ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 18, No. 2 2011

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CONCENTRATIONS OF NITRATES(V) IN WELL WATERS IN THE RURAL AREAS OF PODLASIE PROVINCE AND THE ASSESMENT OF INHABITANTS' HEALTH RISK

STĘŻENIA AZOTANÓW(V) W WODACH STUDZIENNYCH NA OBSZARACH WIEJSKICH WOJEWÓDZTWA PODLASKIEGO I OCENA RYZYKA ZDROWOTNEGO MIESZKAŃCÓW

Abstract: The dug wells in some rural areas make up still the source of supply in potable water. In the period of 2008–2009, in the area of the Podlaskie province, the investigations of the nitrates(V) concentrations were conducted in waters of 11 rural wells in the catchments of Slina river. The area of investigations is characterized by quite intensive agricultural utilization (diary cattle farms).

Investigations showed that the concentration of nitrates(V) follows to the level of 26.40 mg $NO_3 \cdot dm^{-3}$ in well waters. Investigations showed that inappropriate location of the well in the premises of the farm, the improper technical parameters of the well and the migration of the nitrogen pollution from agricultural areas were the main reasons of the contamination of well waters by nitrates. The margin of health safety of people using the well water was assessed. In 3 among 11 of studied wells, water qualify was below the safety health margin. The rest of studied wells contained water about the low safety margin.

Keywords: farmstead, dug wells, well waters, nitrates(V), health risk

According to the data of the end of 2008, in Poland 69.4 % of farmstead on the countryside had the connection to the public water pipe network and used treated water. However, there are essential disproportions between the amount of households located on the countryside and connected to the water pipe network. The most farmstead which use the water pipe network is in following provinces: Lodz (84.3 %), Wielkopolska (81.5 %), Swietokrzyskie (74.3 %) and Opole (72.0 %), but the least in West Pomerania (57.6 %), Warmia and Mazury (58.3 %), Lubuskie (58.8 %) and Malopolska (61.4 %) [1].

Substantial impact on the sanitary state of rural areas has the connection of farmstead to the water-pipe network and sewage treatment plant. In the end of 2008 in Poland

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19.4 % of farmstead used sewerage system. The most of farmsteads, which are seweraged, is in the following provinces: Podkarpackie (35.5 %), Pomerania (29.7 %) and Wielkopolska (24.5 %). The least amount of sewerage farmsteads, is in provinces of: Lublin (9.2 %), Lodz (12.0 %), Lubuskie (13.3 %) and Swietokrzyskie (13.5 %).

In spite of the existing water-pipe networks in the rural areas, it is widely observed that inhabitants of the countryside take water from wells to the direct or farming use but also to water animals and plants. It is caused by economical reasons and in order to cut costs, but it also comes from the conviction that the well water tastes better and is much healthier than piped water, which is not rationally proved. Taking into account chemical and bacteriological properties of dug well water, in many cases it should not be used to direct consumption and to the use in farmsteads.

Rural dug wells are supplied by water coming from first water-bearing layer, below which there are not or are rarely observed waterproof layers, that is why they have the contact with contamination caused by agriculture, mainly by liquid manure or mineral fertilizers. It causes worsening of water quality in the grounds of nitrates and other organic compounds and higher bacteria amount [2, 3]. Usually, this kind of water is not drinkable without previous treatment.

Nitrates(V) and nitrates(III) are ions which can be found in nature and are formed as the result of nitrogen compounds transformation. In natural conditions their concentration in surface water reaches usually some milligrams in 1 dm^3. It is observed the increase of nitrates(V) content in groundwater, which is caused by agriculture intensification. Their concentration can reach the hundreds of milligrams in 1 dm^3 [4, 5]. The presence of nitrates in water is caused by the use of mineral and natural fertilizers in agriculture and sewage discharge to the surface water and to the ground. The main reasons of well waters contamination in the rural areas are:

– percolation to the ground water of liquid manure and others solutions coming from the wastes of animal production like for example from pile of cow dung or pig and cow house,

– natural processes of washing out of nitrates from plough land, pastures and meadows,

– nitrogen mineralisation in organic soils (mainly boggy soils).

Among the farmstead, the animal production usually occurs there. It results in the forming of animal excrements like cow dung, cow manure and poultry excreta. The activity conducted in the area of farmstead is a source of groundwater contamination by fertilizers ingredients, which means mainly nitrogen and phosphorus compounds [5]. Theses elements infiltrate into the depth of the soil profile and penetrate not only to the groundwater, but also as a result of ground outflow, to streams located nearby. The speed of their movement and the quantity of elements going into surface and ground waters depends mainly on the soil type.

Rural wells usually are not deep (with the depth of some to dozens meters). Water in these wells is exposed to contaminations from inappropriate stored animal excrements, but also from water flowing from the area of farmstead. Another source of theses water contaminations is uncontrolled outflow of domestic sewage flowing from households, which are drained usually to closed wells functioning as cesspools. Contaminations, which are introduced to ground by infiltration, penetrate into groundwater. In Poland, the main load of nitrogen compounds coming into shallow ground and surface waters has an origin in agriculture [5]. The land use, but also its intensiveness, influences the quantity of nitrogen load introducing into catchment.

In Podlasie province after 1990, there was observed the increase of milk production and nowadays about 25 % of the country production comes from this region of Poland. The largest farms with the diary cattle breeding of farming character are located in the west part of this province. The clear increase of cattle population and the concentration of this production in this part of the province causes that livestock density is above 3 DJP $\cdot$ ha^{-1} (DJP – *large conversion unit*). Such a numerous livestock density and intensive grassland use can cause the excessive concentration of nitrogen compounds and their migration into the environment [6].

The use of well water, especially coming from shallow wells, can be the reason of periodic poisoning and can cause serious human and animal illnesses [7]. Nitrates(V) harmfulness is caused by their reduction into nitrates(III), which can pose direct risk to health causing methemoglobinemia, anemia, but also as the result of exogenic and endogenic processes they can be the source of carcinogenic nitrosamines [8].

The object of the experiment was the assessment of nitrates(V) concentration in well water in the arable areas in Podlasie province and the assessment of inhabitants health risk in these areas, which is caused by the use of water from ground dug well.

Material and methods

The area of the research was the catchment of the Slina river, which is located in the agricultural area, differentiated on the account of use intensiveness. In order to determine nitrates(V) concentrations in well water in the area of this river catchment, there were chosen 11 rural dug wells. The area of the catchment was divided into four parts, which were differentiated by environmental conditions and the way of ground use.

The wells of number 1–4 are situated on the lower course, where in the areas close to the river are mainly grasslands. Meadows, in majority, occur on boggy peat-muck soils. In this part of the valley, there is observed high concentration of diary cattle breeding (up to do 3 DJP $\cdot$ ha^{-1}) and intensive meadows and pastures use. The doses of mineral fertilization exceed 250 kg NPK $\cdot$ ha^{-1}, while fertilization by liquid manure is also used. Cattle grazing in pastures near the stock yard is also done. Within the farmstead, there are located cow dung piles.

The wells of number 5–8 are located in the middle part of the river catchment and the majority of the areas constitute arable lands but also there are little enclaves of grasslands. In this part, the catchment is medium-intensively used, but there is the possibility of biogens flow from the arable lands which are located higher.

The wells of numbers 9–11 occur in the upper part of the river basin. This part of the catchment covers mainly intensively used meadows and pastures. Livestock density amounts 2–3 DJP $\cdot$ ha^{-1} and there is used mineral fertilization and liquid manure in doses similar to lower part of the basin.

The investigations were done in the period of 2008–2009. In the distance of some meters from analyzed wells, there were done soil pits in order to determine taxonomic unit of soil, take soil samples and determine the level of groundwater. Well water samples were taken in 6 periods in 2008 and 6 periods in 2009, so the sampling frequency was done in accordance with Health Minister Order from 2007 [9]. Nitrates(V) in dug well samples were determined by HACH DR-200 spectrophotometer. Statistic analysis of the results was done with the use of Statsoft Statistica 6.0 program. Chemical analysis results were compared with the norms included in the Health Minister Order considering water quality which is destined to consumption by people [9].

To assess the health risk caused by nitrates taken together with water were used suggestions of Alimentary Commission Codex FAO/WHO [10].

The assessment of nitrates risk caused by nitrates taken together with potable water by inhabitants of analyzed rural area was done by calculating of ADI (*Acceptable Daily Intake*), EDI (*Estimated Daily Intake*) and safety margin.

ADI means the quantity of chemical substance which adult can consume during his or her all life, probably without the damage to his or her health in accordance with the knowledge state. The ADI value for nitrates was determined in 1974 by Expert Committee FAO/WHO [11] on the level of 3.65 mg $NO_3 \cdot kg^{-1}$ body mass per day. Nitrates in potable water make up about 10 % of total value of ADI taken by nutritious way, so the ADI value taken with water can amount 0.365 mg $NO_3 \cdot kg^{-1}$ body mass $\cdot$ day^{-1} [7]. It was accepted that the average body mass is 70 kg so the ADI value amount 25.55 mg $NO_3 \cdot day^{-1}$. The EDI value was calculated on the basis of the formula:

$$EDI = F \cdot R$$

where: F – average daily water consumption [2 $dm^3 \cdot person^{-1} \cdot day^{-1}$],
R – average level of nitrates(V) content in water.
Safety margin = ADI : EDI; the higher index value, the lower health risk.

On the basis of determined safety margin there were accepted the following ranges:
- < 1 – below the safety margin,
- 1–10 – low safety margin,
- 10–20 – medium safety margin,
- 20–30 – high safety margin,
- > 30 – very high safety margin.

Results and discussion

Impact of wells location and their environmental conditions on nitrates(V) concentration in water

The distance of wells supporting potable water for people and farming needs should amount at least 15 meters from farming buildings, cow dung piles and waste containers [12]. In the analyzed area, 7 wells were located closer than 15 meters from farming buildings. These wells were situated on light permeable soils on sandy deposits. The well of number 4 and 7 were quite shallow and located on light soils (Table 1).

Table 1

Localization and characteristics of farm wells

No. of well	Localization	Type of animal production	Distance of well from inventory buildings [m]	Well depth [m]	Groundwater level [m]	Soil type near well
1	Makowo	Dairy cattle	12	8.5	1.8	Podzolic, loose sand
2	Mazury	Dairy cattle	17	7.0	1.3	Pseudo-podzolic
3	Lopuchowo	Dairy cattle	13	5.0	1.2	Brown developed from loams
4	Hermany	Dairy and fattening cattle	12	8.0	1.7	Podzolic
5	Kobylin Pieniazki	Dairy cattle	30	6.0	2.2	Chernozem
6	Kobylin Kruszewo	Dairy cattle	22	7.0	1.4	Strong loamy sands
7	Zawady	Dairy and fattening cattle	12	3.0	2.2	Podzolic, loose sand
8	Bruszewo	Dairy cattle	23	6.0	1.7	Strong loamy dusty sand
9	Szypulki Szymany	Dairy and fattening cattle	7	7.0	1.9	Light loamy sand
10	Zalesie Labedzkie	Dairy cattle	12	6.0	1.5	Weakly loamy sand
11	Jablon Zarzeckie	Dairy cattle	10	5.0	2.4	Podzolic, loose sand

Table 2

Nitrates(V) concentrations in well waters within the of catchment area of Slina river in 2008 [mg $NO_3 \cdot dm^{-3}$], n = 66

No. of well	Determination dates						
	March	May	June	August	September	November	Mean
1	14.4	15.2	8.8	7.6	10.0	14.0	11.7
2	2.8	6.0	3.2	1.9	3.7	4.1	3.6
3	17.2	21.6	19.4	20.1	13.2	14.8	17.7
4	7.4	8.6	4.9	3.3	8.2	2.6	5.8
5	15.2	22.2	8.0	5.4	6.9	7.6	10.9
6	15.6	20.6	9.5	5.9	12.4	19.7	13.9
7	7.2	25.8	18.6	16.8	17.2	16.0	16.9
8	7.4	3.6	3.1	9.4	5.0	4.2	5.5
9	14.8	26.4	10.0	15.0	10.8	20.0	16.2
10	6.2	7.4	6.7	4.6	5.1	4.6	5.8
11	2.0	13.2	7.6	9.9	9.6	10.0	8.7
Minimum	2.0	3.6	3.1	1.9	3.7	2.6	
Maximum	17.2	26.4	19.4	20.1	17.2	20.0	
Mean for 2008				10.6			
Median for 2008				9.1			
SD for 2008				6.2			
Minimum for 2008				1.9			
Maximum for 2008				26.4			

SD – Standard deviation.

Table 3

Nitrates(V) concentrations in well waters within the catchment area of Slina river in 2009 [mg $NO_3 \cdot dm^{-3}$], n = 66

No. of well	Determination dates						
	March	May	June	August	September	November	Mean
1	5.6	9.8	5.2	4.2	7.2	12.8	7.4
2	3.5	5.3	4.3	4.7	3.9	2.6	4.0
3	9.6	17.7	18.8	4.8	10.1	13.2	12.4
4	3.6	6.8	2.1	1.5	3.2	1.2	3.0
5	10.4	17.5	9.3	15.6	17.2	11.2	13.5
6	7.6	16.7	6.2	3.8	1.9	1.2	6.2
7	11.6	17.6	14.4	12.4	12.8	18.0	14.4
8	18.0	12.4	5.0	5.6	3.7	4.3	8.2
9	17.2	22.0	17.6	11.6	11.2	11.6	15.2
10	5.4	5.8	7.0	4.8	4.8	5.2	5.5
11	10.0	9.6	7.8	9.6	5.4	7.0	8.2
Minimum	3.5	5.3	2.1	1.5	1.9	1.2	
Maximum	18.0	22.0	18.8	15.6	17.2	18.8	
Mean for 2009				8.9			
Median for 2009				5.4			
SD for 2009				5.2			
Minimum for 2009				1.2			
Maximum for 2009				22.0			

SD – Standard deviation.

Higher access to water pipe network of the countryside, gives the possibility of higher water use, however while the lack of sewerage systems in most of the villages, it causes sewerage discharge into water, soil and leaky cesspools. The higher concentration of nitrates(V) was observed in wells of number 2, 7 and 9 (Tables 2 and 3), both in researches of 2008 and 2009. It can be assumed that it was caused mainly by little depth of theses wells (3–7 m) but also little distance from inventory buildings.

The concentrations of nitrate nitrogen(V) in analyzed well water were differentiated, both in particular wells but also in particular months. The highest concentrations occurred in May 2008 and 2009.

Nitrates concentration is characterized by seasonal variability. The highest nitrates concentrations occur in early spring, and the least in high vegetation period (Fig. 1).

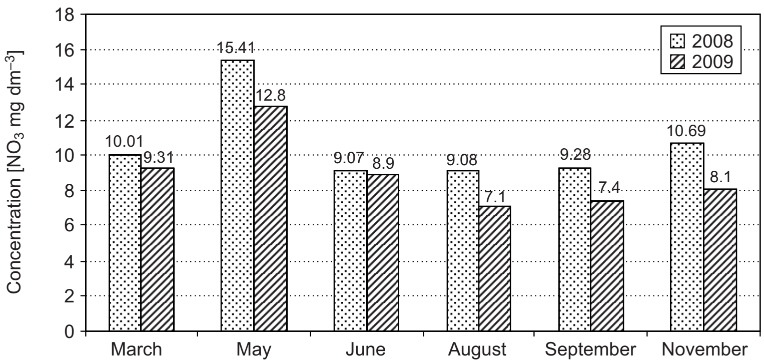

Fig. 1. Seasonal variability of nitrates(V) concentration in well waters in catchment of Slina river

In analyzed well water, there was not found the concentration above the level of 50 mg $NO_3 \cdot dm^{-3}$, so there was not exceed permissible standard for potable water [9]. It is assessed that nitrates move into the depth of ground with the speed of 1 m per year. Deeper layers of groundwater can be contaminated after some time and this contamination is stable and can be felt for many years [3, 5].

Nitrates in surface and shallow groundwater come mainly from rural areas. In surface water they fasten their eutrophication. Supply of these ions to the environment in a form of contaminations, to the large extend, is said to be caused by agriculture and human activity. It is estimated that 50–60 % of nitrogen introduced to Baltic Sea, comes from the area sources, which means agricultural lands. It is found that in water from 50 % of dug wells, the level of nitrates exceed permissible standard of 50 mg $NO_3 \cdot dm^{-3}$ [13].

Calculated median of nitrates concentrations in analyzed water of wells amounted 9.1 mg $NO_3 \cdot dm^{-3}$ in 2008 and 5.4 mg $NO_3 \cdot dm^{-3}$ in 2009, and the range of concentrations fluctuated between 1.2 to 26.4 mg $NO_3 \cdot dm^{-3}$ (Tables 2 and 3). Higher nitrates concentrations were found in researches in 2008, which can be connected with more intensive migration of nitrates caused by higher atmospheric rainfall in this year. The highest nitrate ions concentration was observed in water samples taken in May 2008 and 2009 from the well of number 7 and 9, which can be caused by technical parameters and the location of these wells within the farmstead. In analyzed north-eastern region, vegetation starts far later comparing with the region of middle and western Poland, that is why in early spring nitrates were not taken in by plants and migrated together with surface flow. In this period, there is often used liquid manure on grasslands.

Assessment of inhabitants' health risk caused by nitrates(V) contained in water

Calculated values of ADI (*Acceptable Daily Intake*) and safety margin (Table 4) show that in 3 analyzed wells, nitrates concentration was below safety margin (ADI/EDI < 1). In the rest of 8 analyzed wells, nitrates concentrations were within the low safety margin (ADI/EDI < 10. It can be concluded that water from analyzed wells should not be used as potable water drunk by people.

Table 4

Mean nitrates(V) concentration, value of EDI and safety margin in rural wells waters

No. of well	NO_3 concentration [$mg \cdot dm^{-3}$]	EDI value [$mg\ NO_3 \cdot person^{-1} \cdot day^{-1}$]	Mean safety margin ADI/EDI
1	9.56	19.12	1.33
2	3.83	7.66	3.33
3	15.04	30.08	0.84
4	4.45	8.90	2.87
5	12.20	24.40	1.04
6	10.09	20.18	1.26
7	15.70	31.40	0.81
8	6.80	13.60	1.87
9	15.68	31.36	0.80
10	5.63	11.26	2.27
11	8.47	16.94	1.51
Mean	9.78	19.56	1.31

The researches done by Medical University in Bialystok [7], connected with the assessment of health risk and its estimations caused by nitrates presence in potable water consumed by inhabitants of Podlasie province, showed that 1.79 % of urban dwellers and 4.86 % of rural inhabitants took in nitrates(V) with tap water of lowered safety margin.

Water taken from water pipe network (supported by small intakes) can also be of the potential danger for health, because nitrates which are contained in potable water, due to their transformations, can cause various negative effects in human and animal organisms [14].

Conclusions

1. In intensive agricultural used areas of Podlasie province, there is observed water contamination in dug wells in effect of inappropriate location of wells within the

farmstead, improper technical parameters of wells but also nitrogen compounds migration into the environment.

2. Nitrates(V) concentrations ranged between 1.2 to 26.4 mg $NO_3 \cdot dm^{-3}$. These values do not exceed permissible standards for potable water.

3. There was stated clear seasonal variability of nitrates(V) concentrations, and the highest concentration occurred in early spring months.

4. Water in 3 among 11 analyzed wells, showed the relation of ADI/EDI below safety margin, which can caused negative effect on health in case of longer use.

5. There are needed further investigations on the quality of well and tap water in the rural areas, mainly on the grounds of health reasons.

Acknowledgements

This work was supported by Bialystok Technical University (project No. W/IiŚ/26/08).

References

[1] Informacja o stanie infrastruktury technicznej wsi na koniec 2008 roku. Ministerstwo Rolnictwa i Rozwoju Wsi, Departament Gospodarki Ziemią, Wydział Infrastruktury Technicznej i Techniki Rolniczej 2010 [online] http://bip.minrol.gov.pl.

[2] Bombik T., Kolbuszewski T. and Mazurek J.: Zesz. Nauk. WSRP w Siedlcach, Zoot. 1989, **22**, 193–203 [in Polish].

[3] Durkowski T., Burczyk P., Walczak B. and Wesołowski P.: [in:] Conf. Water as a factor determining the multi-functional development of countryside and agriculture. Proc. of IMUZ 1997, p. 147–152 [in Polish].

[4] Koc J., Ciećko Cz., Janicka R. and Rochweger A.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 175–183.

[5] Sapek A. and Sapek B.: Zesz. Eduk. IMUZ 2005, **10**, 27–38.

[6] Kiryluk A.: Ochr. Środ. Zasob. Natur., IOŚ Warszawa 2008, **35/36**, 88–93.

[7] Szczerbiński R., Karczewski J. and Fiłon J.: Roczn. PZH 2006, **1**, 39–48.

[8] Raczuk J., Biardzka E. and Michalczyk M.: Woda – Środowisko – Obszary Wiejskie 2009, **9**, 1(25), 87–97.

[9] Rozporządzenie Ministra Zdrowia z dnia 29 marca 2007 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi. DzU 2007, nr 61, poz. 417.

[10] Alimentary Commission Codex FAO/ WHO: Progress report by WHO on prediction of dietary intake of pesticides. FAO/WHO CXPR 1994, **94**/4.

[11] Evaluation of certain food additives: Twenty third report of the Joint FAO/WHO Expert Committee on Food Additives. Techn. Rep. Ser. **648**, WHO, Geneva 1980.

[12] Rozporządzenie Ministra Infrastruktury z dnia 12 kwietnia 2002 r. w sprawie warunków technicznych, jakim powinny odpowiadać budynki i ich usytuowanie. DzU 2002, nr 75, poz. 690.

[13] Wiśniowska-Kielian B. and Niemiec M.: Ann. UMCS, Sec. E 2006, **61**, 147–156.

[14] WHO: Guidelines for Drinking-water Quality. Third edition, WHO, Geneva 2004, 417–420.

STĘŻENIA AZOTANÓW(V) W WODACH STUDZIENNYCH NA OBSZARACH WIEJSKICH WOJEWÓDZTWA PODLASKIEGO I OCENA RYZYKA ZDROWOTNEGO MIESZKAŃCÓW

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Abstrakt: Kopane wiejskie studnie przydomowe na niektórych obszarach wiejskich stanowią nadal źródło zaopatrzenia mieszkańców w wodę pitną. W latach 2008–2009 przeprowadzono badania stężeń azotanów(V) w wodach 11 studni wiejskich na obszarze woj. podlaskiego w zlewni rzeki Ślina. Teren objęty badaniami charakteryzuje się dość intensywnym wykorzystaniem rolniczym (intensywne nawożenie, fermy bydła mlecznego).

Badania wykazały, że w wodach studziennych następuje koncentracja azotanów(V) do poziomu 26,40 mg $NO_3 \cdot dm^{-3}$. Głównymi przyczynami zanieczyszczenia wód studziennych azotanami są: niewłaściwe usytuowanie studni w obrębie zagrody, niewłaściwe parametry techniczne studni oraz migracja związków azotu z obszarów rolniczych. Określono margines bezpieczeństwa zdrowotnego mieszkańców korzystających z wód studziennych. Wody z 3 spośród 11 badanych studni wykazują wartość wskaźnika ADI/EDI poniżej marginesu bezpieczeństwa zdrowotnego. Pozostałe badane studnie zawierają wody o małym marginesie bezpieczeństwa.

Słowa kluczowe: zagroda wiejska, studnie kopane, wody studzienne, azotany(V), ryzyko zdrowotne