more stringent than indicated by global guidelines. The requirements of the national Polish regulations were as follows: from 1% of the WHO guidelines to 5% of the EPA guidelines for pyrene, from 10% of the WHO guidelines to 20% of the EPA for benzene, from 6% according to the maximum values given by the WHO to 60% EPA for 1,2 dichloroethane and 20% and 33% of the maximum values for acrylamide and epichlorohydrin (no EPA guidance for these parameters).

In the present study, the average and maximum individual values of all parameters did not exceed the allowable values set in the Polish regulations [8], and US EPA [10] and WHO recommendations [26,39] (Fig. 2). Nevertheless, health concerns resulting from their accumulation in the medium supplied to the body (water) cannot be excluded.

With regard to the requirements of the Minister of Health [8], the highest share of maximum values was recorded for acrylamide and epichlorohydrin (it was about 75% of the MAC), while the lowest was for 1,2-dichloroethane (about 33% of the MAC). The obtained results of xenobiotic concentrations were compared with the acceptable levels recommended by the US EPA [10]. The recorded average values calculated for the 5-years period in relation to the American requirements [10] ranged from 3% of the MAC for benzo[a]pyrene to 17% of the MAC for 1,2-dichloroethane. The maximum concentrations of these parameters did not exceed 20% of the MAC (from 3.5% of the MAC calculated for benzo[a]pyrene, through 10% of the MAC calculated for benzene and vinyl chloride, up to 20% of the MAC calculated for 1,2-dichloroethane). In the context of the WHO recommendations [24], the highest share of the seven substances in the MAC, both in terms of the average and maximum concentrations, was found for vinyl chloride (48% and 50%, respectively) and for epichlorohydrin (22% and 25%). The lowest share was found for benzo[a]pyrene (1% MAC was obtained for both the average and maximum values).

3.2. Assessment of non-carcinogenic risk related to the presence of selected xenobiotics in drinking water

According to the guidelines of the Minister of Health [8], PAH monitoring includes the sum of the concentrations of four compounds, while according to the US EPA, reference doses (RfD) are determined for all substances belonging to the PAH group. Therefore, PAHs were not included in the risk assessment. The non-carcinogenic risk assessment for oral exposure was performed separately for adults and children. Due to the number of samples (n = 18), in accordance with the US EPA [34] recommendations, the maximum values and average estimates were used to estimate the level of health risk, thus assuming a high-risk scenario [40].

3.2.1. Assessment of adults’ exposure arising from water consumption

Doses absorbed as a result of water intake were calculated for each of the chemicals analysed (Table 3). For adults, the maximum CI doses of a chemical absorbed by the oral route ranged from 7.68 × 10⁻⁸ to 1.11 × 10⁻⁸ mg/kg/d, while the average values ranged from 6.64 × 10⁻⁸ to 9.45 × 10⁻⁸ mg/kg/d. For both parameters, extreme values were obtained for benzo[a]pyrene (lowest) and for 1,2-dichloroethane (highest), which is reflected in the concentrations of these substances determined in water.

The maximum exposure index values (HI) for the substances analysed descended in the following order: 1,2-dichloroethane (1.85 × 10⁻³) > benzene (1.39 × 10⁻³) > vinyl chloride (7.38 × 10⁻⁴) > acrylamide (4.17 × 10⁻⁴) > benzo[a]pyrene (2.56 × 10⁻⁴) > epichlorohydrin (1.39 × 10⁻⁴). The same order was observed for the average HI values: 1,2-dichloroethane (1.57 × 10⁻³) > benzene (1.39 × 10⁻³) > vinyl chloride (7.15 × 10⁻⁴) > acrylamide (4.17 × 10⁻⁴) > benzo[a]pyrene (2.21 × 10⁻⁴) > epichlorohydrin (1.22 × 10⁻⁴). For acrylamide, both the maximum and average values of HI were identical, which is reflected in the same maximum and average concentrations of this compound in the water tested and in the size of doses absorbed by the oral route. None of the substances exceeded the allowable non-carcinogenic risk limit HI<sub>allow</sub> = 1. The total maximum HI for the xenobiotics administered via the oral route for adults was 4.79 × 10⁻³, which is 0.48% of the acceptable risk value. On the other hand, the total average HI level was 4.44 × 10⁻³, which corresponds to 0.44% HI<sub>allow</sub>. The share of the maximum risk for individual parameters in relation to the allowable level ranged from 0.19% to 0.01% HI (Fig. 3).

3.2.2. Assessment of children’s exposure arising from water consumption

As was the case with adults, doses of the substances absorbed by the oral route were calculated for children. The maximum CI values of the xenobiotics ranged from 2.95 × 10⁻⁸ mg/kg/d for benzo[a]pyrene (with an average dose of 2.55 × 10⁻⁸ mg/kg/d) to 4.27 × 10⁻⁸ mg/kg/d for 1,2-dichloroethane (for an average dose of 3.63 × 10⁻⁸ mg/kg/d). Both average and maximum extreme values were obtained for benzo[a]pyrene (lowest) and for 1,2-dichloroethane (highest), which was also the case with adults. The maximum children’s exposure to the consumption of water containing the xenobiotics tested did not exceed the allowable value. The total exposure to selected xenobiotics for children was 1.83 × 10⁻³ (maximum exposure level) and 1.70 × 10⁻³ (average exposure level), which is 0.18% and 0.17% of the acceptable HI value, respectively. The order of the maximum HI risk values calculated for children for individual parameters
Fig. 2. Average concentrations (av.) in water: (a) benzo(a)pyrene, (b) PAH, (c) benzene, (d) acrylamide, (e) epichlorohydin, (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.
was as follows: 1,2-dichloroethane \( (7.12 \times 10^{-4}) \) > benzene \( (5.33 \times 10^{-4}) \) > vinyl chloride \( (2.84 \times 10^{-4}) \) > acrylamide \( (1.60 \times 10^{-4}) \) > benzo[a]pyrene \( (9.83 \times 10^{-5}) \) > epichlorohydrin \( (5.34 \times 10^{-5}) \). The order obtained for the average exposure level was the same (Table 4).

In children, just like in the case of adults, the highest share in the acceptable risk level was recorded for 1,2-dichloroethane (0.071% HI accept), while the lowest for epichlorohydrin (merely 0.005% HI accept) (Fig. 4).

When comparing the HI values of the indicated age groups, the exposure value for children was approximately 38% of the calculated risk for adults. The significantly lower level of non-carcinogenic risk for children compared to adults is most likely due to the differences in the amount of daily water consumption (adults approx. 2.5 dm³/d, children approx. 0.78 dm³/d), different body weight and exposure duration taken into account in the calculations under the adopted residential scenario. These factors have already been pointed out by, among others, Kicińska and Wysowska [41] in the risk analysis for selected metals in water from various types of intakes.

The exposure sequence of individual xenobiotics (HQ) in their maximum HI for both adults and children was identical. The maximum share of individual HQs in the total HI was found for: 1,2-dichloroethane (almost 39%), benzene (approx. 29%), and vinyl chloride (15%). The HQ for acrylamide was approx. 9%, for benzo[a]pyrene approx. 5%, and for epichlorohydrin approx. 3% of the HI was calculated for both adults and children (Fig. 5).

### Table 3

<table>
<thead>
<tr>
<th>Xenobiotic</th>
<th>RfD (mg/kg/d)</th>
<th>Max. CW (mg/dm³)</th>
<th>Cl (mg/kg/d)</th>
<th>HI</th>
<th>Av. CW (mg/dm³)</th>
<th>Cl (mg/kg/d)</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>3 \times 10^{-3}</td>
<td>6.9 \times 10^{-6}</td>
<td>7.68 \times 10^{-9}</td>
<td>2.56 \times 10^{-4}</td>
<td>5.96 \times 10^{-6}</td>
<td>6.64 \times 10^{-8}</td>
<td>2.21 \times 10^{-4}</td>
</tr>
<tr>
<td>Benzene</td>
<td>4 \times 10^{-3}</td>
<td>4.99 \times 10^{-4}</td>
<td>5.55 \times 10^{-6}</td>
<td>1.39 \times 10^{-4}</td>
<td>4.99 \times 10^{-4}</td>
<td>5.55 \times 10^{-6}</td>
<td>1.39 \times 10^{-4}</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>2 \times 10^{-3}</td>
<td>7.49 \times 10^{-4}</td>
<td>8.34 \times 10^{-7}</td>
<td>4.17 \times 10^{-4}</td>
<td>7.49 \times 10^{-4}</td>
<td>8.34 \times 10^{-7}</td>
<td>4.17 \times 10^{-4}</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>6 \times 10^{-5}</td>
<td>7.49 \times 10^{-6}</td>
<td>8.34 \times 10^{-7}</td>
<td>1.39 \times 10^{-4}</td>
<td>7.49 \times 10^{-4}</td>
<td>8.34 \times 10^{-7}</td>
<td>4.17 \times 10^{-4}</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>3 \times 10^{-3}</td>
<td>1.99 \times 10^{-4}</td>
<td>2.21 \times 10^{-6}</td>
<td>1.39 \times 10^{-4}</td>
<td>1.93 \times 10^{-4}</td>
<td>2.15 \times 10^{-6}</td>
<td>7.15 \times 10^{-4}</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>6 \times 10^{-3}</td>
<td>9.99 \times 10^{-4}</td>
<td>1.11 \times 10^{-5}</td>
<td>1.39 \times 10^{-4}</td>
<td>8.49 \times 10^{-4}</td>
<td>9.45 \times 10^{-6}</td>
<td>1.57 \times 10^{-3}</td>
</tr>
</tbody>
</table>

RfD – Reference dose of the chemical (mg/kg/d); CW – Substance concentration in water (mg/dm³); Cl – Dose of the chemical substance taken by the oral route (mg/kg/d); HI – Exposure index of the chemical for a given route of exposure; *according to US EPA (IRIS, 2020); **according to US EPA (RAIS, 2020).

![Fig. 3. The share of risk for the analyzed substances is in the acceptable level of non-carcinogenic risk for adults.](image_url)
of the highest level of carcinogenic risk (CR$_{\text{max}}$) for the parameters tested was $2.69 \times 10^{-7}$ and did not exceed the value of CR = $10^{-6}$, which is, according to the literature on the subject [9], the limit value of the acceptable risk level. The estimated CR$_{\text{max}}$ was 26.89% of the acceptable risk level. According to the US EPA [10] recommendations, the acceptable level is CR = $10^{-4}$, but the study uses a more conservative calculation variant.

The largest share in the calculated CR$_{\text{max}}$ was demonstrated for vinyl chloride (approx. 60%), 1,2-dichloroethane (38%), and benzene (11%). The share of remaining parameters in the total CR$_{\text{max}}$ ranged from 3% (benzo[a]pyrene, epichlorohydrin) to 0.2% (acrylamide).

### 3.4. Estimation of the safe concentration levels of selected xenobiotics

On the basis of the calculated non-carcinogenic risk (for adults and children) and carcinogenic risk, the acceptable and safe concentration levels (RBRL) of selected xenobiotics in water were estimated for oral exposure. Following the risk prevention principle, the least favourable results of the health risk calculated, obtained for the highest recorded concentrations of the tested substances, were adopted for the calculations.

In the case of the maximum oral exposure of adults, RBRL values in terms of non-carcinogenic risk were (data in mg/dm$^3$): $2.7 \times 10^{-2}$ for benzo[a]pyrene, $1.8 \times 10^{-1}$ for acrylamide, $2.7 \times 10^{-1}$ for vinyl chloride, $3.59 \times 10^{-1}$ for benzene, and $5.39 \times 10^{-1}$ for 1,2-dichloroethane and epichlorohydrin (Fig. 6).

For children, these were (data in mg/dm$^3$): $7 \times 10^{-2}$ for benzo[a]pyrene, $4.68 \times 10^{-1}$ for acrylamide, $7 \times 10^{-1}$ for vinyl chloride, $9.36 \times 10^{-1}$ for benzene, and 1.4 for 1,2-dichloroethane and epichlorohydrin (Fig. 7).

Table 4

<table>
<thead>
<tr>
<th>Xenobiotic</th>
<th>RfD (mg/kg/d)</th>
<th>Max. CW (mg/dm$^3$)</th>
<th>Max. Cl (mg/kg/d)</th>
<th>Max. HI CW</th>
<th>Av. CW (mg/dm$^3$)</th>
<th>Av. Cl (mg/kg/d)</th>
<th>Av. HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>$3 \times 10^{-6}$</td>
<td>$6.9 \times 10^{-6}$</td>
<td>$2.95 \times 10^{-6}$</td>
<td>$9.83 \times 10^{-5}$</td>
<td>$5.96 \times 10^{-4}$</td>
<td>$2.55 \times 10^{-4}$</td>
<td>$8.49 \times 10^{-5}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>$4 \times 10^{-3}$</td>
<td>$4.99 \times 10^{-4}$</td>
<td>$2.13 \times 10^{-6}$</td>
<td>$5.33 \times 10^{-4}$</td>
<td>$4.99 \times 10^{-4}$</td>
<td>$2.13 \times 10^{-4}$</td>
<td>$5.33 \times 10^{-4}$</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>$2 \times 10^{-3}$</td>
<td>$7.49 \times 10^{-3}$</td>
<td>$3.20 \times 10^{-7}$</td>
<td>$1.60 \times 10^{-4}$</td>
<td>$7.49 \times 10^{-5}$</td>
<td>$3.20 \times 10^{-7}$</td>
<td>$1.60 \times 10^{-4}$</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>$6 \times 10^{-3}$</td>
<td>$7.49 \times 10^{-3}$</td>
<td>$3.20 \times 10^{-7}$</td>
<td>$5.34 \times 10^{-5}$</td>
<td>$6.55 \times 10^{-5}$</td>
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<td>$4.67 \times 10^{-5}$</td>
</tr>
<tr>
<td>Vinyl chloride</td>
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<td>$1.99 \times 10^{-4}$</td>
<td>$8.51 \times 10^{-7}$</td>
<td>$2.84 \times 10^{-4}$</td>
<td>$1.93 \times 10^{-4}$</td>
<td>$8.24 \times 10^{-7}$</td>
<td>$2.75 \times 10^{-4}$</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
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<td>$9.99 \times 10^{-4}$</td>
<td>$4.27 \times 10^{-6}$</td>
<td>$7.12 \times 10^{-4}$</td>
<td>$8.49 \times 10^{-4}$</td>
<td>$3.63 \times 10^{-6}$</td>
<td>$6.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>S HI:</td>
<td></td>
<td></td>
<td></td>
<td>$1.83 \times 10^{-5}$</td>
<td></td>
<td></td>
<td>$1.70 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

RfD – Reference dose of the chemical (mg/kg/d); CW – Substance concentration in water (mg/dm$^3$); CI – Dose of the chemical substance taken by the oral route (mg/kg/d); HI – Exposure index of the chemical for a given route of exposure; *according to US EPA (IRIS, 2020); **according to US EPA (RAIS, 2020).
Table 5
Carcinogenic risk (CR) index for selected xenobiotics

<table>
<thead>
<tr>
<th>Xenobiotic</th>
<th>SF (mg/kg/d)</th>
<th>Max concentration (mg/dm³)</th>
<th>CDI_{max} (mg/kg/d)</th>
<th>CR_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>1.00 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>7.68 \times 10^{-8}</td>
<td>7.68 \times 10^{-8}</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.50 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>5.55 \times 10^{-8}</td>
<td>3.05 \times 10^{-8}</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>5.50 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>8.43 \times 10^{-7}</td>
<td>4.17 \times 10^{-7}</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>9.90 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>8.34 \times 10^{-7}</td>
<td>8.25 \times 10^{-7}</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>7.20 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>2.21 \times 10^{-6}</td>
<td>1.59 \times 10^{-6}</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>9.10 \times 10^{-14}</td>
<td>6.9 \times 10^{-6}</td>
<td>1.11 \times 10^{-5}</td>
<td>1.01 \times 10^{-5}</td>
</tr>
</tbody>
</table>

SF – Slope factor appropriate for oral exposure; CDI – Dose of a carcinogenic substance taken by a given route of exposure; *according to US EPA (IRIS, 2020); **according to US RAIS (2020).

Fig. 5. Shares of the maximum HQ of individual xenobiotics in the total HI.

Fig. 6. Share of the maximum annual concentrations of the substance in the determined safe concentration level (RBRL) for the maximum non-carcinogenic exposure (HI) for adults (oral exposure).
share in relation to RBRL was found for vinyl chloride (16%), while the lowest for acrylamide (0.04%) and benzo[a]pyrene (0.77%).

The total safe local concentrations of the xenobiotics analysed should not exceed the value of RBRL = 1.91 mg/dm$^3$ for adults, and 4.98 mg/dm$^3$ for children, while according to the requirements of the Minister of Health [8], the total MAC for the substances tested is $4.81 \times 10^{-3}$ mg/dm$^3$, which is a much lower value. However, it should be noted that the limit values set for drinking water in the Polish regulations refer to the concentration of the substance at a given moment, while the values of the calculated risk (HI, CR) and RBRL refer to the concentrations of the substance based on many years of exposure. Due to the fact that the calculated RBRL significantly differed from the Polish guidelines [8], the obtained results were adjusted. The worst variant was adopted, in which all the substances had a toxic effect on the same human organ or internal system. The adjusted safe local concentration of the substance (ABRBL) amounted to 0.32 mg/dm$^3$ for adults, and 0.83 mg/dm$^3$ for children. In the case of an additional tightening of the criteria, the obtained levels of xenobiotic concentrations were significantly below the upper limits. The total average concentrations of the xenobiotics tested in the years 2012–2019 were approx. 0.20% of ABRBL for children, and 0.53% for adults. The total maximum concentrations were 0.22% of ABRBL for children and approx. 0.58% for adults.

4. Discussion

The results of the study were compared with findings reported by other researchers. Water pollution by oil derivatives and its potential effects on health were studied by several research teams, including Zhang et al. [42], Tongo et al. [43], and Yu et al. [44]. A study by Zhang et al. [42] analysed 16 different PAHs in drinking water from selected cities in China. The average sum of the concentrations of the substances tested was $56.25 \times 10^{-1}$ ng/dm$^3$. The authors showed that the use of water from water supply systems is characterized by a lower exposure to PAH contamination. A similar study was conducted by Song et al. [45]. The authors analysed samples of water and sediments from three water treatment plants in Guangzhou (China). The calculated exposure based on
the US EPA guidelines, both total (HI) and separate for each of the PAHs (HQ), did not exceed the acceptable level (HI = 1). The carcinogenic exposure assessment also showed a negligible level of risk. An analysis of carcinogenic risk resulting from dermal contact and consumption of water contaminated with PAHs was performed by Karyab et al. [46]. The calculated carcinogenic exposure exceeded the limit proposed by the WHO, and the authors paid special attention to exposure resulting from dermal contact with contaminated water. The greatest risk of cancer was found in children aged over 16 (almost 93%). The problem of benzene in food products was discussed by Heshmati et al. [47]. These authors assessed health risk for this parameter in selected food samples from the Iranian market. Recently, the contamination of water with benzene in Texas (USA) was also investigated by the research in Lyon was conducted on raw water, however, that the results of the research described in this paper concern water directed to the water supply system, while the research in Lyon was conducted on raw water from piezometers.

5. Conclusions

Qualitative assessment in the context of health risk creates opportunities to determine the potential long-term impact of consuming treated water on the health of its recipients and to determine local achievable safe risk levels. Based on the analyses, it was found that:

- The long-term maximum and average concentrations of the xenobiotics analysed in water did not exceed the limit values set in the Polish regulations, and the WHO and US EPA guidelines.
- Comparing the recommended maximum contents of the xenobiotics analysed, it was noted that the Polish (EU) requirements are much more stringent compared to the US EPA and WHO recommendations, except for those pertaining to vinyl chloride levels in drinking water.
- The calculated maximum non-carcinogenic risk associated with drinking water for adults was $4.79 \times 10^{-3}$, corresponding to 0.48% of the acceptable risk value, and $1.83 \times 10^{-3}$ for children which is 0.18% HI$_{acc}$. The level of non-carcinogenic exposure for children was significantly lower than for adults and amounted to approx. 38% of that for adults.
- The calculated maximum potential carcinogenic risk was estimated at the level of $2.69 \times 10^{-7}$ and constituted 26.89% of the acceptable risk level.
- The largest share in the calculated non-carcinogenic risk for both adults and children was found for 1,2-dichloroethane. This parameter also showed a significant share in the calculated carcinogenic risk (approximately 30%).
- The highest level of carcinogenic exposure was reported for vinyl chloride (about 60%), and the lowest for acrylamide (0.2%).
- The determined RBRL for selected xenobiotics in water, did not exceed the actual concentrations recorded, even when the cumulative effect of the substances on the same organs of the human body was taken into account – the recorded total maximum concentrations of the xenobiotics constituted 0.22% of ARBRL for children and about 0.58% for adults.

In light of new emerging challenges for the external environment and new health threats, this subject requires more in-depth research. The obtained results confirmed that the technological processes used to ensure the safety of water provided to consumers are effective. The authors emphasise the need to continue research in order to address the issue of inhalation and dermal risks, as well as to extend the analysis to include further parameters that may affect human health. It is underlined that scientific research in the field of drinking water safety is still insufficient and requires constant updating.

Author contributions

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, A.K. and E.W.; Writing-Review & Editing, A.K. and E.W.; Visualization, A.K. and E.W.; All authors have read and agreed to the published version of the manuscript. A.K – 40%, EW – 60%.

Conflicts of interest

The authors declare no conflict of interest.

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