

# **MACROELEMENTS: ZINC AND IRON IN WELL WATER IN THE UPPER NAREW RIVER CATCHMENT\***

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## Abstract

The aim of the present study was to evaluate the spatial distribution of concentrations of some elements in shallow ground waters as well as to find the main sources of their origin. The investigations were carried out in 8 villages in Podlasie region. The water sampling sites were in the villages Sobótka, Narew, Cieluszki, Kaniuki, Zawyki, Uhowo, Topilec, and Złotoria, all on or near the Narew River. Water samples were collected in spring, summer, and autumn of 2006. The samples underwent determinations of calcium, magnesium, sodium, potassium, zinc, and iron concentrations by means of AAS and EAS techniques after previous filtering through micro-pore filters ( $d=0.45\ \mu\text{m}$ ). None of the tested water samples met the standards for potable water specified in the Decree of the Ministry for Health of 2007 as they exceeded permissible concentrations of iron ions. Regarding potassium ions, the well waters were classified to underground waters quality class V. The waters with the highest values of the tested parameters were found in wells in Kaniuki, Złotoria and Zawyki.

**Key words:** well, macroelements, potassium.

## **MAKROELEMENTY, CYNK I ŻELAZO W WODACH STUDZIENNYCH DOLINY GÓRNEJ NARWI**

## Abstrakt

Celem pracy było określenie rozkładu przestrzennego stężenia wybranych składników płytkich wód podziemnych oraz określenie głównych czynników ich pochodzenia. Badania przeprowadzono w 8 wsiach położonych w województwie podlaskim. Miejsca poboru próbek wody wyznaczono w miejscowościach: Sobótka, Narew, Cieluszki, Kaniuki, Zawyki, Uhowo, Topilec,

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Złotoria, zlokalizowanych wzdłuż rzeki Narew w jej bezpośrednim sąsiedztwie. Próbkę wody pobierano w terminach: wiosna, lato, jesień 2006 r. W próbkach oznaczono stężenie jonów wapnia, magnezu, sodu, potasu, cynku i żelaza metodą AAS i ESA po ich przefiltrowaniu przez filtry mikroporowate o średnicy porów 0,45  $\mu\text{m}$ . Badane wody nie odpowiadały standardom wody przeznaczonej do spożycia określonym w Rozporządzeniu Ministra Zdrowia z 2007 r., z powodu przekroczenia wartości dopuszczalnych stężenia jonów żelaza. Ze względu na stężenie jonów potasu wody badanych studni zakwalifikowano do V klasy jakości wód podziemnych. Wody o najwyższych wartościach stężenia badanych parametrów stwierdzono w studniach zlokalizowanych we wsiach Kaniuki, Złotoria i Zawyki.

Słowa kluczowe: studnia, makroelementy, potas.

## INTRODUCTION

The monitoring of shallow ground waters in Poland is not performed regularly and lacks uniform water quality criteria. It is accepted that chemical composition of shallow ground waters is very similar to that of water disposed through drainage system (IGRAS 2000).

Unsatisfactory water quality in wells in rural households has been indicated by several authors (SAPEK, SAPEK, RZEPIŃSKI 1993, MISZTAŁ, SAPEK 1997, SIKORSKI 1997, OSTROWSKA et al. 1999, PIETRZAK 1997, SAPEK 2002, SAPEK 2002).

Depending on their type, technical status and capacity, sites where natural fertilizers are stored (manure plates, reservoirs for liquid and solid manure) are the gravest hazard to soil and ground water, including the nearest water flows and small water reservoirs, as they can be a source of such elements as phosphorus, nitrogen, potassium, heavy metals and other ingredients contained in farm animal fodder (CHADWICK, CHEN 2002, RITTER, BERGSTROM 2001, DE VRIES et al. 2002).

The aim of the present study was to evaluate the spatial distribution of concentrations of some elements in shallow ground waters and to identify the main sources of their origin.

## MATERIAL AND METHODS

The investigations were carried out in 8 villages situated in Podlasie, a region in the east of Poland. One dug well in each village was selected among farmsteads which are involved in agricultural production. All the wells were filled with water from the first water-bearing layer. The study embraced well water within the river Narew section from Sobótka to Złotoria villages. The sites where the water was collected were set up in the villages Sobótka, Narew, Cieluszki, Kaniuki, Zawyki, Uhowo, Topilec, and Złotoria, all on or very near the Narew River (Figure 1).

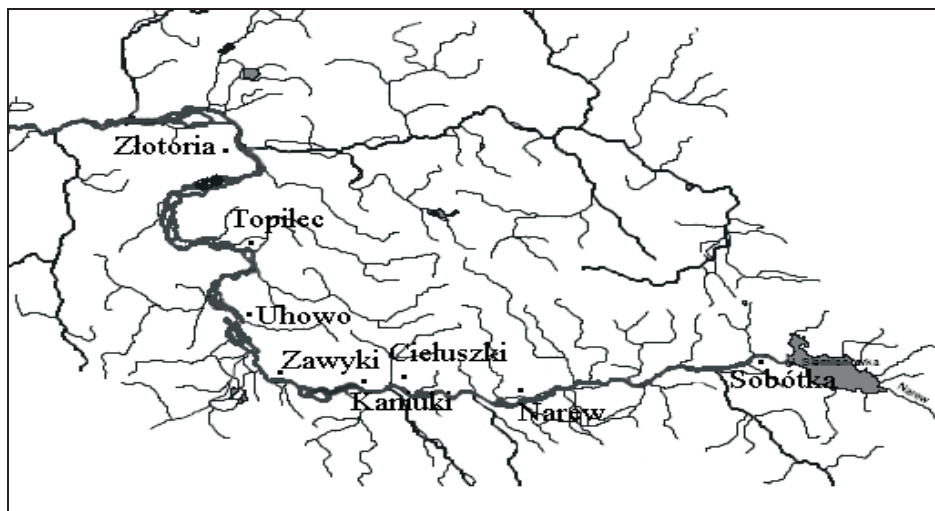


Fig. 1. Location of the well water sampling points

The water samples were collected in spring, summer, and autumn of 2006. The samples underwent determinations of calcium, magnesium, sodium, potassium, zinc, and iron concentrations by means of AAS and EAS after previous filtering through micro-pore filters ( $d=0.45\ \mu\text{m}$ ). In the AAS and EAS techniques, oxidizing flame air-acetylene was applied as an atomization source.

The precision and accuracy was estimated by testing the recovery of analytes from 5 model samples with various concentrations of the analyzed metals. Specific conductivity measurements were made *in situ* during the sample collection. Soluble forms of the above components were studied. Correctness of the determinations of soluble Ca, Mg, Na, Zn, and Fe forms was verified using the reference material SRM 1643e (Trace Elements in Water, NIST). Parameters of the analytical methods were adjusted to recommendations set in the Decree of the Ministry for Environment (2004). The data thus obtained enabled us to calculate arithmetic means for concentrations of the metals in the samples collected from 3 wells in each village on three sampling dates. Factorial analysis (FA), which is a multi-dimensional analysis applied to describe and explore a large sets of data, was used for statistical computations. The present study supplied 576 measurement results, which were subsequently analyzed. In order to isolate factors, the main components method, which uses a primary correlation matrix for calculations, was applied. This method is used in hydrochemistry to investigate processes occurring in underground waters and to identify the supplying and origin sources which shape the chemical composition of waters (SIMEONOVA et al. 2003, Simeonov et al. 2004). In order to interpret the factorial analysis results, it

was assumed that associations of primary variable with a factor are strong when absolute values of its charges are greater than 0.70 (EVANS et al. 1996, PUCKET, BRICKER 1992).

## RESULTS AND DISCUSSION

The concentrations of the elements analyzed were found to be variable. The highest concentration of calcium ions was determined in well water from Złotoria ( $178.97 \text{ mg} \cdot \text{dm}^{-3}$  – II quality class for underground waters), while the lowest one – in Cieluszki ( $104.65 \text{ mg} \cdot \text{dm}^{-3}$  – II quality class for underground waters) – Figures 2, 3, 4. Similarly, the highest

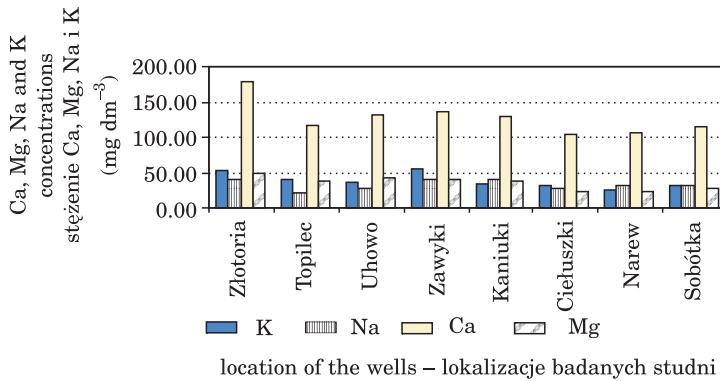


Fig. 2. Arithmetic mean values of concentrations of macroelements in well waters  
Rys. 2. Wartości średniej artmetycznej ze stężenia makroelementów studziennych

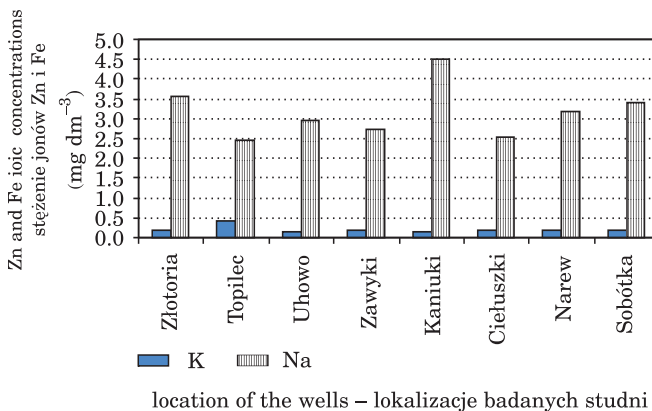


Fig. 3. Arithmetic mean values of zinc and iron ionic concentrations in well waters  
Rys. 3. Wartości średniej artmetycznej ze stężenia jonów cynku i żelaza w wodach studziennych

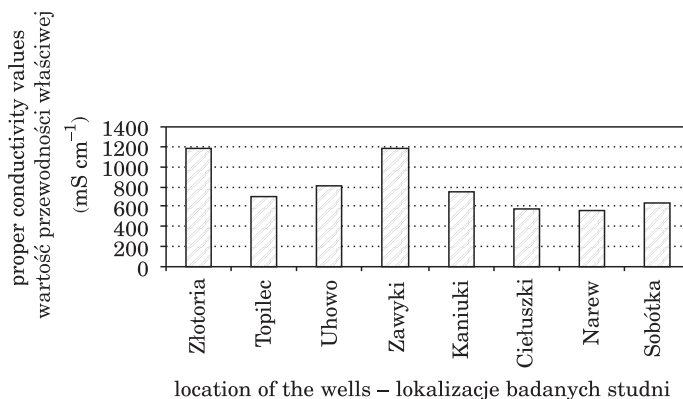


Fig. 4. Arithmetic mean values of well water proper conductivity

Rys. 4. Wartości średniej arytmetycznej przewodności właściwej w wodach studziennych

content of magnesium ions ( $48.19 \text{ mg} \cdot \text{dm}^{-3}$  – II quality class for underground waters) was observed in well water from Złotoria, whereas the lowest one – in Narew ( $23.60 \text{ mg} \cdot \text{dm}^{-3}$  – I quality class for underground waters). In these villages, the distribution of potassium ions was similar: Złotoria –  $52.27 \text{ mg} \cdot \text{dm}^{-3}$ , Narew –  $26.43 \text{ mg} \cdot \text{dm}^{-3}$  (higher than V quality class for underground waters).

According to JASZCZYŃSKI et al. (2006), elevated levels of potassium ions was caused by agricultural activity, because potassium content in crops or plants growing under natural conditions is over 100-fold higher than that of sodium (also in plants from natural potassium-deficient soils).

CHADWICK and CHEN (2002) as well as FOY and O'CONNOR (2002) identify point sources next to area contamination from which potassium and organic matter are transferred from natural fertilizers to water systems. These authors claim that silage liquids which penetrate into the ground water and soil, together with fertilizers components, cause soil acidification, which accelerates their migration in a soil profile and, consequently, their washing out.

The concentration of sodium ions followed a similar pattern to that of calcium – the highest value of sodium was recorded in well water from Złotoria –  $39.77 \text{ mg} \cdot \text{dm}^{-3}$ , while the lowest occurred in Cieluszki –  $26.85 \text{ mg} \cdot \text{dm}^{-3}$  (I quality class for underground waters). The highest specific conductivity values were measured in well water from Złotoria ( $1184 \text{ mS} \cdot \text{cm}^{-1}$ ), while the lowest ones – in Narew ( $558 \text{ mS} \cdot \text{cm}^{-1}$  – II quality class for underground waters). The highest iron concentration was found in water from Kaniuki ( $4.50 \text{ mg} \cdot \text{dm}^{-3}$ ), the lowest – in Topilec ( $2.44 \text{ mg} \cdot \text{dm}^{-3}$  – III quality class of underground waters). The highest zinc content was recorded in water collected in Topilec ( $0.43 \text{ mg} \cdot \text{dm}^{-3}$ ), the lowest – in Uhowo ( $0.17 \text{ mg} \cdot \text{dm}^{-3}$ ); both values are within the range corresponding to I quality class for underground waters.

The so-called pre-mixes, that is mineral fodder concentrates used in animal feeding, except plant ones, are a source of microelements and heavy metals such as zinc in natural fertilizers. Their excess which has not been absorbed by farm animals is found in their excreta and, consequently, in natural fertilizers (KLOCEK, OSEK 2001, DE VRIES et al. 2002).

None of the tested water samples met the norms of the Ministry for Health (2007) due to high concentrations of iron ions.

The results of the statistical multi-factorial analysis implied the main factor responsible for supplying of the well waters with such ions as Ca, Mg, and K as well as increasing the specific conductivity value (Figure 5). The factor seems to be associated with the fact that, according to SKORBIŁOWICZ et al. (2001), well water receives macroelements through the elution of geological environment and migration of elements from organic fertilizers stored on a farm. The analysis revealed another source of iron and sodium in well waters. The low quality of the well waters we studied caused by high concentrations of iron was probably caused by the influx of water characterized by a much inferior quality from the central fragments of the upper Narew River valley.

All the wells lie near the Narew River (from 50 m to only 200 m). High levels of iron ions in water samples from most of the wells can also be attributed to a constant contact of well waters with the so-called long distance underground waters, which are rich in iron. The analysis of the changes in the values of the factors (Figure 6) revealed that the intensification of factor I was the strongest in Złotoria and Zawyki, whereas that of factor II – in Kaniuki.

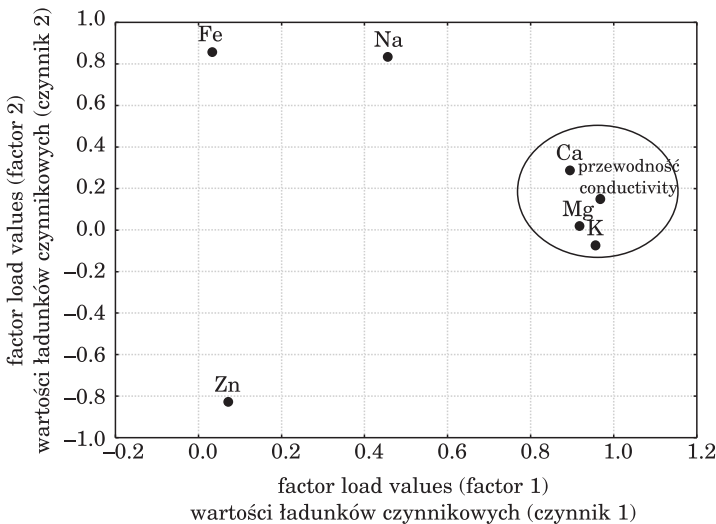


Fig. 5. Results from factorial analysis (rotation method - normalized varimax); determined loads are  $> 0.7$

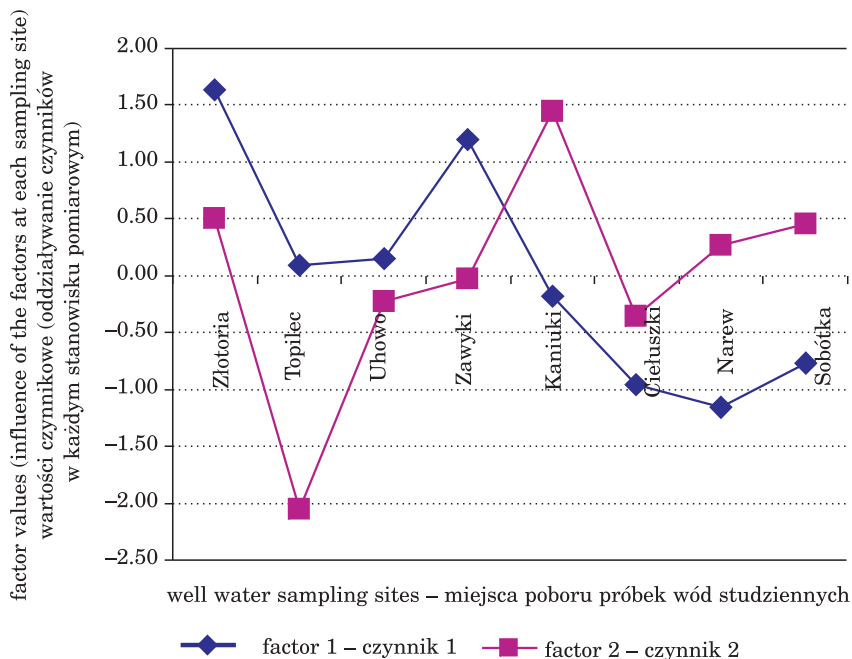


Fig. 6. Changes in the dynamics of the factors at sampling points  
Rys. 6. Zmiany dynamiki czynników w punktach poboru próbek

## CONCLUSIONS

1. The water samples we analyzed failed to meet the potable water standards specified in the Decree of the Ministry for Health of 2007 as they exceeded permissible concentrations of iron ions.

2. Regarding potassium ions, the water from the wells was classified to underground waters quality class V.

3. Water samples yielding the highest values of the parameters we examined were collected from the wells in Kaniuki, Złotoria and Zawyki.

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