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ORIGINAL PAPER

OCCURRENCE OF IRON, MANGANESE, AND SELECTED TRACE ELEMENTS IN WATER FROM HOUSEHOLD WELLS EXPOSED TO THE IMPACT OF A MINING AREA

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Abstract

Groundwater often contains excessive concentrations of mineral and organic substances, in particular iron and magnesium. While iron, manganese and trace metals occur naturally in the environment, some amounts of these elements can originate from anthropogenic sources. Industrial plants create a threat of chemical contamination to groundwater. This research tested concentrations of selected compounds in water from wells located on private premises in the vicinity of a copper ore tailings impoundment. Water from wells in from 11 locations was analyzed for Fe, Mg and trace elements such as Cu, Ni, Zn and Cr. The results were compared to standards for drinking water. Analyses of samples of well water in the research area revealed that the concentrations of trace metals in most wells were below the acceptable groundwater standard limits for Cu, Ni, Zn and Cr. The average concentration of Cu in groundwater varied from 0.009 - 0.038 mg dm^{-3}, Ni: 0.003 - 0.009 mg dm^{-3}, Zn: 0.030 - 0.826 mg dm^{-3} and Cr: 0.002 - 0.003 mg dm^{-3}. Meanwhile, the analyzed water samples are characterized by frequent excessive amounts of iron and magnesium and average concentrations of these metals ranged between 0.1 and 1.1 mg dm^{-3} for iron and 0.0001 and 0.4 mg dm^{-3} for magnesium. However, there were significant differences between the examined years and sites. Consequently, water from the wells was unsuitable for drinking. Nevertheless, the presence of the copper ore tailings impoundment did not impact the the quality of water drawn from the analyzed wells.

Keywords: water pollution, wells water, water quality, heavy metals, trace elements, Zelazny Most.

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INTRODUCTION

Water is crucial for all living organisms, and its contamination may cause various diseases. Pollutants, bacterial contamination, the chemization and mechanization of agriculture or industrialization all create serious health hazards. On a municipal scale, there are some processes implemented for water purification like chemical and mechanical treatment methods (e.g. coagulation, sedimentation or filtration). Water is also disinfected before it can be delivered to users and usually chlorine is added to water in order to remove bacteria and viruses. During coagulation, water is enriched with aluminum sulphate or ferric chloride, and compounds in water like NOM (natural organic matter) can interact with chlorine thus creating new compounds in a process called disinfection by-products, DBP (Malczewska, Benjamin 2016). Another problem which can appear on a municipal scale is insufficient removal of alkali metal salts. Reverse osmosis can be a good solution to remove these compounds along with bacteria, viruses, pesticides, and some heavy metal ions (e.g. lead, cadmium, chromium, nickel), nitrite, nitrate, or chloroform (Greenlee at al. 2009). Regardless of which water treatment is implemented, water supplied through waterworks is under permanent monitoring, whereas water from privately owned wells is not. However, an appropriate monitoring of groundwater quality is important, especially in areas close to industrial zones (Szerszeň et al. 1999, 2004, Kabała et al. 2008, Karczewska et al. 2010, Jain et al. 2015, Różkowski et al. 2015, Dobrzański et al. 2017). Despite the significant progress in the development of waterworks, water from household wells continues to be used, which can contribute to bigger groundwater pollution (Jóźwiakowski et al. 2014, Paweska et al. 2017). Moreover, water drawn from wells is usually is consumed with little or no treatment, which adds to the health hazard.

Metal ions such as iron, copper, zinc, and manganese are important for many biological processes and necessary for the survival of living organisms (Porcheron et al. 2013, Jain et al. 2015). Iron is responsible for the correct functioning of the blood system, and manganese is a natural part of many food products.

Iron is usually present in groundwater in amounts dependent on the structure and mineral composition of the geological foundation. In addition to intensifying the colour and turbidity, iron contributes to a poor taste and odour of water. Manganese usually co-occurs in water with iron.

The purpose of the present study was to determine the quality of water in wells in the context of selected metals in the water drawn from wells located close to cooper tailings ponds.

MATERIAL AND METHODS

This study was conducted in 1999-2015 and comprised analyses of selected metals in water sampled at the following locations: Bytkow, Dabrowa, Grodowiec, Grodziszcze, Juszowice, Komorniki, Krzydlowice, Rudna, Rynarcice, Tarnowek and Zelazny Most (Figure 1). To ease the presentation of

Fig.1 Location of sampling sites

statistical data, the wells are denoted with acronyms (*S1-S11*). The villages are located from 600 to 4500 m from a cooper tailings pond called Zelazny Most (Figure 1). The facility (PIWU – Plant for Industrial Waste Utilization) is located in the Legnica-Głogow Copper Mining District, in south-eastern Poland, and is one of the largest sites of this type in Europe (DUDA 2014).

Sources of groundwater for quality analyses are household wells, from which water was sampled every two years (total eight samples per well) from a depth between 2 and 6 m.

Samples were randomly collected from 11 location and analyzed in accordance with the analytical reference method and the *Regulation of the Polish Minister of Health* (13.11.2015) *on the quality of water intended for human consumption* (Dz.U. 2015 item 1989). The determination of selected metals in water was carried out by atomic absorption spectrometry on a graphite furnace. The principles and procedures for determining trace metals such as Fe, Mg, Cu, Ni and Cr in surface water, groundwater and drinking water are described in details in ETAAS PNEN ISO 15586:2005 standard and PN-ISO 8288:2002 method. A standard method was applied for Zn determination.

Cluster analysis of the wells was performed to analyze the quality of well water (concentrations of tested elements) at all sampling sites. The vertical axis presents the distance or dissimilarity between clusters, and the horizontal axis of the dendrogram represents the objects and clusters and the closeness of either individual data points or clusters. The Ward's hierarchical method was used for cluster analysis with the squared Euclidean distance as the distance measure.

Study area

The region is characterized by significant weather variability, presenting the characteristic of a climate affected by an ocean, including mild and short winters. The warmest month is July with an average temp. exceeding 18°C. The coldest months are January and February with average monthly subzero temperatures, between –1.7°C and –2.1°C. The average annual temperature of air at the station in Polkowice was 8.4°C (Czaban 2017).

A Quaternary aquifer is a substantial water resource in this area. Quaternary formations, of variable thickness, are mainly clays, fluvioglacial sands and gravels as well as holocene sediments. The Tertiary aquifer is mostly composed of clays and silty loams and sands (Czaban 2017). The hydro-geochemical background of the investigated area is presented in Table 1.

RESULTS AND DISCUSSION

What influences groundwater is typically the geology (pleistocene glacial material in the form of moraine clay, sandy loam, fluvioglacial sand and gravel, lake sediments and Holocene river deposit), the anthropogenic impact (e.g. mining or other industrial activity) or the underground reservoir. Regular monitoring of soil and plants in the surroundings of Zelazny Most tailings pond (PIWU on Figure 1) has been conducted since 1996 (Medynska et al. 2009, Czaban et al. 2017). But water in wells located on private premises in the close vicinity of the cooper tailings ponds has not been monitored.

The study was conducted to investigate concentration of chosen metals and their distribution in wells in the surroundings of the cooper tailings

Table 1

Concentrations of the analyzed metals in the wells

Item	Fe	Mn	Cu	Ni	Zn*	Cr
1	2	3	4	5	6	7
The highest allowed value	0.2	0.05	2.0	0.02	3.0	0.05
Hydrogeochemical background	0.020 5.000	0.010 0.400	0.001 0.020	0.001 0.005	0.000 0.020	0.0001 0.010
	(mg dm^{-3})	(mg dm^{-3})	(mg dm^{-3})	(mg dm^{-3})	(mg dm^{-3})	(mg dm^{-3})
S1, approximate distance from the PIWU 2.9 km						
Min.	0.100	0.000	0.001	0.001	0.024	0.001
Average	0.200	0.400	0.009	0.003	0.046	0.003
Max.	0.300	0.700	0.021	0.007	0.068	0.005
SD	3.200	3.100	3.195	3.197	0.921	3.040
Median	0.200	0.400	0.010	0.003	0.046	0.002
S2, approximate distance from the PIWU 2.7 km						
Min.	0.000	0.000	0.002	0.001	0.016	0.001
Average	0.200	0.000	0.016	0.005	0.074	0.002
Max.	0.700	0.100	0.059	0.020	0.231	0.005
SD	3.900	3.900	4.138	4.140	2.075	3.894
Median	0.100	0.000	0.010	0.005	0.034	0.002
S3, approximate distance from the PIWU 1.8 km						
Min.	0.000	0.000	0.001	0.001	0.004	0.001
Average	0.100	0.300	0.012	0.005	0.110	0.002
Max.	0.400	4.000	0.050	0.054	0.302	0.005
SD	7.600	7.600	7.939	7.940	3.605	7.684
Median	0.100	0.000	0.010	0.003	0.100	0.002
S4, approximate distance from the PIWU 2.0 km						
Min.	0.000	0.000	0.003	0.001	0.009	0.001
Average	0.100	0.300	0.018	0.009	0.212	0.002
Max.	0.600	6.200	0.070	0.057	1.058	0.005
SD	6.800	6.900	7.213	7.214	3.454	6.932
Median	0.100	0.000	0.011	0.005	0.050	0.002
S5, approximate distance from the PIWU 4.5 km						
Min.	0.000	0.000	0.001	0.001	0.036	0.001
Average	0.300	0.200	0.028	0.004	0.247	0.002
Max.	2.200	2.200	0.337	0.012	0.444	0.005
SD	4.700	4.700	4.905	4.910	2.020	4.703
Median	0.100	0.000	0.010	0.003	0.256	0.002

cont Table 1

1	2	3	4	5	6	7
S6, approximate distance from the PIWU 2.1 km						
Min.	0.000	0.000	0.005	0.001	0.040	0.001
Average	0.900	0.300	0.038	0.003	0.091	0.002
Max.	8.300	1.700	0.578	0.010	0.226	0.005
SD	4.700	4.400	4.590	4.595	1.831	4.374
Median	0.200	0.100	0.010	0.003	0.048	0.002
S7, approximate distance from the PIWU 1.8 km						
Min.	0.000	0.000	0.001	0.001	0.007	0.001
Average	0.100	0.000	0.011	0.004	0.181	0.003
Max.	0.400	0.100	0.031	0.034	0.753	0.005
SD	5.700	5.700	6.005	6.006	2.656	5.751
Median	0.100	0.000	0.010	0.003	0.040	0.002
S8, approximate distance from the PIWU 1.5 km						
Min.	0.000	0.000	0.005	0.001	0.010	0.001
Average	0.300	0.000	0.0153	0.003	0.118	0.002
Max.	2.600	0.000	0.042	0.007	0.605	0.005
SD	5.700	5.700	6.004	6.006	2.670	5.751
Median	0.100	0.000	0.012	0.003	0.042	0.002
S9, approximate distance from the PIWU 1.8 km						
Min.	0.000	0.000	0.003	0.001	0.026	0.001
Average	0.200	0.100	0.037	0.005	0.174	0.003
Max.	2.000	3.700	0.951	0.022	1.120	0.005
SD	7.500	7.600	7.873	7.876	3.599	7.553
Median	0.100	0.000	0.014	0.003	0.067	0.002
S10, approximate distance from the PIWU 0.6 km						
Min.	0.000	0.000	0.002	0.001	0.003	0.001
Average	1.100	0.200	0.011	0.005	0.030	0.003
Max.	8.900	3.100	0.052	0.024	0.173	0.009
SD	6.800	6.600	6.859	6.859	3.032	6.638
Median	0.100	0.000	0.010	0.003	0.012	0.002
S11, approximate distance from the PIWU 3.3 km						
Min.	0.000	0.000	0.002	0.001	0.010	0.001
Average	0.200	0.000	0.023	0.004	0.826	0.002
Max.	2.900	0.400	0.625	0.027	3.300	0.006
SD	8.100	8.100	8.485	8.487	3.458	8.249
Median	0.100	0.000	0.010	0.003	0.142	0.002

* Zn concentration in groundwater is presently not regulated by the Polish Standards, therefore its concentration was evaluated based on previously binding standards.

ponds. Statistically processed data, including the minimum, maximum and standard derivation (SD), are presented in Table 1.

Iron (Fe) is quite widespread in the environment, and may originate from a variety of mineral and organic sources. Its excessive concentration in potable water can contribute to a detectable change in taste and odour. Average concentrations of Fe detected in our study ranged between approximately 0.1 mg dm^{-3} and 1.1 mg dm^{-3}. The lowest concentration of iron was 0.0001 mg dm^{-3} and the maximum content was 8.9 mg dm^{-3}, but the mean (median) concentrations in particular years were quite similar (between 0.2 and 0.1 mg dm^{-3}). Excessive iron concentrations were recorded in the examined water samples. However, groundwater usually contains iron in a very wide range of concetrations. And in Poland, an increased content of iron was observed in the compositions of the quaternary level (Moryl et al. 2008, Paweska et al. 2016). Iron is considered to be an element necessary for biological life, but it can also be a potential threat.

The calculated average manganese concentrations ranged between approximately 0.0001 and 0.4 mg dm^{-3}. The maximum content was 6.2 mg dm^{-3}, and the mean (median) concentrations in particular years varied between 0.0001 and 0.4 mg dm^{-3} (Table 1).

Having analyzed the results of this research into the chemical quality of water, in terms of the iron and manganese content, it appeared that the water from the examined wells should not be used for drinking.

Evaluation of trace metals in the well water for drinking purposes depends on specific standards set in the drinking water standards of the WHO (2011) and the *Regulation of the Polish Minister of Health* (2015). Therefore, in this study, changes in the values of selected trace metals were evaluated and confronted with these regulation.

Chromium (Cr) is usually found in water from old mining process runoffs leaching into groundwater, cement-plant emissions, mineral leaching and waste incineration (Reddy et al. 2012). In the studied area, average concentrations of chromium (Cr) varied between 0.002 and 0.009 mg dm^{-3}. The lowest Cr concentration was found to be 0.001 mg dm^{-3} and the maximum content was 0.009 mg dm^{-3}, the mean (median) concentrations in particular years were between 0.002 and 0.003 mg dm^{-3}. Over the whole analyzed period of time, the permissible concentration was exceeded only in a few cases. However, the SD indicated significant dispersion of data.

Nickel (Ni) in water may occur as a result of infiltration. Usually, the presence of nickel in water is connected with the leaching of metals in contact with water. Its concentration in groundwater depends on the land use, pH, and depth of sampling (Cempel, Nikel 2006).

The average concentration of Ni in well water ranged from 0.003 up to 0.009 mg dm^{-3}. The lowest concentration of Ni was found to be 0.001 mg dm^{-3}, and the maximum content was 0.057 mg dm^{-3}. The mean Ni content did not exceed the allowable concentration, but the SD suggested that the data points are spread out over a wider range of values (Table 1).

Zinc (Zn) can be found naturally in water, but can also originate from mined areas. Typical sources comprise industrial waste, metal plating, and plumbing. None of the analyzed samples contained zinc in concentrations above 3.3 mg dm^{-3}. However, the WHO guideline is set at 3.0 mg dm^{-3} for zinc in drinking water (WHO 2011). Thus, the content of this study area could be attributed to natural rather than human sources.

Copper (Cu) concentrations in drinking-water vary widely as a result of variation in water characteristics, such as pH, hardness and copper availability in the distribution system. And dissolved copper can change the water colour and taste (WHO 2011). Since the evaluated area is close to the tailings dam, there was a risk of water pollution by compounds originating from the dam. The results of the metal analysis of water samples from the investigated sites are presented in Table 1. The analysis indicated that cooper concentrations were below the maximum allowed concentration. The potable water standard set by the World Health Organization for Cu is at 2.0 mg dm^{-3} (WHO 2011). The Cu concentrations calculated in our study ranged between approximately 0.001 mg dm^{-3} and 0.951 mg dm^{-3}.

The concentration of nickel was found to be above the permissible limits in a few wells (S3, S4), but the recorded cases were either a single accident or a natural phenomenon. In the case of nickel concentrations, the SD reflects a large amount of variation (Table 1).

Usually, the median gives a better representation of the central tendency than does the average value. Taking into account medians, the concentrations of the evaluated elements were within acceptable limits, with one exception (S1, where the manganese concentration exceeded the permitted value eight times). Overall median concentrations were 0.2, less than 0.1, 0.012, 0.003, 0.256 mg dm^{-3} for iron, manganese, cooper, nickel, zinc and chromium, respectively. These concentrations of the analyzed elements in wells are below the drinking water standards. However, the concentrations of the elements were unevenly distributed during the analyzed period of time.

Figure 2 depicts the major branches (clusters) in the dendrogram. The variation among the various parameters assayed in water sampled from the different sampling sites did not show a significant pattern of impairment. EMAD et. al. (2012) used a similar technique and discovered that the variation in water quality parameters measured in sampling sites is in good agreement with the degree of pollution. Dendrograms classifying the analyzed elements by the type and origin are presented in Figure 2.

Most of the dendrograms indicated two significant cluster groups that had no apparent visual cluster separation. The concentration of iron (Fe), shown in a dendrogram (Figure 2*a*), classified samples into two main groups: *S1* (cluster I) and others sampling sites (cluster II). The most significant as-

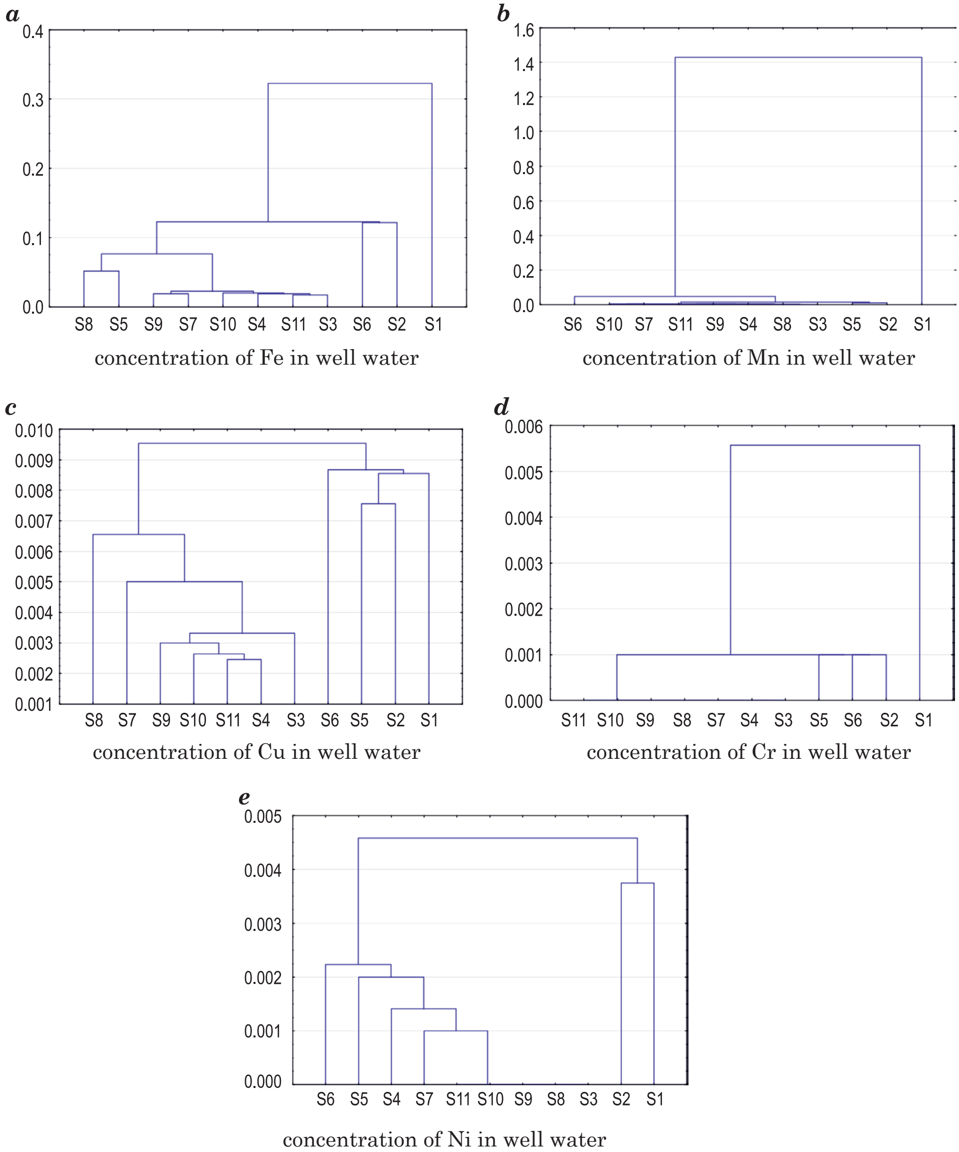

Fig. 2. The visual representation of the correlation between compounds and well water ain a hierarchical clustering dendrogram

sociation was between *S11, S3, S4, S10* (with a similarity or height of 0.02) and *S9, S7* sampling site (with a similarity or height of 0.03). The concentration of magnesium (Mn), classified data into two main groups: *S1* (cluster I) and others sampling sites (cluster II). As for cooper concentrations, the sampling sites were grouped into two statistically significant clusters: cluster I including sampling site *S6, S5, S2, S1*, and cluster II comprising the others sampling sites. The most significant association was between S11 and S4 (with a similarity or height of 0.0026).

The concentration of chromium (Cr), shown in a dendrogram, classified samples into two main groups: *S1* (cluster I) and others sampling sites (cluster II). The most significant association was between S5, S6, S2 and S10. As for nickel (Ni), the sampling sites were grouped into two statistically significant clusters: cluster I included sampling site *S2* and *S1* and clutser II composed of the other sampling sites.

Based on concentrations of the elements, all the analyzed well water samples were divided by cluster analysis into two major clusters. In most cases, the concentration in sampling point S1 differed significantly and usually created a single cluster or, less often, a multi-site *cluster*.

CONCLUSIONS

The results show that concentrations of some metals such as Fe, Mn and Cr in water samples are higher than the Polish and WHO standards. And since the water from the tested wells is not subjected to any purification processes, it is unsuitable for drinking. Moreover, the research results reveal that the quality of water from privately owned wells differs significantly.

Water from the wells was unsuitable for drinking, but the presence of the copper ore tailings impoundment did not affectd the water quality in the analyzed wells. The research did not reveal any strong or significant metal-location relationships in the water from the wells submitted to the investigation. The concentrations of the evaluated metals in wells did not have any correlation to the distance of the wells from Zelazny Most.

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