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*Original Research*

# Health Risk Assessment of Exposure to Nitrates in Drinking Water Depending on the Source of Its Origin

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## Abstract

The purpose of this study was to assess and compare selected parameters of drinking water quality monitored by state authorities and compare with water from individual ground wells not subject to official control, as well as to assess the exposure of the studied area inhabitants to nitrates, taking into account the method of treatment for the water supply. The study collected well water samples from 52 randomly selected households in Rybnik county located in south-western Poland. Nitrate concentration was determined in the tested water samples using the DR 3900 spectrophotometer. The lowest determined concentration of nitrate was; the average value was – 41.2 mg/L. This publication estimates the potential risk to human health due to consumption of drinking water from public water systems and private shallow wells in Rybnik County, Poland. In the case of well water samples HQ value was greater than 1 in 50% of samples in case of children exposure, in 40% in case of teenagers exposure and 33% in case of adults.

**Keywords**: nitrates, well water, rural areas, water quality monitoring, health risk assessment

## Introduction

According to the World Health Organization (WHO), 80% of all diseases of modern civilization are related to the quality of drinking water. It is estimated that around 840 000 people die every year in the world due to diarrhea caused by consuming contaminated drinking water or lack of access to water necessary for basic hygiene, e.g. washing dirty hands [1, 2]. Access to potable water is a fundamental right and health policy goal at a national, regional and local level [3]. Currently, the problem on a global scale is the rational management of limited water resources and protection against pollution caused by human activities. This problem applies to developing countries and those with limited water resources, in addition to more established nations [4]. Water that meets all safety conditions – specific

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microbiological requirements, as well as requirements for the content of chemical substances, is essential for drinking food preparation and personal hygiene [5, 6]. Using a local water supply system ensures access to water of adequate quality, given that water utilities must supply water that meets the requirements for drinking water and for the economy. This water is subject to constant control, monitoring and systematic assessment on the basis of applicable law [7].

The latest scientific reports, including in its scope exposure to nitrates contained in well water, mainly concern countries such as Iran, India and China. There are few publications from Europe or the United States covering this topic. According to Musacchio et al. [8], despite the European Nitrate Directive being issued almost 30 years ago, groundwater nitrate contamination is still a serious threat to ecosystems and human health. Nitrate trends over 11 years show that most regions from the Lombardy Plain (Italy) present steady or increasing concentrations, highlighting how contamination can affect supposedly resistant and resilient aquifers [8]. As reported by Chaudhuri and Mimi [9] about 30% of rural households in India had privilege to tap water sources (treated + untreated), as compared to about 70% for the urban areas. Moreover, only about 18% of rural households accessed "treated" tap water as against 62% for urban households. About 65% of rural households relied on shallow groundwater sources (well – covered and uncovered, hand pump or tube-/bore-well) compared to only about 20% for urban areas. According to Maupin et al. [10], in the USA nearly 280 million people supplied by over 170,000 public water systems benefit from regular water quality monitoring, approximately 45 million mostly rural Americans (about 14% of the population) dependent on private well water, or roughly one in every seven households, do not. The quality and safety of water from domestic wells are not regulated by the Federal Safe Drinking Water Act or, in most cases, by state laws. Instead, individual homeowners are responsible for maintaining their domestic well systems and for monitoring water quality.

In Poland, despite significant progress in the expansion of the water supply and sewage network in rural areas, a large proportion of Polish residents still use water from shallow groundwater wells. Household wells in rural areas are still often the only source of drinking water. This is mainly due to major logistical difficulties associated with connecting the house to the water supply. Often, the financial expenditures associated with taking this action exceed the economic resources of individual households. In rural areas, where household wells are often the only source of drinking water, water quality often deviates from relevant requirements [11]. This is due to the fact that waters from wells are not covered by the compulsory monitoring controls, and are not subject to any official monitoring and verification. The regulations on water quality in Poland do not include consideration of individual intake differences, and the fact that regular use of water from the household well can be an important source of exposure to many chemicals [6].

The effects from chemical drinking water contaminants differ from those associated with microbial contamination. Chemicals cause undesirable health effects as a result of short-term and long-term exposure. Nitrites cause the oxidation of divalent iron found in hemoglobin to trivalent iron, resulting in the formation of methaemoglobin, which lacks oxygen binding capacity. This causes the symptoms of so-called methaemoglobinaemia, which is due to its lack of oxygen binding capacity [12]. The toxic effects of nitrates are the most dangerous when young children are exposed to them because their blood contains fetal hemoglobin, which is more susceptible to oxidation. Nitrates (V) can transform into nitrates (III), forming toxic substances with carcinogenic effects, including nitrosamines. Nitrosamines can lead to the formation of malignant tumors of the liver, colon, lungs, pancreas, stomach, kidneys, bladder, esophagus and tongue [12, 13].

Requirements for nitrate and nitrite in drinking water are contained in the Regulation of the Minister of Health of 2017 "On the quality of water intended for human consumption" [14], and enforced by the State Sanitary Inspectors. Obligatory supervision forces monitor the water quality in Poland. As a result recipient receives water that is fit for consumption. This does not apply to recipients who obtain drinking water from private sources, because it is not subject to statutory control. Hence, it was assumed that water from domestic wells may be of poorer physical and chemical composition in relation to the water supplied by the water supply system.

The study assumed that the concentration of nitrates and nitrites in well water will be higher than in tap water, which will have a negative impact on the health of the population of people supplied with drinking water from the well. Therefore, the purpose of this work was to assess and compare selected parameters of drinking water quality monitored by state authorities and water from individual ground wells not subject to official control, as well as to assess health exposure of the studied area inhabitants to nitrates, taking into account the nature of the water supply (public versus private).

## Material and Methods

### Description of Study Area

The study carried out a chemical analysis of well water samples from 52 randomly selected domestic wells (which are not subject to mandatory monitoring) located in Rybnik County, located in the south-west of Poland (Fig. 1). Rybnik County (50°06′N, 18°31′E) covers an area of 224 km$^2$, and is inhabited by a population over 78 thousand [15].

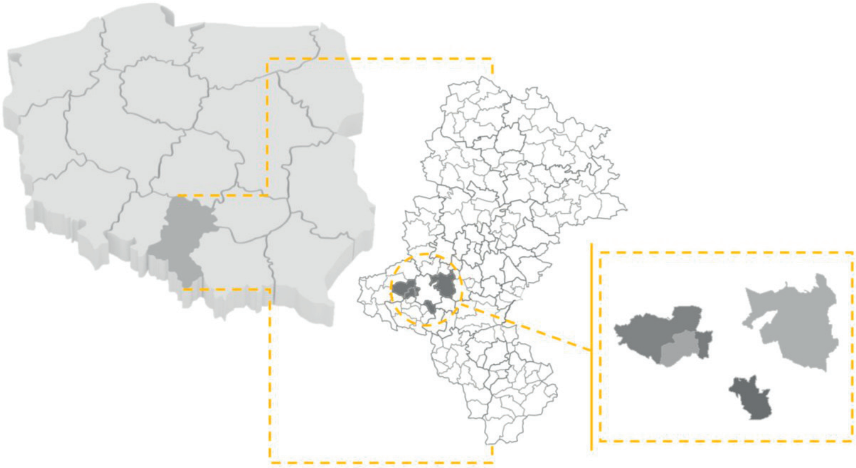

Fig. 1. Location of the Rybnik County against the background of Poland and Silesia Province.

Physicochemical analysis included determination of pH, electrical conductivity, as well as the nitrite and nitrate concentrations. In addition, the study was also based on results of drinking water testing from public systems (n = 145 samples), obtained as part of control monitoring in the years 2014-2018 in the Rybnik County. Monitoring is carried out by the District Sanitary and Epidemiological Station (DSES) in Rybnik, in accordance with applicable in Poland requirements from the Minister of Health [14].

## Sample Collection

The water samples were collected in accordance with Polish standard PN-EN ISO 5667-3:2018 "Water quality - Sampling - Part 3: Preservation and handling of water samples" [16] and PN-ISO 5667-5:2017-10 "Water quality - Sampling - Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems" [17]. According to the guidelines, the samples were collected in plastic bottles with a capacity of 2 $dm^3$ closed with plastic caps. Each time, the bottles were rinsed with the tested water and filled under the cork, pouring a small stream on the walls of the bottle (which prevents the sample from becoming aerated). Samples from individual shallow groundwater wells were taken in clean containers and delivered to the laboratory under refrigeration conditions (5±3ºC) where the analysis of selected water quality parameters was carried out.

As part of the control monitoring the results of water sample tests, covering the years 2014-2018, were obtained. The number of samples analyzed in individual years is shown in Table 1. The number of collection points and the number of samples analyzed in individual years results varied depending on the system annual water sampling plans, legal drinking water sampling guidelines, which were amended in 2015 and 2017, respectively [14, 18].

Table 1. Number of water samples (n) analyzed as part of the control monitoring in 2014-2018.

| Year | pH | Electrical conductivity | $NO_3^-$ | $NO_2^-$ |
|---|---|---|---|---|
| 2014 | 43 | 43 | 19 | 19 |
| 2015 | 42 | 35 | 17 | 17 |
| 2016 | 16 | 16 | 16 | 16 |
| 2017 | 22 | 22 | 21 | 22 |
| 2018 | 22 | 22 | 21 | 9 |

## Performed Measurements

Determination of water samples was carried out in accordance with the methodology specified by Polish standard PN-EN ISO 10523:2012 "Water quality - Determination of pH" [19]. Each well water sample was poured into three 50 $cm^3$ beakers, followed by three pH and temperature measurements. After each measurement, the pH electrode was rinsed with deionized water, and the arithmetic mean calculated from the three measurements. Both the pH measurements and the measurement of electrical conductivity were performed using a pH-meter CP-401 (Elmetron, Poland). Subsequently, 25 mL of water was added to a 50 $cm^3$ beaker and the specific electrical conductivity was measured. The results of the determinations are given in units [µS/cm]. Determination of electrical conductivity was performed using the methodology, developed from Polish standard PN-EN 27888:1999 [20].

The nitrite concentration in the tested samples was determined in accordance with the Polish standard PN-EN 26777:1999 "Water quality - Determination of nitrite - Molecular absorption spectrometric method [21]. For analysis, 40 ml were taken from each sample and transferred to a 50 ml flasks. Then 1 ml of colored reagent (sulfanilamide - $C_6H_8N_2O_2S$, phosphoric acid - $H_3PO_4$ and N-(1-Naphthyl)ethylenediamine dihydrochloride) was added. The sample was diluted with distilled water to a volume of 50 $cm^3$ and mixed. After 20 minutes the individual sample results were measured using the DR 3900 spectrophotometer (HACH, USA) at a wavelength of $\lambda$ = 540 nm. The limit of detection (LOD) and the limit of quantitation (LOQ) were 0.004 and 0.007 mg/L for nitrite, respectively.

The content of nitrates in water samples was determined in accordance with the Spectrophotometric methodology described by Polish standard PN-82/C-04576/08 [22]: 10 ml of the test sample was measured into a porcelain dish, then 2 drops of 0.5% sodium hydroxide (NaOH) solution and 1 ml of sodium salicylate ($C_6H_4COONa$) were added; the content of the porcelain dish was evaporated to dryness on a water bath. The evaporated sample was cooled and then 1 ml of concentrated sulfuric acid ($H_2SO_4$) was added. The resulting precipitate was digested using a baguette, then 20 ml of distilled water and 7 ml of alkaline sodium potassium tartrate solution were added. The content of the dish were transferred to a flask and made up with distilled water to make a total volume of 50 $cm^3$. The sample was poured into the optical cuvette and then read with an DR 3900 spectrophotometer (HACH, USA) at a wavelength of $\lambda$ = 410 nm. For both nitrate and nitrite, the reading was made relative to the reference - blank. The limit of detection (LOD) and the limit of quantitation (LOQ) were 0.007 and 0.009 mg/L for nitrate, respectively.

### Non-Carcinogens Health Risk Model

According to the US EPA, human health risk assessment is the process used to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media [23]. In the present study, the quantitative human health risk assessment for nitrate as a result of consumption of drinking water from shallow groundwater wells was estimated for residents of Rybnik County. The study population was divided into four age groups (taking into account physiological and behavioral differences): infants (<2 years), children (2 to<6 years), teenagers (6 to< 16 years) and adults ($\geq$16 years) [24, 25]. The daily exposure to nitrite or nitrate was calculated using the following formula [26]:

$$EDI = Cf \times Cd / BW$$

where: EDI – estimated daily intake (mg/kg); Cf – nitrite or nitrate concentration in drinking water (mg/L); Cd – average daily drinking water intake (L/day: 0.08 for infants, 0.85 for children, 2.00 for teenagers and 2.50 for adults); BW – body weight (kg: 10 for infants, 15 for children, 50 for teenagers and 78 for adults [24, 25, 27-29].

Using the following equation, a non-carcinogenic hazard quotient (HQ) was calculated for nitrite and nitrate [30]:

$$HQ = EDI / RfD$$

where RfD is the reference dose of a specific pollutant expressed in units of mg/kg body weight per day. The oral reference dose is based on the assumption that thresholds exist for certain toxic effects such as cellular necrosis. In general, the RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. According to the Integrated Risk Information System, RfD for nitrate is 1.6 mg/kg-day [31]. HQ is the ratio of the potential exposure to a substance compared to the concentration (mg/L) at which no adverse effects are expected (calculated as the exposure divided by the appropriate chronic or acute value). A hazard quotient lower than or equal to 1 means adverse non-cancer effects are unlikely, and thus the exposure is considered to have a negligible risk for causing an adverse effect. Hazard Quotient greater than 1 indicates a significant risk for causing non-carcinogenic effects [30]. For both nitrite and nitrate the adverse effect associated with the RfD is methemoglobinemia, a condition where the hemoglobin in the red blood cells loses its ability to bind with and transport oxygen.

## Results and Discussion

The problem of groundwater pollution by nitrate and nitrite is the subject of research around the world. Analyzes carried out in different years show that water pollution with nitrogen compounds is a common problem in various regions of the world [32-37]. Unfortunately, private wells are often places in unsuitable locations where as a result of high top soil permeability, low depth and the absence of a well protection zone, water from shallow domestic wells used for drinking has often exceeded the quality standards in terms of both physical and chemical parameters [36].

### Results of Analysis of Water Samples Taken from Domestic Wells

The pH results obtained from the analyzed water samples varied. The lowest determined pH was 5.36 when measured at a temperature of 20.8ºC, while the highest was 8.12 at a temperature of 21.0ºC. Compared to the normative values of pH 6.5-9.5, specified in the Polish Regulation [14], over 44% of all well water samples taken for testing had a pH value lower than the lower limit of normative range. Reasons for a low water pH are usually acidic rain, high content of humic acids and acid wastewater. Acid rain also leads to the acidification of surface waters, which in turn penetrate deep into the soil and pollute groundwater. The water pH also changes during the year. The biggest changes occur during the snowmelt runoff period [38]. Electrical conductivity is also an indicator of water quality, providing information on the degree of water mineralization. Water without solutes is a weak electrical conductor. Low electrical conductivity may also indicate greater purity of water. The test results for the electrical conductivity indicate that no result exceeded the permissible value, i.e. 2500 µS/cm. The results obtained range from 213 to 940 µS/cm (n = 52).

Nitrite concentrations in all tested water samples taken from domestic wells were lower than the normative value (0.5 mg/L) set out in the Regulation [14]. The average content of nitrite in the tested well water samples was 0.044±0.036 mg/L, and the highest determined concentration was 0.123 mg/L. Nitrite in drinking water is more toxic to humans than nitrate [11]. Obtaining such low values in the tested samples is therefore very beneficial and may suggest a low content of nitrite in other domestic wells, that were not tested. Nitrate was the form of nitrogen that occurred in the highest concentrations in ground water. The determined amounts of nitrate in the tested well water samples were very diverse. The lowest determined concentration was 1.1 mg/L, while the highest was as high as 194.8 mg/L. The average value for the obtained nitrate concentrations was 41.2 mg/L (n = 52). In the tested water samples, according to the Regulation [14], the normative value equal to 50 mg/L was exceeded in water samples taken from 17 domestic wells or 33% of all samples included in the study. The sample with the highest nitrate concentration was 400% higher than the normative value, with a low pH (6.21).

Studies conducted in the United States from 1941 to 1995 have shown that the cause of methaemoglobinaemia is that the concentration of nitrates in water above exceeds 10 mg/L. In the United States, the Maximum Contaminant Level (MCL) and the Maximum Contaminant Level Goal (MCLG) for nitrate is 10.0 mg/L (expressed as nitrogen) and for nitrite 1.0 mg/L (expressed as nitrogen). In turn, monthly average nitrate concentrations in England and Scotland, recorded in drinking water, were at the level of 22.94 and 2.07 mg per liter, respectively in the years 1986-1990 [39]. In British Colombia (Canada), nitrate values over 10 mg/L were reported for over 60% of 450 groundwater samples. The average concentration of nitrates in water in British Colombia is gradually increasing as the population and agricultural activity increase [33]. The results obtained from semi-arid regions of Peddavagu in Central Telangana (PCT), South India, showed that nitrate concentrations in groundwater in this region vary from 17 to 120 mg/L, with a mean of 58.74 mg/L [40]. About 57% of samples exceeded the maximum acceptable limit of Indian drinking water standard (45 mg/L) [41]. Nitrate concentration in groundwater samples, collected from Yerraguntla Mandal, South India, ranged from 2.50 to 760.12 mg/L, with a mean value of 86.13 mg/L. Most of the samples also exceeded the permissible limits of nitrate, designated in this country [42]. In the study of Sadler et al. [43] concentrations of nitrate in drinking water samples, collected from 52 drinking water wells in rural Central Java, Indonesia, had a range of 0.01-84 mg/L, a mean of 20 mg/L and a medium of 14 mg/L. Only two of the 52 samples exceeded the WHO guideline values of 50 mg/L for infant methaemoglobinaemia. The number of wells was the same as in the own study, however, in this study in 17 cases (33% of all samples) the value of 50 mg/L was exceeded. Barakat et al. [44] results from Morocco showed that the nitrate content of groundwater fall between 0 and 82.08 mg/L (mean 24.73 mg/L), with 38.10% of groundwater samples exceed the Moroccan and WHO limits for drinking. Average nitrate levels in groundwater in most European countries have been stable at around 17.5 mg/L. Average concentrations are lowest in Finland (around 1 mg/L) and highest in Malta (58.1 mg/L) [45]. Comparing own results with the results of other authors, the mean concentration of nitrates in the water in individual countries was as follows: India > Malta > Poland > Morocco > England > Indonesia > Canada > Scotland > Finland.

## Results of the Analysis of Water Samples from the Water Supply Network Obtained from the Sanitary-Epidemiological Station

Results of drinking water quality tests carried out in 2014-2018 as part of the control monitoring by District Sanitary and Epidemiological Station in Rybnik is presented in Fig. 2. Among the analyzed parameters, exceeding the normative values was noted twice for pH and five times for nitrate concentration. The determined nitrate showed the largest differences between the minimum and maximum values. Similar differences were also observed in the results of the nitrate content obtained in the study of well waters in Rybnik County. The highest, average nitrate concentration was recorded at 57.8 mg/L for water samples collected in 2015 (Fig. 2). In the case of the nitrite concentration and specific electrical conductivity, no exceedances of limit values [14] were reported. The average values for electrical conductivity in water samples from the water supply system taken in the years 2014-2018 ranged from 352 to 410 µS/cm. The highest value for electrical conductivity was recorded in 2016 (1026 µS/cm), and is within the range of the norm specified in the Regulation [14] which is equal to 2500 µS/cm (Fig. 2).

## Drinking Water Quality Differences between the Public Water Systems and Private Wells Based on the 2018 Data

The results indicate that there are significant differences between the average, maximum and minimum values obtained for pH and nitrate. For

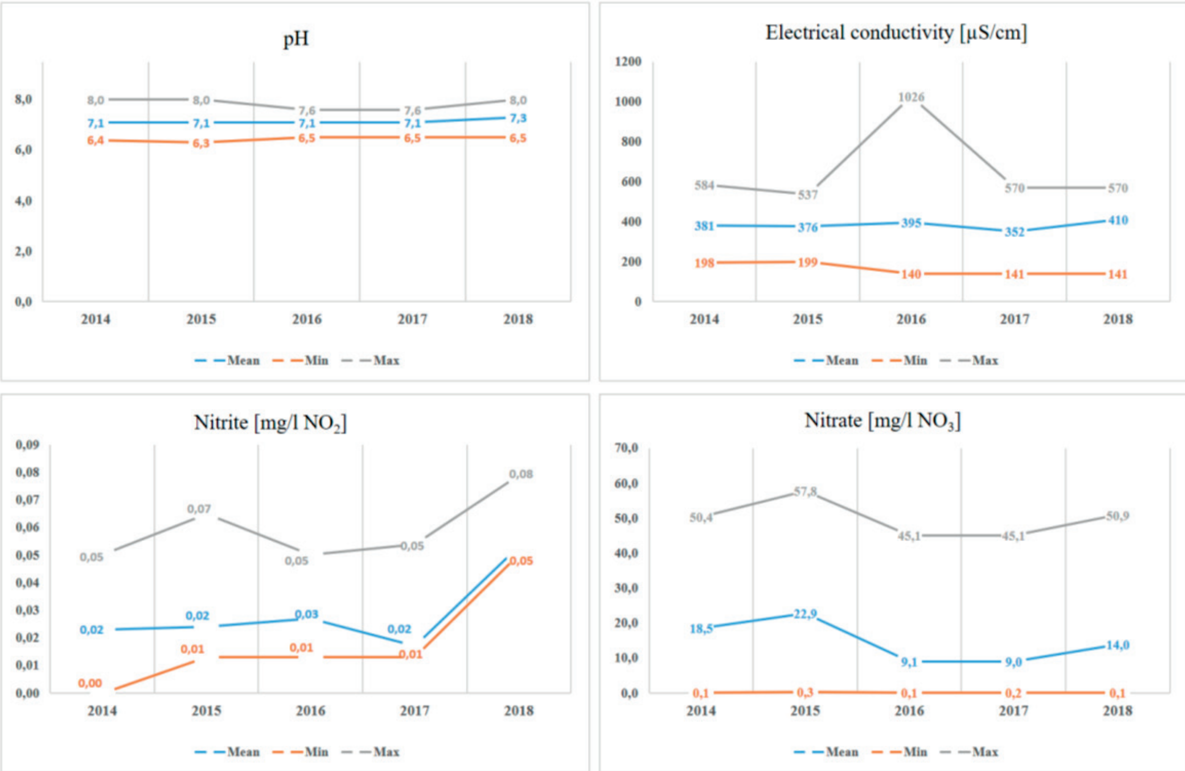


Fig. 2. Drinking water quality parameters analyzed in the water samples covered by monitoring in the years 2014-2018.

Public Water System water samples taken as part of the required monitoring program, the average value for the pH was 7.3, while for samples taken from domestic wells it was 6.5. In both cases the value falls within the lower range of the value allowed by the Regulation [14]. The minimum pH values obtained for samples from the public water supply system and private wells were 6.5 and 5.4 respectively. The biggest difference between water from the water supply and water taken from private wells was noted in the case of nitrate. The highest recorded concentration of these compounds, determined in water samples taken from wells, exceeded the normative value almost 4 times, however, according to the applicable law, water from private wells is not subject to official control (Table 2).

Table 2. Comparison of basic descriptive statistics for the results of the analysis of tap water samples covered by control monitoring and well water samples.

| Parameter | Mean | Min | Max | SD |
|---|---|---|---|---|
| pH | | | | |
| Tap water | 7.3 | 6.5 | 8.0 | 0.42 |
| Well water | 6.5 | 5.4 | 8.1 | 0.57 |
| Electrical conductivity [µS/cm] | | | | |
| Tap water | 410 | 141 | 570 | 143.2 |
| Well water | 534 | 213 | 940 | 147.7 |
| $NO_3^-$ [mg/L] | | | | |
| Tap water | 14.0 | 0.1 | 50.9 | 19.9 |
| Well water | 41.2 | 1.1 | 194.8 | 38.1 |
| $NO_2^-$ [mg/L] | | | | |
| Tap water | 0.053 | 0.050 | 0.079 | 0.010 |
| Well water | 0.044 | <LOQ | 0.123 | 0.036 |

## Human Health Risk Assessment

Detailed concentration values determined in well water samples and results obtained for EDI and HQ are presented in Table 3. The HQ values obtained in the studied groups increased in the following order children>teenagers>adults>infants. HQ value was greater than 1 for 50% of samples in case of children exposure (26 samples), in 40% in case of teenagers exposure (21 samples) and 33% in case of adults (17 samples). For infants, HQ reached 1 in only one case. It is worth noting that in 9 cases the HQ value (mostly in children but also in teenagers group) was greater than 1 despite the fact that the maximum permissible level of nitrates was not exceeded (Table 3; samples No. 6,8,14,15,22,24,25,27,30). For the samples in question, the nitrate content was between 31.0 and 44.3 mg/L. Taking into account the average, minimum and maximum values as well as the standard deviation obtained for individual nitrate concentrations, the EDI and HQ were calculated and compared for tap and well water samples (Table 4). Considering the maximum HQ value obtained for well and tap water, in all groups except infants the HQ value was greater than 1 (Fig. 3). However, in the case of well water and the infants group, the HQ value was on the border (0.97). For well water, HQ>1 was also noted for the mean and SD value for the group of children and teenagers (Mean: 1.47 and 1.04, SD: 1.5 and 1.10, respectively). For tap water, no other maximum HQ value was greater than 1 in all consumer

Table 3. Nitrate concentrations, estimated daily intake and hazard quotient for four groups of well water consumers.

| No. | $NO_3^-$ [mg/L] | EDI [mg/kg] | | | | HQ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Infants | Children | Teenagers | Adults | Infants | Children | Teenagers | Adults |
| 1 | 15.9 | 0.127 | 0.901 | 0.636 | 0.510 | 0.1 | 0.6 | 0.4 | 0.3 |
| 2 | 64.2 | 0.514 | 3.638 | 2.568 | 2.058 | 0.3 | 2.3 | 1.6 | 1.3 |
| 3 | 88.6 | 0.709 | 5.021 | 3.544 | 2.840 | 0.4 | 3.1 | 2.2 | 1.8 |
| 4 | 70.8 | 0.566 | 4.012 | 2.832 | 2.269 | 0.4 | 2.5 | 1.8 | 1.4 |
| 5 | 6.2 | 0.050 | 0.351 | 0.248 | 0.199 | 0.0 | 0.2 | 0.2 | 0.1 |
| 6 | 44.3 | 0.354 | 2.510 | 1.772 | 1.420 | 0.2 | 1.6 | 1.1 | 0.9 |
| 7 | 1.8 | 0.014 | 0.102 | 0.072 | 0.058 | 0.0 | 0.1 | 0.0 | 0.0 |
| 8 | 44.3 | 0.354 | 2.510 | 1.772 | 1.420 | 0.2 | 1.6 | 1.1 | 0.9 |
| 9 | 53.1 | 0.425 | 3.009 | 2.124 | 1.702 | 0.3 | 1.9 | 1.3 | 1.1 |
| 10 | 26.6 | 0.213 | 1.507 | 1.064 | 0.853 | 0.1 | 0.9 | 0.7 | 0.5 |
| 11 | 93.0 | 0.744 | 5.270 | 3.720 | 2.981 | 0.5 | 3.3 | 2.3 | 1.9 |
| 12 | 1.1 | 0.009 | 0.062 | 0.044 | 0.035 | 0.0 | 0.0 | 0.0 | 0.0 |
| 13 | 22.1 | 0.177 | 1.252 | 0.884 | 0.708 | 0.1 | 0.8 | 0.6 | 0.4 |
| 14 | 35.4 | 0.283 | 2.006 | 1.416 | 1.135 | 0.2 | 1.3 | 0.9 | 0.7 |
| 15 | 44.3 | 0.354 | 2.510 | 1.772 | 1.420 | 0.2 | 1.6 | 1.1 | 0.9 |
| 16 | 62.0 | 0.496 | 3.513 | 2.480 | 1.987 | 0.3 | 2.2 | 1.6 | 1.2 |
| 17 | 70.8 | 0.566 | 4.012 | 2.832 | 2.269 | 0.4 | 2.5 | 1.8 | 1.4 |
| 18 | 70.8 | 0.566 | 4.012 | 2.832 | 2.269 | 0.4 | 2.5 | 1.8 | 1.4 |
| 19 | 22.1 | 0.177 | 1.252 | 0.884 | 0.708 | 0.1 | 0.8 | 0.6 | 0.4 |
| 20 | 26.6 | 0.213 | 1.507 | 1.064 | 0.853 | 0.1 | 0.9 | 0.7 | 0.5 |
| 21 | 194.8 | 1.558 | 11.039 | 7.792 | 6.244 | 1.0 | 6.9 | 4.9 | 3.9 |
| 22 | 35.4 | 0.283 | 2.006 | 1.416 | 1.135 | 0.2 | 1.3 | 0.9 | 0.7 |
| 23 | 79.7 | 0.638 | 4.516 | 3.188 | 2.554 | 0.4 | 2.8 | 2.0 | 1.6 |
| 24 | 31.0 | 0.248 | 1.757 | 1.240 | 0.994 | 0.2 | 1.1 | 0.8 | 0.6 |
| 25 | 39.9 | 0.319 | 2.261 | 1.596 | 1.279 | 0.2 | 1.4 | 1.0 | 0.8 |
| 26 | 88.6 | 0.709 | 5.021 | 3.544 | 2.840 | 0.4 | 3.1 | 2.2 | 1.8 |
| 27 | 35.4 | 0.283 | 2.006 | 1.416 | 1.135 | 0.2 | 1.3 | 0.9 | 0.7 |

Table 3. Continued.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 28 | 26.6 | 0.213 | 1.507 | 1.064 | 0.853 | 0.1 | 0.9 | 0.7 | 0.5 |
| 29 | 8.9 | 0.071 | 0.504 | 0.356 | 0.285 | 0.0 | 0.3 | 0.2 | 0.2 |
| 30 | 44.3 | 0.354 | 2.510 | 1.772 | 1.420 | 0.2 | 1.6 | 1.1 | 0.9 |
| 31 | 119.6 | 0.957 | 6.777 | 4.784 | 3.833 | 0.6 | 4.2 | 3.0 | 2.4 |
| 32 | 13.3 | 0.106 | 0.754 | 0.532 | 0.426 | 0.1 | 0.5 | 0.3 | 0.3 |
| 33 | 26.6 | 0.213 | 1.507 | 1.064 | 0.853 | 0.1 | 0.9 | 0.7 | 0.5 |
| 34 | 66.4 | 0.531 | 3.763 | 2.656 | 2.128 | 0.3 | 2.4 | 1.7 | 1.3 |
| 35 | 10.6 | 0.085 | 0.601 | 0.424 | 0.340 | 0.1 | 0.4 | 0.3 | 0.2 |
| 36 | 5.3 | 0.042 | 0.300 | 0.212 | 0.170 | 0.0 | 0.2 | 0.1 | 0.1 |
| 37 | 57.6 | 0.461 | 3.264 | 2.304 | 1.846 | 0.3 | 2.0 | 1.4 | 1.2 |
| 38 | 8.9 | 0.071 | 0.504 | 0.356 | 0.285 | 0.0 | 0.3 | 0.2 | 0.2 |
| 39 | 12.8 | 0.102 | 0.725 | 0.512 | 0.410 | 0.1 | 0.5 | 0.3 | 0.3 |
| 40 | 20.4 | 0.163 | 1.156 | 0.816 | 0.654 | 0.1 | 0.7 | 0.5 | 0.4 |
| 41 | 5.3 | 0.042 | 0.300 | 0.212 | 0.170 | 0.0 | 0.2 | 0.1 | 0.1 |
| 42 | 5.3 | 0.042 | 0.300 | 0.212 | 0.170 | 0.0 | 0.2 | 0.1 | 0.1 |
| 43 | 1.8 | 0.014 | 0.102 | 0.072 | 0.058 | 0.0 | 0.1 | 0.0 | 0.0 |
| 44 | 18.6 | 0.149 | 1.054 | 0.744 | 0.596 | 0.1 | 0.7 | 0.5 | 0.4 |
| 45 | 8.9 | 0.071 | 0.504 | 0.356 | 0.285 | 0.0 | 0.3 | 0.2 | 0.2 |
| 46 | 1.3 | 0.010 | 0.074 | 0.052 | 0.042 | 0.0 | 0.0 | 0.0 | 0.0 |
| 47 | 21.3 | 0.170 | 1.207 | 0.852 | 0.683 | 0.1 | 0.8 | 0.5 | 0.4 |
| 48 | 7.1 | 0.057 | 0.402 | 0.284 | 0.228 | 0.0 | 0.3 | 0.2 | 0.1 |
| 49 | 18.6 | 0.149 | 1.054 | 0.744 | 0.596 | 0.1 | 0.7 | 0.5 | 0.4 |
| 50 | 115.1 | 0.921 | 6.522 | 4.604 | 3.689 | 0.6 | 4.1 | 2.9 | 2.3 |
| 51 | 93.0 | 0.744 | 5.270 | 3.720 | 2.981 | 0.5 | 3.3 | 2.3 | 1.9 |
| 52 | 57.6 | 0.461 | 3.264 | 2.304 | 1.846 | 0.3 | 2.0 | 1.4 | 1.2 |

groups (Table 4, Fig. 4). According to results obtained, long-term exposure to nitrate through consumption of well water increases the likelihood of non-carcinogenic risk, and the exposure to nitrate in the exposed population is not safe during the present study period.

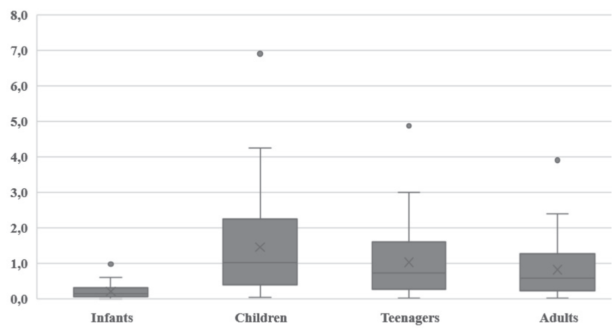


Fig. 3. Distribution of nitrate exposure for four groups of water consumers (based on HQ).

Water used for drinking should not pose a risk to human health. The nitrate exposure assessment reported in this study indicates that water collected from domestic wells is a significant health risk, especially for children (HQ = 6.90) and adolescents (HQ = 4.87). The same situation, i.e. the highest, was recorded in the study of groundwater collected in rural areas in Iran. However, the calculated HQ values were at a significantly lower level than the results reported in this work (1.74 and 1.23, respectively) [25]. The hazard quotient (HQ) values for 41% of children and infants were above the safety level in the studies of Qasemi et al. [46] carried out in villages of Azadshahr, Iran. The Li et al. [47] nitrate exposure assessment in groundwater in China showed that nearly 50% of the samples tested had HQ>1, and the highest HQ values were several times higher (11.24 – adults, 19.86 – children) than the results obtained for well water samples taken in Poland. In the aforementioned study of Suvarna et al. [42] from South India, HQ values for infants, children, male and female ranges from 0.05 to 14.25, 0.06 to 18.53, 0.04 to

Table 4. Descriptive statistics of nitrate concentration, estimated daily intake and hazard quotient for four groups of consumers obtained for well and tap water.

| Type of sample | Parameter | $NO_3^-$ [mg/L] | EDI [mg/kg] | | | | HQ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Infants | Children | Teenagers | Adults | Infants | Children | Teenagers | Adults |
| Well water | Mean | 41.2 | 0.332 | 2.354 | 1.662 | 1.332 | 0.21 | 1.47 | 1.04 | 0.83 |
| | Min | 1.1 | 0.001 | 0.006 | 0.004 | 0.003 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max | 194.8 | 1.558 | 11.039 | 7.792 | 6.244 | 0.97 | 6.90 | 4.87 | 3.90 |
| | SD | 38.1 | 0.351 | 2.486 | 1.754 | 1.406 | 0.22 | 1.55 | 1.10 | 0.88 |
| Tap water | Mean | 14.0 | 0.112 | 0.793 | 0.560 | 0.449 | 0.07 | 0.50 | 0.35 | 0.28 |
| | Min | 0.1 | 0.001 | 0.006 | 0.004 | 0.003 | 0.00 | 0.00 | 0.00 | 0.00 |
| | Max | 50.9 | 0.407 | 2.884 | 2.036 | 1.631 | 0.25 | 1.80 | 1.27 | 1.02 |
| | SD | 19.9 | 0.159 | 1.128 | 0.796 | 0.638 | 0.10 | 0.70 | 0.50 | 0.40 |

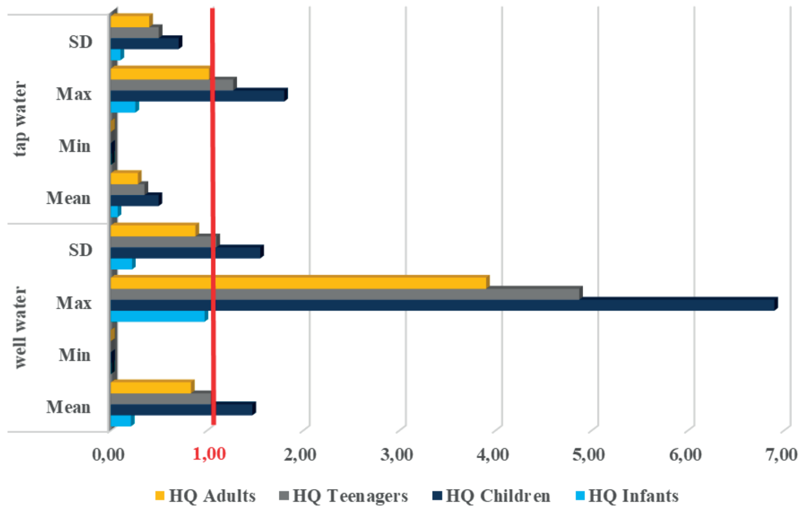


Fig. 4. HQ values obtained for four groups of tap and well water consumers.

12.18 and 0.05 to 14.62, respectively. In our study, this range was from 0.0 in all groups to 1.0 for infants, 6.9 for children, 4.9 for teenagers and 3.9 for adults.

Human impacts on the quality of water resources is extremely complex and multifaceted. As a result of using well water contaminated with nitrates for economic purposes, such as watering locally grown vegetables, there is a high probability of contamination of agricultural products with these compounds, not only as a result of using nitrogen fertilizers, but also from watering vegetables with contaminated water. Study conducted by Taneja et al. [37] showed that the average nitrate concentration in 59 drinking water samples exceeded the normative value, which is 45 mg/L in India. It was found that in rural and urban areas the average concentration of nitrates in drinking water was 45.69±2.08 mg/L and 22.53±1.97 mg/L, respectively. The study of vegetables grown in the area from which water samples were taken, and watered with water from the studied wells, showed that the maximum average nitrate concentration was recorded in beets (1349.38 mg/kg), then in spinach (1288.75 mg/kg) and in amaranth (1007.64 mg/kg), therefore the nitrate pollution of vegetables was as high as that of water [37].

The massive introduction of nitrogen fertilizers, necessary to maximize global food production, has increased the amount of residual nitrite and nitrate not only in groundwater, but also in food products such as meat, dairy and fish. Study results of Iammarino et al. [47], obtained during 5 years of official controls and monitoring, showed nitrite and nitrate content in 1785 samples of meat, dairy products, fish products and leafy vegetables. In addition, high nitrate concentrations were recorded in some leafy vegetables and mussels, while high nitrite concentrations were recorded in some spinach samples.

## Conclusions

The present study showed that the exceedances of the normative values of selected parameters of drinking water quality in the tested well water samples taken from the Rybnik County concern the pH values (57% of the water samples) and the nitrate (V) content (29% of the water samples). In none of the 52 tested well water samples, the permissible value determined for the specific conductivity and for nitrates (III) was exceeded. Drinking water samples taken from domestic wells are of worse quality in terms of the parameters tested, compared to water samples subject to constant official control. According to results obtained, long-term exposure to nitrate through consumption of well water increases the likelihood of non-carcinogenic risk.

Reducing the concentration of nitrates in drinking water by regulating the excessive use of fertilizers on agricultural crops is insufficient. Therefore, it is necessary to supervise and control not only tap water, but also well water, in order to reduce health hazards resulting from exposure to nitrate and nitrite, which are often present in well waters. Integrated groundwater and surface water management is recommended [48]. The compulsory monitoring of well water will exclude the existence of a legislative gap that may affect the misinterpretation of drinking water quality results in Poland obtained during official controls carried out to date.

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## Conflict of Interest

The authors declare no conflict of interest.

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