

Estimation of potential health and environmental risk associated with the presence of micropollutants in water intakes located in rural areas

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Received 17 February 2020; Accepted 24 April 2020

ABSTRACT

The issue of health risk assessment about drinking water was first indicated by the American National Research Council of the Academy of Sciences in 1983, whereas in the Environmental Protection Agency US EPA procedure – in 1998. Also in 1998, the issue of health risk was regulated in Council Directive of the European Union 98/83/EC on the quality of water intended for human consumption. The EU regulations were implemented into Polish legislation, which was expressed in 2007 by the publication and implementation of the Regulation of the Minister of Health on the quality of water intended for human consumption. Further changes to the regulations, both EU and national, were introduced in 2017. Currently, a lot of attention is paid, among others, to estimating health risks. The health risk is assessed based on characteristics of potential negative health effects for humans, resulting from exposure to specific harmful factors. The risk assessment procedure distinguishes hazard identification, the assessment of the dose-response relationship, the assessment of toxicity and exposure and risk characterization related to the penetration of pollutants into the body (water consumption, absorption, and inhalation). In the case of water, the risk associated with its quality is an important element in the prevention of diseases and thus has an impact on the shaping of public health. However this problem has been widely discussed concerning public drinking water supplies, the data on the quality and risk connected with the presence of organic micropollutants in the ground (well) water in rural areas. This kind of water resources is frequently intaken without control and used for various purposes. The work aimed to estimate the potential risk with selected organic micro-pollutants the most frequently found in well waters. Concentrations of these pollutants were collected from various data, toxicological data were also presented. Both health and environmental risk were calculated for the compounds identified as the most frequently present in well water. The added value of the paper is that not only toxicological data but also these on biodegradation were taken into consideration, and treatment strategies for the waters polluted by the most dangerous pollutants were proposed.

Keywords: Health risk; Environmental safety; Well water; Organic micropollutants

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1. Introduction

Control of the quality of drinking water is a key issue in public health policies. There are many approaches to the risk assessment, some of them are recommended by governmental agencies such as EPA [1–3], some are required by national laws. For example, in Poland, the legitimacy of performing health risk assessments is provided by the Regulation of the Minister of Health of December 7, 2017, on the quality of water intended for human consumption [4].

Generally, most of the currently used health risk assessment methodologies for drinking water are derived from the United States Environmental Protection Agency (US EPA) procedures that were developed for polluted environmental media. The procedures for health risk analysis and assessment were presented for the first time in 1983 (version updated in 1994) by the American National Research Council of the Academy of Sciences. In the methodologies mentioned above health risk is assessed based on the characteristics of potential negative health effects for humans (population) resulting from exposure to specific harmful factors. The steps in the procedure are hazard identification, dose-response relationship assessment, exposure assessment, and risk characteristic [1–3].

The European International Life Science Institute (ILSI) aims to create universal methods for comparing the health benefits and risks associated with water consumption. One of the main goals is to create a scientific basis that would be a base for information about benefits and risks, widely available to the public throughout the European Union. The following research and development programs are/were implemented [5–7]: risk assessment of chemicals in water, procedures for assessment of scientific support for claims on water, quality of life – integrated benefit and risk assessment, best practices in benefit-risks analysis. Each time these programs are implemented according to the scheme: methodology – building the model, case study – model testing, consensus – implementation of the model.

Although there are official procedures on health risk assessment many researchers still working on improving the methodologies. The reasons for this are that [8–10]:

- drinking water plays a very important role in the potential prevention of diseases, which makes the risk analysis necessary for public health,
- in the assessment of risk (chances and harm), there are recommendations often based on subjective judgments,
- an extremely important and characteristic feature of the benefit and risk models is the possibility of pure, that means net, determination of the impact of pollutants contained in the water on human health,
- the methods of health risk assessment and the possibilities of their practical application in the decision-making process related to the monitoring of drinking water quality are not sufficiently known in the countries.

The circumstances mentioned above make us think about the need to popularize research in this field and discuss the adoption of basic principles for health risk assessment in terms of deviations from the normative for quality of water for consumption [8–10].

It should be emphasized that risk assessment methodologies are mainly focused on higher delivery capacities and business activity. Water from individual water intakes, for example, wells in rural areas are not monitored and risk connected with the use of this kind of water is not often evaluated. Moreover, parametric evaluation of water quality is focused on biological parameters and selected physiochemical macropollutants mainly inorganic, including only selected organic micropollutants such as benzene, benzo(a)pyrene, vinyl chloride, 1,2-dichloroethane, epichlorohydrin, pesticides, trichloroethene and tetrachloroethene, total PAHs (sum of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene), indeno-1,2,3-cdperylene, trihalomethanes [4,11,12].

Whereas the assessment of the situation in the rural areas needs also to evaluate the risk connected with the presence of other micropollutants, most frequently present in drinking water from wells, such as antibiotics, pesticides, or pharmaceuticals.

The paper aimed to present the quality of water in wells from a rural area in the aspect of the pollution with the most frequently present micropollutants, and estimation of the risk both health and environmental, by various methods. The environmental risk connected with the presence of micropollutants in water from wells was evaluated by taking into consideration acute and chronic toxicity as well as susceptibility to biodegradation. Although well water had no such effect on the environment as surface one, it can be used, for example, for irrigation of ponds, and as a result, having impact also on water organisms. Data on susceptibility to biodegradation are also important in this context. That is the reason why when we consider the risk for health we should also analyze the environmental risk of the pollutants present in well water.

Moreover, for the most dangerous pollutants, treatment/removal strategies are presented.

2. Contamination of water in rural areas by organic micropollutants – concentrations and properties

About pollution of drinking water in rural areas by micropollutants is still little known. Chinese research studies on 1,300 organic micropollutants in the groundwater samples collected from 13 drinking water wells distributed across five rural regions of Liaodong Peninsula in China indicated that about 80 various micropollutants have been detected including 12 polycyclic aromatic hydrocarbons (PAHs), 11 alkanes, 9 pesticides, substituted phenols, 7 perfluoroalkyl acids, 6 heterocyclic compounds, 5 alcohols, 5 phthalic acid esters, 5 pharmaceutical and personal care products, 3 ketones, 2 polychlorinated biphenyls (PCBs), 2 alkylbenzenes, and 2 chlorinated benzenes [13]. The study on screening organic-micropollutants in groundwater made by Kong et al. [14] confirmed that in groundwater samples organic chemicals are often present. Seventy-eight organic micropollutants were found by the authors including PAHs, pesticides, plasticizers, antioxidants, pharmaceuticals, and other emerging compounds. The most frequently found chemicals were 2-ethyl-1-hexanol, 2-phenoxy-ethanol, acetophenone, pentamethylbenzene, nitrobenzene, and dimethyl phthalate. Also, such pesticides

as 1,4-dichlorobenzene, oxazolyl, diflubenzuron, carben-dazim, diuron, and dimethomorf were found, as well as naphthalene and its alkylated derivatives. The studies of Meffe and de Bustamante [15] in Italy have indicated that the most frequently present micropollutants in groundwater were the ones of industrial origin and pesticides. Antimicrobial compounds such as josamycin were found, whereas estrogens were under detection limits.

Also, Spanish research studies on groundwater contamination by organic micropollutants [16] have indicated that both in rural and industrial regions groundwater was polluted by pesticides, pharmaceuticals active compounds, some industrial compounds, drugs, estrogens, and personal care products.

In Poland, the results on the quality of groundwater can be obtained from the monitoring system made by the governmental agency Inspectorate of Environmental Protection [17]. In 2017, ninety-seven samples of groundwater in Poland were examined for 59 organic micropollutants, including mainly PAHs and pesticides. The results indicated that contaminants of the highest concentrations were PAHs: phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and benzo(1,2,3-cd)perylene. The most frequently found compound was phenanthrene with concentration up to 440 ng/L. Also, dieldrin was frequently present in groundwater samples in Poland, followed by toluene and benzene. Average concentrations of the pollutants the most frequently present at the highest concentrations in Polish groundwater as a function of time are presented in Fig. 1.

Research survey made in India [18] showed that all examined wells located nearby villages were contaminated by drugs, in several wells such drugs as ciprofloxacin, enoxacin, cetirizine, terbinafine, and citalopram were found at concentrations higher than 1 µg/L.

The research studies made by other authors have indicated that if irrigation of arable areas with wastewater occurred, sulfamethoxazole was constantly present in groundwater [19] at an average concentration of less than 5 ng/L. The highest concentrations in groundwater showed caffeine (12 ng/L), trimethoprim (7 ng/L), and cotinine

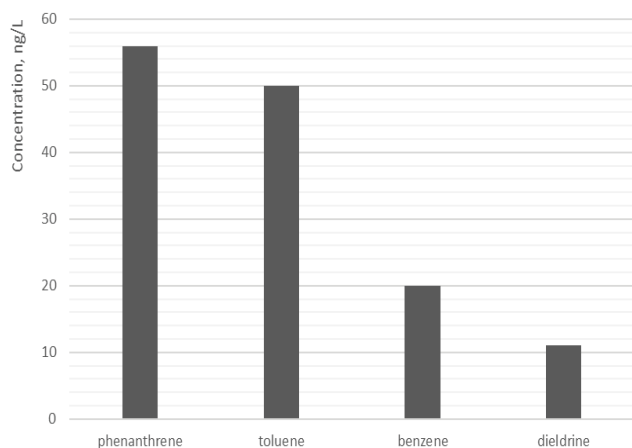


Fig. 1. Average concentrations of phenanthrene, dieldrin, toluene, and benzene in Polish groundwater in 2017 [17].

(9 ng/L). Very interesting data on the pollution of groundwater by pharmaceuticals have been given by Sui et al. [20]. They have reported that according to the data given from 2012 to 2014 the frequency of selected pharmaceuticals in groundwaters was as presented in Fig. 2. The pharmaceuticals found at the highest concentrations in groundwaters were salicylic acid, azithromycin, clofibrac acid, ibuprofen, gemfibrozil, norfloxacin, metoprolol, ofloxacin, diclofenac, and caffeine (Fig. 3).

Taking into consideration concentration and frequency of detection the following compounds were selected for further analysis: polycyclic aromatic compounds (phenanthrene, fluoranthene), pesticide (dieldrin), and pharmaceuticals (salicylic acid, sulfamethoxazole, and caffeine).

3. Toxicological properties of the contaminants the most frequently found in well water in rural areas

The physicochemical properties of the chemical compound chosen for risk analysis are presented in Table 1.

As can be seen from the data given in Table 1, the chemical compounds differ a lot in terms of their physicochemical properties, for example, from practically non-soluble in water (dieldrin) to the ones very well soluble (salicylic acid, caffeine). Such compounds as dieldrin were designed for killing insects at low concentrations. Their presence in groundwater could be especially dangerous for humans. Such compounds as caffeine or salicylic acid are not designed for killing, but act as pharmaceuticals and stimulants; as a result at low concentrations are not expected to have negative effects on humans. The last group of compounds chosen for risk analysis is selected polyaromatic hydrocarbons, which are by-products of combustion processes. A comparison of the toxicological properties of the selected compound is given in Table 2.

Compounds the most frequently present in groundwaters in wells differ a lot in terms of their chronic and acute effects on organisms. The data given in Table 2 were selected taking into consideration two aspects, toxicity for mammals (based on LD50) and toxicity for aquatic organisms (including acute and chronic effects).

From the compounds listed in Table 2, the most toxic one is dieldrin with oral LD50 for male rats equal to 46 mg/kg of body mass, followed by caffeine and salicylic acid. These data are very important, taking into consideration that both salicylic acid or its derivatives and caffeine are common ingredients of pharmaceuticals or stimulants. A comparison of acute toxicity values to the concentrations of the compounds in groundwater indicate that acute intoxication of the human via drinking water is almost impossible. The compounds mentioned above are however much more toxic for water organisms. For some of them reference concentrations were set, for example, Canadian guidelines for water protection have set a safe concentration of phenanthrene at level 0.4 µg/L and for fluoranthene at level 0.04 µg/L [50]. Phenanthrene is moreover considered as the persistent compound with a half-life in the water environment higher than 8 weeks [50].

Despite acute toxicity other side effects of the compounds are important, for example, dieldrin has been recognized as a potential carcinogen and neurotoxicant [51]

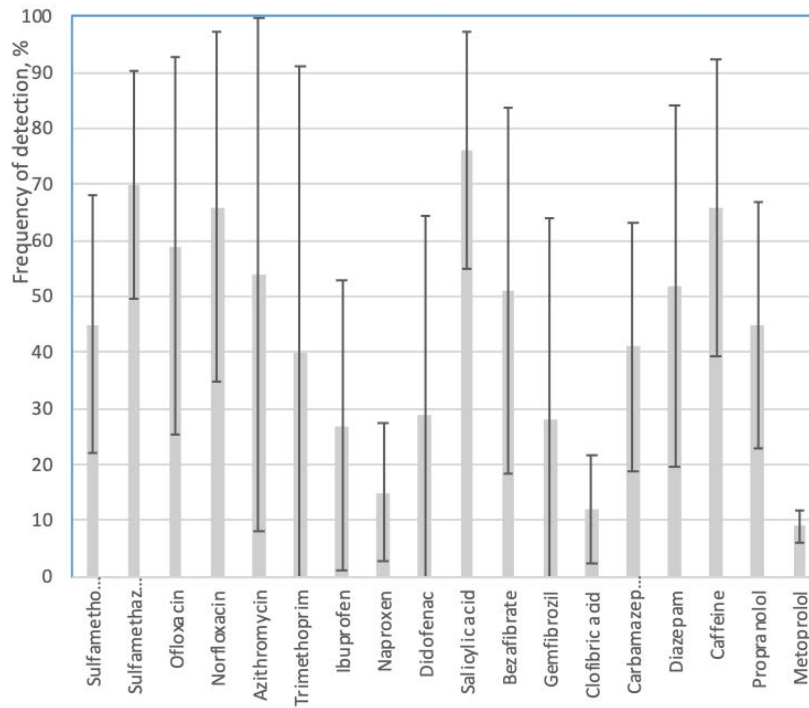


Fig. 2. Frequency of detection of selected pharmaceuticals in groundwater according to the data selected by Sui et al. [20].

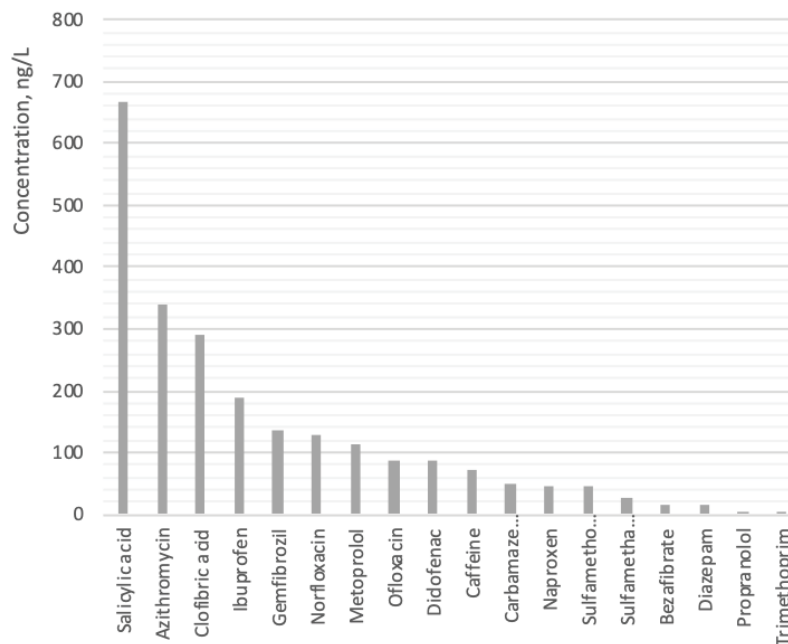


Fig. 3. Pharmaceuticals found in groundwater at the highest concentrations according to the data selected by Sui et al. [20].

whereas it shows low phytotoxicity. Its acute toxicity for aquatic organisms vary however a lot, and insects are the most sensitive group to this pesticide.

What is important salicylic acid, which is a common ingredient of medicines shows mutagenic properties, for example, causes a mutation in microorganisms *Sacchceromyces cerevisiae* at concentration 1 mmol/L/3H and inhibition of

DNA of the mouse at 100 mg/kg. It also shows teratogenic activity in rats after oral ingestion of 1,050 mg/kg (TDLo – the lowest dose causing a toxic effect) [52]. Caffeine lethal concentration for the human is at the level 80 – 100 mg/L of blood. This level can be reached if a human ingests about 10 g of caffeine, whereas one cup of coffee contains up to 150 mg of this compound [53]. Taking into consideration

Table 1
Selected physicochemical properties of the contaminants the most frequently analyzed in groundwater in rural areas [21–27]

Compound	Molecular formula	Solubility in water mg/L	LogK _{ow}	Susceptibility to hydrolysis	Boiling point, °C
Phenanthrene	C ₁₄ H ₁₀	1.6 at 15°C 1.1 at 25°C	4.46	Does not contain a group amenable to hydrolysis	340
Fluoranthene	C ₁₆ H ₁₀	0.2–0.26	5.16	Lacks functional groups that hydrolyze under environmental conditions	384
Dieldrin	C ₁₂ H ₈ Cl ₆ O	0.195 at 25°C	5.40	Hydrolysis half-life of dieldrin has been reported as greater than 4 y	330
Sulfamethoxazole	C ₁₀ H ₁₁ N ₃ O ₃ S	610 at 37°C	0.89	Did not undergo hydrolysis under field conditions	482
Salicylic acid	HOOC ₆ H ₄ COOH	2,240 at 25°C	2.26	Lack of functional groups that hydrolyze under environmental conditions	211
Caffeine	C ₈ H ₁₀ N ₄ O ₂	21,160 at 25°C	–0.07	Hydrolysis half-life of caffeine in water is reported to be >1 y	178

the average concentration of caffeine in groundwater (about 80 ng/L) lethal dose would be reached by drinking 1.25 m³ of drink. It is practically impossible. For microorganisms caffeine EC50 for activated sludge is >1,000 mg/L [26,54]. Sulfamethoxazole shows a teratogenic effect at high concentrations, equal to 533 mg/kg of body mass of rat [27].

In Table 3, the data on the susceptibility of the selected organic micropollutants to biodegradation is collected. They indicate that only caffeine is readily biodegradable in the environment and can be utilized by microorganisms as a sole source of nitrogen and energy. The remaining compounds could be readily degraded or be inherently biodegradable in the environment, for example, fluoranthene half-life time is more than 2 months, phenanthrene 306 d, dieldrin even 1,000 d. The available literature data often differ a lot, for example, under laboratory conditions sulfamethoxazole was classified as neither readily nor inherently biodegradable, but in full-scale WWTPs its removal rate was about 49%.

4. Health and environmental risk evaluation methodologies used in the study

Both health and environmental risk have been evaluated for the six chosen compounds, the most frequently present in water from wells.

4.1. Health risk estimation

The health risk was estimated based on the separate methodology for carcinogenic and non-carcinogenic compounds. In the case of non-carcinogenic compounds hazard quotient (HQ) was calculated based on chronic daily intake value and reference dose [61]:

$$HQ = \frac{CDI}{RfD} \quad (1)$$

where CDI is the chronic daily intake via ingestion with water, mg/kg of body weight/d; CDI can be calculated using the following equation:

$$CDI = \frac{(C.EF.IR.ED)}{(BW.AT)} \quad (2)$$

where C is the mean concentration of a compound in water, mg/L; EF is the exposure frequency, d/y, estimated as 365 d; IR is the ingestion rate, 2 L/d (adult, 90th percentile); ED is the exposure duration, years it was estimated as 70 y; BW is the body weight; the weight of 50% of the corresponding WHO age-weight curve was considered for 15 y old and older as 70 kg; AT is the averaging time, a period over it the exposure is averaged, d; RfD is the maximum acceptable oral dose of a toxic substance, mg/kg/d.

CDI values and reference doses for the contaminants considered in this study are listed in Table 4. Also, data on carcinogenicity are given. Of all chemicals considered in the context of health risk only one – dieldrin – has been classified as probable human carcinogen however there is no clear evidence given to support this thesis. Because of this during calculations, both non-carcinogenic and carcinogenic compounds methodology was used in the case of this compound.

The results of HQ calculations are given in Table 5.

If HQ is less than 1.0, there should be no significant risk or systemic toxicity. Ratios above 1.0 could represent a potential risk. In the study for all components, the ratio was significantly below 1.0. It means that at average concentrations of compounds present in well water there is no risk of using it for drinking purposes. It should be however emphasized that when exposure involves more than one chemical the sum of individual hazard quotients should be taken into consideration as a measure of the potential for harm. Individual micropollutants are not very harmful to human health, but if 100 or more compounds are present they can pose a serious risk. Moreover, the problem is when unexpected, high concentrations will appear in the water, however, this risk is common mainly in surface water, rarely it takes place in the case of groundwater [61].

In the case of potentially carcinogenic dieldrin also carcinogenic risk should be estimated based on incremental lifetime risk of cancer (R). To calculate it the following equation can be used [61]:

Table 2
Selected toxicological properties of the contaminants the most frequently analyzed in groundwater in rural areas [21,22,28–49]

Compound	LD ₅₀	LC ₅₀	EC ₅₀	NOEC	LOEC
Phenanthrene	700 mg/kg (mouse oral)	<100 mg/L (fish, 96 h)	0.23 mg/L <i>Pseudokirchneriella subcapitata</i>	0.082 mg/L <i>Daphnia magna</i>	0.163 mg/L <i>Daphnia magna</i>
			0.7 mg/L <i>Daphnia magna</i>	Reinbow trout	8 mg/L reinbow trout
Fluoranthene	2,000 mg/kg Rat oral	0.043 mg/L <i>Chironomus riparius</i> , larvae, 48 h 117 mg/L <i>Daphnia magna</i> , 48h 350 mg/L <i>Daphnia pulex</i> , 48 h	<i>Pseudokirchneriella subcapitata</i>	<0.06 mg/L	
			0.036 mg/L	0.013 mg/L	0.096 mg/L
			<i>Scenedesmus vacuolatus</i>	0.063 mg/L	<i>Chironomus riparius</i>
			<i>Anabaena flosaque</i>	<i>Diporeia</i> sp. 0.058 mg/L <i>Chironomus tentans</i> 0.017 mg/L	
Dieldrin	46 mg/kg mammals	0.0123 µg/L <i>Macrobrachium faustinum</i> , 96 h 0.0012 mg/L fish 0.23 mg/L <i>Daphnia magna</i> , 48 h 562.5 mg/L <i>Oryzias latipes</i> , 96 h	<i>Dario reiro</i>	0.058 µg/L <i>Macrobrachium faustinum</i>	
			1.0 mg/kg of body mass (NOEL)		
Sulfamethoxazole	2,300 mg/kg (mouse, oral)		>8 mg/L fish	132.5 µg/L <i>Bacillus stearothermophilus</i>	
			0.25 mg/L <i>Daphnia</i> sp. 0.006 mg/L algae		
Salicylic acid	480 mg/kg Oral mouse 1,300 mg/kg rabbit oral	90 mg/L <i>Leuciscus idus</i> , 48 h 460 mg/L <i>Phimephales promelas</i> , 96 h	5.6–10 mg/L <i>Daphnia</i> sp. 14 mg/L aspirin, <i>Desmodesmus subcapitatus</i>	0.004 mg/L <i>Cyprinus carpio</i>	
			724 mg/L		
			0.3 mg/L fish		
Caffeine	150–200 mg/kg (for human) 367 mg/kg (for rats)	87 mg/L <i>Leuciscus idus</i> , 96 h 395 mg/L <i>Daphnia magna</i>	0.12 mg/L	0.608 µmol/L 7 d, <i>Lemna gibba</i> – frond number	
			<i>Daphnia magna</i> , 48h <100 mg/L <i>Scenedesmus subcapitatus</i>	6.25 mg/L <i>Scenedesmus subcapitatus</i> 50–60 mg/L <i>Pimephales promelas</i>	

Table 3
Results of the biodegradation OECD test for the compounds considered in the study [55–60]

Compound	OECD biodegradation test results	Results of other biodegradation tests
Phenanthrene	In 28 d OECD test using 100 mg/L of phenanthrene and 30 mg/L of sludge 54%–67% degradation after 4 weeks based on BOD measurement – no clear results, in the first test this compound did not fulfill the criteria to be considered as readily biodegradable, in the second test it met them	Is not considered as readily biodegradable in MITI test; half-life in the environment 67 d
Fluoranthene	No data	Half-life in the environment 306 d; degradable under laboratory conditions, however it tends to persist longer in contaminated environments
Dieldrin	No data	Half-life in the environment 792–1,000 d
Sulfamethoxazole	Neither readily nor inherently biodegradable in standard OECD tests over 28 d	In full-scale working sewage treatment plants (STP) the median removal rate amounts to 49%
Salicylic acid	Inherent biodegradability; in 14 d OECD test using 100 mg/L of salicylic acid and 30 mg/L of sludge over 88% biodegradation efficiency was obtained; in an OECD guideline 301F test, salicylic acid showed a biodegradation of 94% within 28 d	No data
Caffeine	No data	Readily biodegradable in the environment, bacteria can utilize caffeine as a sole source of nitrogen, carbon, and energy for growth, however, some studies have shown the mutagenic effect of caffeine through DNA repair inhibition in bacteria

Table 4
Reference dose and CDI values for the contaminants considered within the study [62–70]

Compound	CDI values (mg/kg/d)	RfD (mg/kg/d)	Carcinogenicity	References
Phenanthrene	1.6×10^{-6}	0.03	Not classifiable as to human carcinogen	[62,63]
Fluoranthene	0.2×10^{-6}	0.04	Not classifiable as to human carcinogen	[64]
Dieldrin	0.3×10^{-6}	0.00005	Probable human carcinogen	[65]
Sulfamethoxazole	1.3×10^{-6}	0.13	No evidences for carcinogenic effects in human	[66]
Salicylic acid	19×10^{-6}	0.014	No evidences for carcinogenic effects in human	[67,68]
Caffeine	2.3×10^{-6}	0.0025	Not considered as human carcinogen	[69,70]

$$R = \text{CDI} \times \text{PF} \quad (3)$$

where CDI is the chronic daily intake, the amount of chemical at the exchange boundary, mg/kg/d; PF is the potency factor (30 in the case of dieldrin), mg kg/d.

For dieldrin, R is equal to 9×10^{-6} .

From a cancer risk standpoint, the risk over this period of exposure is at the level of 9×10^{-6} . The acceptable risk level is in the range of 1×10^{-4} [61], so the water should be safe.

4.2. Environmental risk

Environmental risk of compounds was estimated according to three procedures: EPA protocol, procedure based on susceptibility to degradation (screening of environmental risk), and Schröberl's methodology.

According to the EPA method [72], risk assessment is based on a deterministic approach or the quotient method. The deterministic approach uses risk quotient (RQ), which is calculated by dividing a point estimate of exposure by a point estimate of effects. It is necessary to collect the data on estimated environmental concentration (EEC) and compare it to the effect level, for example, LC50. This is a quite simple method to evaluate environmental risk. To calculate RQ for water organisms EC50 or LC50 values should be known and they must be compared to peak (acute RQ) or average (chronic RQ) chemical compound concentration. The lowest tested EC50 or LC50 is taken into consideration. The result of the compounds analyzed in the study is presented in Table 6. Based on the data presented in Table 6, it can be stated that taking into consideration acute RQ the toxic compounds could be ranked as follows: dieldrin,

fluoranthene, phenanthrene. Taking into consideration data concerning chronic RQ as follows: fluoranthene and phenanthrene. No data about chronic toxicity NOEC levels are available for dieldrin which making calculations for this compound difficult.

The RQ values obtained based on the calculations for the pollutants the most frequently present in well water were compared to EPA's Level of Concern (LOC). If RQ is less than LOC, it is generally regarded that the risk is acceptable. For acute and chronic RQ values LOC values are as in Table 7.

Based on the values of chronic and acute RQ it can be stated that all analyzed compounds can be considered as environmentally safe at average concentrations present in groundwater. The second test for the elimination of the most dangerous compounds of the frequently analyzed in groundwater was based on criteria given by Biziuk [74] – Table 8. This methodology could support acute and chronic RQ or PEC/PNEC calculations.

Both data on toxicity and biodegradation under environmental conditions indicate that the most dangerous of the

considered compounds were phenanthrene, anthracene, and dieldrin.

To confirm environmental risk assessment also Schröberl's method has been used for calculations of environmental risk. As a result, the values for water organisms presented in Table 9 have been obtained.

The results confirmed that in concentrations present in well water the toxicants are not environmentally dangerous ($PEC/PNEC < 1$). For terrestrial organisms, the risk will be lower because the route of contact of them with contaminants present in well water is much more hindered. More of them will be degraded or adsorbed on soil particles. Therefore risk for water organisms is sufficient to estimated environmental risk.

5. Removal possibilities of the contaminants the most frequently found in water in rural areas and the most dangerous

Phenanthrene and fluoranthene are PAHs. Their presence in well water can pose a serious risk for humans or living organisms. They have been classified by US-EPA as prominent mutagens and carcinogens and included in the list of the priority pollutants [75]. Biological methods for removal of these pollutants from well water are not applicable because of the long half-life in the environment. The preferred method should allow for removing these pollutants quickly and effectively from water. It also should be cheap and not complicated. Another factor is that the method should be flexible to achieve the preferred effects despite the variations in concentrations of the mentioned organic micropollutants. The method should be also not selective because not only aromatic hydrocarbons but also other pollutants are expected to be removed from the water.

Table 5
Results of health risk analysis of the compounds in well water (used for drinking purposes)

Compound	HQ	Carcinogenicity
Phenanthrene	5.3×10^{-5}	No
Fluoranthene	0.5×10^{-5}	No
Dieldrin	0.006	Potential carcinogen
Sulfamethoxazole	10^{-5}	No
Salicylic acid	0.001	No
Caffeine	0.0009	No

Table 6
Acute and chronic RQ values for the compounds the most frequently analysed in groundwater

Compound	Acute RQ fish	Acute RQ invertebrates	Acute RQ algae	Chronic RQ fish	Chronic RQ invertebrates	Chronic RQ algae
Phenanthrene	5.6×10^{-7}	8×10^{-7}	2.4×10^{-4}	1.1×10^{-2}	7×10^{-4}	9.3×10^{-4}
Fluoranthene	1.6×10^{-4}	5.9×10^{-8}	1.9×10^{-4}	1.9×10^{-4}	4.1×10^{-4}	5.3×10^{-4}
Dieldrin	9.2×10^{-3}	0.89	1.1×10^{-4}	No data	No data	No data
Sulfametoxazole	8×10^{-8}	5.3×10^{-7}	8.6×10^{-5}	5.6×10^{-6}	1.8×10^{-4}	7.5×10^{-3}
Salicylic acid	7.5×10^{-6}	6.5×10^{-6}	8.7×10^{-6}	2.2×10^{-3}	1.2×10^{-4}	4.8×10^{-5}
Caffeine	9.2×10^{-7}	4.4×10^{-7}	8×10^{-7}	1.6×10^{-6}	6.7×10^{-3}	1.3×10^{-5}

Table 7
LOC values for risk presumptions [73]

Risk presumption	Risk quotient (RQ)	LOC
Acute high risk	EEC/lowest EC50 or LC50	0.5
Acute restricted use	EEC/lowest EC50 or LC50	0.1
Acute endangered species	EEC/lowest EC50 or LC50	0.05
Chronic risk	EEC/lowest NOAEC or NOEC	1.0

Table 8
Criteria used for the classification of chemical compounds as dangerous for the environment [74]

Toxicity, susceptibility for biodegradation	Toxicity limits	Compounds classified as
Acute toxicity, very toxic	LC50 or EC50 (fish or crustacean) < 1 mg/L LD50 orally (rat) 25 mg/kg = or LC50 (dermal/inhalation, rat) < 0.5 g/L	Phenanthrene: EC50 <i>Daphnia magna</i> 0.7 mg/L, log K_{ow} 4.46
Acute toxic and bioaccumulative	LC50 or EC50 (fish or crustacean or algae) < 100 mg/L LD50 orally (rat) 200 mg/kg K_d for fish > 100 or log K_{ow} > 3.0	Dieldrin: LD 50 = 46 mg/kg, EC50 algae 0.1 mg/L, log K_{ow} = 5.40
Acute toxic substance, not biodegradable	LC50 or EC50 (fish or crustacean or algae) < 100 mg/L LD50 orally (rat) 200 mg/kg Negative results in 28 d OECD biodegradation test BOD/COD < 0.2	–
Potentially bioaccumulative, non-biodegradable	LC50 or EC50 (fish or crustacean or algae) < 100 mg/L LD50 orally (rat) 200 mg/kg No positive results in 28 d OECD biodegradation test BOD/COD < 0.5	–

Table 9
Environmental risk assessment based on PEC and PNEC values

Index/compound	Water organisms		
	Phenanthrene	Fluoranthene	Dieldrin
PEC mg/L	56×10^{-9}	710^{-9}	10^{-9}
PNEC mg/L	10^{-4}	3×10^{-4}	10^{-3}
PEC/PNEC	5×10^{-4}	2.3×10^{-3}	10^{-6}

As a result of treatment, no harmful by-products should be generated. The method, which meets all the requirements given above is sorption or sorption with oxidation (in the case of highly polluted water). Also, membrane methods should be considered.

In Table 10, data on effectiveness and parameters of sorption in the removal of phenanthrene and fluoranthene are listed. As can be seen from the collected data removal efficiencies of phenanthrene and fluoranthene by sorption on various adsorbents are over 80%. Individual sorption capacities for phenanthrene vary from 0.04 to over 97.4 mg/g and for fluoranthene about 0.02 mg/g. Based on the results it can be stated that under individual conditions sorbent should be chosen based on water quality (kind and concentration of pollutants).

Dieldrin removal by adsorption was investigated among others by Bandala and Octaviano [85]. It was stated that this pesticide was effectively (removal efficiency over 93%) adsorbed on activated carbon. Sorption was more effective than oxidation. As showed by Ormad et al. [86] oxidation by chlorine removed about 60% and ozonation about 70% of initial dieldrin concentration. Oxidation can be used as a preliminary step in micropollutants removal. This usually takes place in water treatment plants treating surface water. In the case of groundwater taken from wells, this will not be

effective because of the danger of by-products generation during the oxidation process. For households, oxidation equipment, that needs chemical agents is also not effective and can be considered only if high quantities of water are pumped (it will allow saving sorbent). These installations, however, undergo standards for drinking water set by national or state law. The effectiveness of membrane processes in the removal of phenanthrene, fluoranthene, and dieldrin are presented in Table 11.

In Table 12, the literature data on the effectiveness of sorption and membrane processes in the removal of pharmaceuticals are presented.

The methods of pharmaceuticals removal from water are activated carbon adsorption on granulated beds and membrane processes (UF, NF, and RO) and, in the case of wastewater treatment, membrane bioreactors MBR. The effectiveness of the membrane processes is comparable to the one obtained during sorption on activated carbon. Also, alternative sorption agents can be considered. In the individual case of using them in engineering should be chosen individually. Studies focused on the removal of PAHs using RO and NF showed the retention coefficient of PAHs in the range from 85.9% to 99%, independently of the molecular weight of a compound. This is important when we design the technology for well water treatment. According

Table 10
Removal efficiency and technical parameters of phenanthrene and fluoranthene by sorption

Compound	Type of adsorbent	Removal efficiency	HRT or contact time	Other parameters	Source
Phenanthrene	Magnetically modified rice husk biochar	up to 90%	<2 h	The maximum adsorption capacity 97.6 mg g ⁻¹ , initial concentration of phenanthrene 5–70 mg/L, 25°C	[76]
	Biochar	Up to 80%	At time lower than 2 h	Initial concentration of phenanthrene 5–70 mg/L, 25°C	[76]
	Activated carbon prepared from orange rind	Over 95%	Up to 90 min.	Adsorption capacity 70.92 mg/g	[77]
	Steel slag	No data	Up to 24 h	Maximum adsorption capacity 0.043 mg/g, initial concentration 1–5 mg/L	[78]
	<i>Sargassum hemiphyllum</i>	92%–97% removal	Up to 24 h	Initial concentration 500–1,000 µg/L, adsorption capacity 430–460 µg/g	[79]
Fluoranthene	Graphene wool	99.9%	Up to 24 h	adsorption capacity 5 mg/g	[80]
	Clinoptilolite modified with cetyl pyridinium chloride	Over 80% within 15 min. and over 93% over 24 hours	Up to 24 h	No data	[81]
	Expanded clay aggregate	Over 92%	Up to 21 h	Initial concentration 0.02 mg/L	[82]
	Zeolites modified with surfactants	Over 95%	No data	No data	[83]
	Granular activated carbon	Up to 100%	No data	Initial concentration 408 ng/L, adsorption capacity 242 mg/g	[84]

Table 11
Membrane methods efficiency in phenanthrene, fluoranthene, and dieldrin removal

Compound	Phenanthrene	Fluoranthene	Dieldrin	Reference
Ultrafiltration	up to 99%		up to 60%	[87,88]
	Micellar enhanced ultrafiltration up to 95%	–	The best separation properties are exhibited by membranes with cut-off about 1–2 kDa	[89,90]
Nanofiltration	Ultrafiltration process using amphiphilic polymer nanoparticles			
	BDXN-70 membrane, aromatic polyamide compound, >95% under optimal conditions	BDXN-70 membrane, aromatic polyamide compound, >95% under optimal conditions	up to 90% (NF-70 and NF-200B)	[91,92]
Reverse osmosis	NF90 membrane, 96%	–		
	>60% (landfill leachate)	>98%	CA membrane 99.88% NS-100 membrane 100%	[93,94] [95,96]

to literature data, the greater efficiency in the retention of PAHs is obtained for RO [97]. In the case of dieldrin – from pesticides group – it can be effectively removed from water during NF or by integrated systems of MF or NF and activated carbon adsorption (powdered or granulated) [97]. NF

shows the retention coefficient from 50% to 100% in the case of pesticides, depending on molecular weight and concentration. Also, other coupled processes should be considered, for example, the integrated system: coagulation – reverse osmosis [97,98].

Table 12
Efficiency of selected processes in pharmaceuticals removal [97–99]

Compound	Process	Parameters	Removal efficiency
Sulfamethoxazole	Sorption on powered activated carbon (PAC)	Dosage: 8–43 mg/L	2%–62%
	Membrane coupled biological processes MBR reactor	Full scale: SRT: 10–15 d; HRT: 1 d	7%–60%
	UF	Pilot scale, laboratory scale	91%–93%
	NF	Full scale	45%–94%
	NF	laboratory scale	50%–85%
Caffeine	Sorption on granulated activated carbon (GAC)	Full scale; contact time: 15 min	45%
	UF coupled with sorption on granulated activated carbon (GAC)		up to 90%
Salicylic acid	NF, RO	Laboratory scale	90%–92%

6. Conclusions

Based on the data given above, it can be concluded that:

- Organic micropollutants are often present in well water in rural areas.
- The most frequently present organic micropollutants are pesticides, hydrocarbons, and pharmaceuticals.
- At average concentrations present in groundwater, from literature data, the most frequently present compounds such as phenanthrene, naphthalene or dieldrin shall not result in it both health and environmental risk.
- Risk analysis of micropollutants in water should be based not only on acute and chronic toxicity, but also on biodegradation data.
- Methods used for micropollutants removal from well water should be simple to operate cheap and, what is very important, individually adjusted. The recommended ones should be sorption or membrane processes.

Acknowledgments

The article was supported by scientific subvention of Czestochowa University of Technology.

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