Monitoring of Groundwater Chemical Composition in Areas of Crop Production

Joanna Fronczyk[1], Mariusz Lech[2], Maja Radziemska[3], Anna Sieczka[4], and Zbigniew Lechowicz[5]

***Abstract*—**The main objective of the research presented in the paper was the monitoring of contaminant indicators in the groundwater in the area of precision cultivation of winter wheat in the northern, southern and central part of Poland. On each of the experimental sites, 6 piezometers were located, from which samples for chemical analysis were taken. The following parameters were determined: pH, electrical conductivity, nitrogen compounds, phosphates, sulphates, and heavy metals (Cu, Pb, Zn).

The results obtained revealed that fertilization has impact on the level of phosphorus, which in most of the analyzed samples, according to Polish legal provisions, was characteristic of III Class of groundwater quality (0.5 – 1.0 mgPO_4/L). The concentration of NO_3 was below the highest acceptable concentration of that parameter in drinking water recommended by WHO (50 mg NO_3/L). Nitrites, copper and lead concentrations did not exceed the maximum limits under Polish legal provisions for water intended for human consumption. In addition, sulphate ions had in most samples a concentration characteristic of III Class of groundwater quality (60 – 250 MgSO_4/L), and in samples collected at the Chociwel site - of IV Class (250 – 300 mgSO_4/L). However, the increased levels of this parameter did not result from fertilization. The study shows that the applied precision nitrogen fertilization could influence the acceptable concentration of nitrates in groundwater, while the inadequacy of the phosphoric fertilizer to the needs of the plants could have resulted in the increased concentrations of phosphate in the analyzed groundwater samples.

***Keywords*—**ammonium nitrate, fertilization, groundwater quality, phosphate fertilizers, precision agriculture.

I. Introduction

The intensification of agricultural production may cause increasing stress on the ecosystem [1]. Plant production, inter alia wheat as the third most-produced cereal in the world, is widely recognized as a branch of economy that affects the environment negatively, especially due to the contamination of surface and groundwater with nutrients (nitrogen and phosphorus) and pesticides. Because of their mobility in the soil-water environment, nitrates and phosphates may primarily migrate into groundwater. This phenomenon takes place because due to their anionic form nitrates and phosphates are not retained by soil particles and thus may cause eutrophication of groundwater and surface water [2], [3]. As Sharpley et al. [4] and Ulrich et al. [5] have reported, the over-enrichment of nitrogen (N) and phosphorus (P) are a pervasive water quality concern. According to CSO data [6], an average of 75.5 kg/ha of nitrogen fertilizers and 24.3 kg/ha of phosphorus was used in Poland in 2014, which resulted in the consumption of 1,098.4 thousand tons of nitrogenous fertilizers and 341.1 thousand tons of phosphate fertilizers. In Poland, the most commonly used are nitrogenous fertilizers, among which the most popular are ammonium nitrate, urea and nitro-chalk.

Runoff from agricultural areas is considered the main source of groundwater pollution by nitrogen compounds, which in Poland may cause eutrophication of the Baltic Sea. Approx. 5% of the monitoring stations in Poland have recorded groundwater nitrate concentrations above 50 mg/L, approx. 3% - a concentration between 40 and 50 mg/L and approx. 87% - a concentration below 25 mg/L. Based on average annual data from all monitoring stations of surface fresh water in EU-27, approx. 86% of the stations have recorded nitrate concentrations below 25 mg/L, slightly more than 2% have shown a concentration between 40 and 50 mg/L, and just over 2% have indicated a concentration greater than 50 mg/L [7]. Therefore, it is necessary to take measures aimed at reducing the concentration of nitrogen in surface water and groundwater, and to monitor the nitrogen cycle in soil and its migration in the aquifer. Limitation of nutrient losses and thus their spread into the environment is achieved through precision agriculture, which allows adjustment of the dose of fertilizer precisely to the needs of the crops. One of the possibilities to limit the migration of the nutrient in the subsoil used in the world is the application of permeable reactive barriers [8], [9]. This method utilizes the properties of various reactive materials to remove contaminants from groundwater [10]-[13].

The EU Water Directive [14] recommends the use of principles of sustainable development in the management of surface water and groundwater, and sets out a timetable of measures to ensure good quality of all waters in Europe.

Joanna Fronczyk[1] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Mariusz Lech[2] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Maja Radziemska[3] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Anna Sieczka[4] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

Zbigniew Lechowicz[5] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences - SGGW, Nowoursynowska 159, 02-776 Warsaw, Poland

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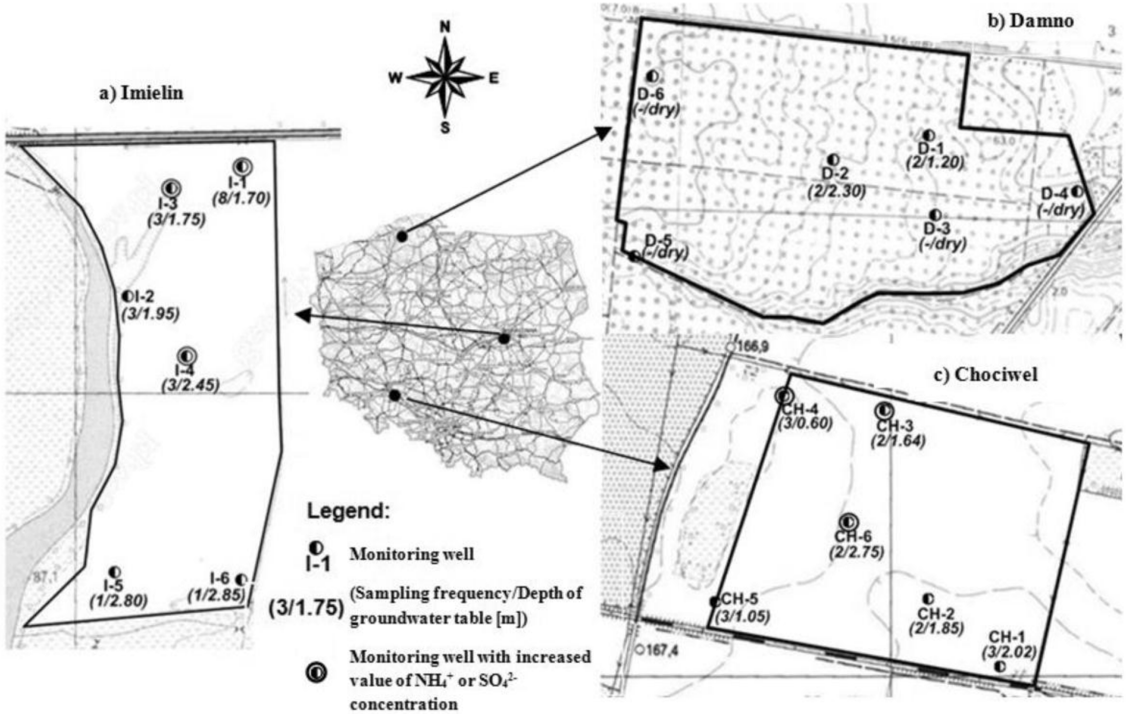

Fig. 1 Location of groundwater monitoring wells; experimental sites at a) Imielin; b) Damno; and c) Chociwel

The Council Directive 91/676/EEC [15] concerning the protection of waters against pollution caused by nitrates from agricultural sources aims at reducing water pollution and preventing such pollution through the monitoring of all types of uniform bodies of water, designation of vulnerable zones of nitrate pollution, establishing codes of good agricultural practice, and submitting the progress of implementation of the Directive every four years to the Commission.

The aim of the studies presented in the paper was the monitoring of contaminant indicators in groundwater in the area of precision cultivation of winter wheat in southern (Chociwel experimental site), northern (Damno experimental site) and central (Imielin experimental site) Poland.

II. Material and Methods

A. Experimental sites

Monitoring studies were conducted at three experimental sites located in various parts of Poland. The research was carried out in areas of crop production fertilized with the use of precision farming tools, but differing in terms of physical, geographical and climate conditions. The location of the experimental sites and the groundwater monitoring wells is shown in Fig. 1.

The Chociwel site (20 ha) is located near Wroclaw city in southern Poland. The area of the crop field is flat and devoid of characteristic forms of topography. In addition, to the west the field lies adjacent to wetlands, and approximately 200 m to the south of the field there are small ponds filling former clay pits. In the subsoil, below a 0.5 m thick soil layer, occur silty clays (1.5 m thick) and medium sands. In the vicinity of groundwater monitoring wells Ch-4 and Ch-5 was noted a significant thickness of organic soils to a depth of approx. 1.2 m below the surface.

The Damno site (40 ha) is located near Słupsk city in northern Poland. The study area is located in the zone of a glacial deposit moraine. In the subsoil, below the soil layer, occur silty clays and sandy clays.

The Imielin site (22 ha) is located near Warsaw in central Poland. In the subsoil, below the soil layer, silty clays with a thickness of up to 1 m have been identified. In the area of groundwater monitoring wells I-3 and I-5, the thickness of this layer reaches up to 2 m. Below occur silty sands and medium sands. To the west, the experimental site is bordered by Gwoździe Lake.

In each of the experimental sites, 6 groundwater monitoring wells were installed using the Edelman sampler. Water samples were collected from the monitoring wells, after stabilization of the groundwater table, into plastic containers (1.5 L) using a submersible pump. To stabilize the chemical composition of water prior to sample collection, it was necessary to pump three volumes of water stored in the monitoring well. In order to avoid the transfer of pollution, the submersible pump and pipes were washed with distilled water. The frequency of groundwater sampling varied depending on the location (Fig. 1). The depths of the groundwater table are given in brackets in Fig. 1. It should be noted that groundwater monitoring wells D-3 to D-6 were dry. The results of the monitoring studies were analyzed to determine the effects of fertilization on groundwater quality, as well as the depth of the water table and characteristics of the subsoil.

TABLE I
ELECTRICAL CONDUCTIVITY AND PH OF GROUNDWATER COLLECTED IN THE EXPERIMENTAL SITES

Parameter	Ch-1	Ch-2	Ch-3	Ch-4	Ch-5	Ch-6	D-1	D-2	I-1	I-2	I-3	I-4	I-5	I-6
Median EC	699	685	1,269	911	678	928	392	428	830	462	552	649	601	431
Mean EC	931	649	1,246	838	662	923	392	428	814	439	502	617	601	431
Median pH	8.31	7.32	7.89	7.25	7.64	7.87	7.20	7.49	7.54	8.01	8.36	8.08	7.3	6.97
Mean pH	8.07	7.50	7.95	7.31	7.54	7.85	7.20	7.49	7.53	7.77	7.86	7.93	7.3	6.97

B. Chemical analysis

Electrical conductivity (EC) and pH were measured in the field immediately after collecting of groundwater samples using a multi-parameter device (SCHOTT, Germany). The water samples were then filtered through a 0.45 µm filter, cooled to 2°C and transported to the laboratory. In the laboratory, the contents of PO_4, NH_4, NO_3, NO_2, SO_4 were measured by the spectrophotometric method using a DR-6000 UV-VIS equipment (Hach Lange, USA), whereas the content of metals (Cu, Pb and Zn) was measured by atomic absorption spectroscopy using an iCE-3000 spectrometer (Thermo Scientific, USA). All chemical analyses were made twice and in further calculations were used averaged values. The test results were analyzed using XLSTAT statistical software for Microsoft Excel.

III. RESULTS AND DISCUSSION

A. Physical parameters

The electrical conductivity of the groundwater samples ranges from 350.9 to 1,441.0 µS/cm (Table I). The highest values were observed in samples collected in Chociwel (from 551 to 1,441 µS/cm), and slightly lower values were noted in Imielin (from 385 to 898 µS/cm) and Damno (from 351 to 505 µS/cm). In Chociwel, the majority of the samples was characterized by EC values exceeding background values (200-700 µS/cm), but not exceeding the values characteristic of Class II of groundwater quality – 2,500 µS/cm [16]. In Imielin, all samples collected from well I-1 and one sample from well I-4 exceed the background value of 700 µS/cm, whereas in Damno in both monitoring wells the EC value did not exceed the background values. Measurement of this parameter allows monitoring both water quality and potential migration of contaminants because every change of the substance dissolved in water causes a change in the EC [17]. Some authors suggest that EC values above 1000 µS/cm in shallow groundwater may have resulted from anthropogenic pollution of water [18]. However, in EU countries the maximum admissible value of EC in potable water is 2,500 µS/cm. This value is also the limit of good groundwater quality.

The pH of the collected groundwater samples reached values ranging from 6.26 to 8.69 (Table I): in Chociwel from 7.12 to 8.69, in Damno from 6.26 to 8.13 and in Imielin from 6.79 to 8.38. With the exception of three samples (collected in September from wells Ch-1 and Ch-3 and in March collected from well D-1), the obtained values were characteristic of background values. In addition, only the pH of the sample taken in March from well D-1 in Damno was lower than the admissible value for good groundwater quality. According to EU rules, water with a pH ranging from 6.5 to 9.5 is allowed for human consumption.

B. Nitrogen compounds

The concentration of nitrate in groundwater samples from the analyzed experimental sites ranged from 0.1 to 16.2 $mgNO_3/L$ (Fig. 2). The largest variability of NO_3 concentration was observed in samples taken from monitoring wells located in Chociwel (0.2-16.2 $mgNO_3/L$), but only in one sample the nitrate concentration was characteristic of Class II of groundwater quality (16.2 $mgNO_3/L$). In Imielin, the nitrate concentration ranged from 0.1 to 1.6 $mgNO_3/L$ and therefore was within a range of concentrations typical of background values (0-5 $mgNO_3/L$). Groundwater in Damno had a concentration of NO_3 larger than the background values but still not exceeding the admissible value for Class I of groundwater quality (7.9-9.5 $mgNO_3/L$). Because of high solubility and anionic form, only to a small extent subject to sorption processes, nitrates are a common form of nitrogen migration in shallow groundwater, especially from fertilization sources [19]. High NO_3 concentration (>50 $mgNO_3/L$) has been recorded in numerous aquifers all over the world, e.g. in Canada [20] and Portugal [21]. However, in the case of the experimental sites, no significant anthropogenic effect was observed in the NO_3 content and the nitrate concentrations did not exceed the maximum concentrations allowed by EU and WHO in water intended for human consumption and the limit value of good quality of groundwater (50 $mgNO_3/L$).

In the analyzed experimental sites, nitrite concentration ranged from 0.001 to 0.436 $mgNO_2/L$ in groundwater (Fig. 2). The highest values were observed in Chociwel in samples taken in March from wells Ch-1 (0.436 $mgNO_2/L$), Ch-2 (0.333 $mgNO_2/L$) and Ch-3 (0.148 $mgNO_2/L$), and in May from well Ch-6 (0.156 $mgNO_2/L$). All the samples, with the exception of well Ch-3, exceeded the value of the concentration limits for Class II of groundwater quality, but did not exceed the limit value for good groundwater quality (0.5 $mgNO_2/L$). In most samples, the nitrite content in groundwater samples from Chociwel and Imielin did not exceed typical background values (0-0.03 $mgNO_2/L$), whereas the nitrite concentration in the samples collected in Damno was characteristic of Class II of groundwater quality (0.03-0.15 $mgNO_2/L$). Some authors assume that the nitrite content above 0.010 $mgNO_2/L$ in the shallow groundwater may be evidence of pollution from e.g. liquid manure or natural and

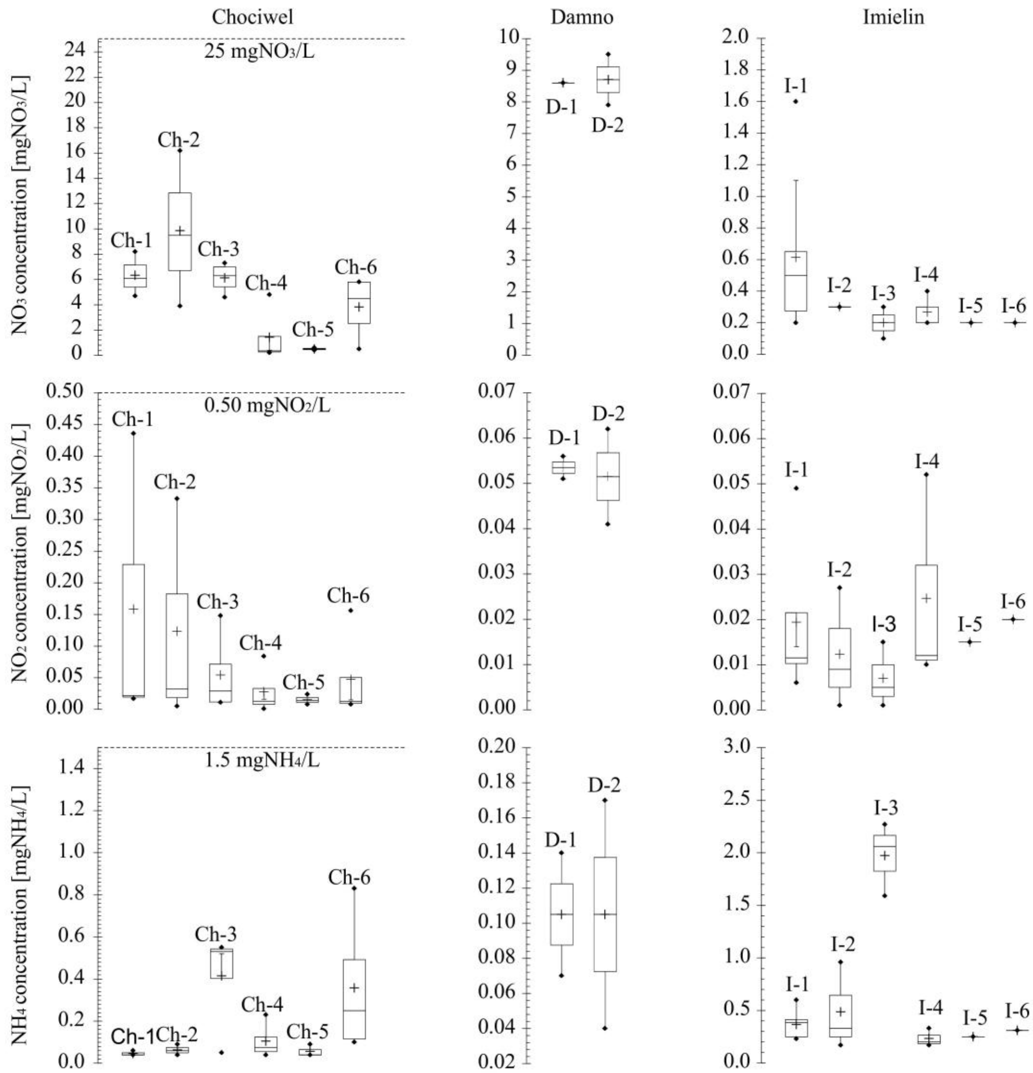

Fig. 2 Concentration of nitrates (NO_3), nitrites (NO_2) and ammonium (NH_4) in groundwater collected in the experimental sites

artificial fertilizers [18]. Furthermore, due to the unstable nature of nitrite, its higher amounts may be an important indicator of water contamination by organic substances. The measured concentrations did not exceed the limit EU values in water intended for human consumption and the limit for good groundwater quality (0.5 $mgNO_2$/L).

It is commonly recognized that ammonium is a typical indicator of pollution, especially in shallow groundwater [22]. The content of ammonium ions in the analyzed groundwater samples ranged from 0.04 to 2.27 $mgNH_4$/L (Fig. 2). The largest concentrations ranging from 0.17 to 2.27 $mgNH_4$/L were observed in Imielin, and slightly smaller in Chociwel (0.04-0.83 $mgNH_4$/L) and Damno (0.04-0.17 $mgNH_4$/L). Most of the analyzed samples, with the exception of samples taken in Imielin from well I-3, did not show concentrations greater than those typical for the background (0 - 1 $mgNH_4$/L). Throughout the measuring period, the concentration of ammonium ions in well I-3 exceeded the threshold of good groundwater status (1.5 $mgNH_4$/L) and permissible concentrations in water intended for human consumption (0.5 $mgNH_4$/L). Well I-3 is located in a local depression, which also collected organic material such as organic fertilizers. Decomposition of organic matter can be a source of ammonium ions in concentrations characteristic of poor groundwater quality. Maximum concentrations in water intended for human consumption has also been exceeded in wells Ch-3 and Ch-6. However, it must be noted that the migration of ammonium ions in groundwater is inhibited through sorption by the material of the aquifer [22] [23].

C. Phosphates

The phosphate concentration in the analyzed samples of groundwater ranged from 0.3 to 1.0 $mgPO_4$/L (Fig. 3.). The highest concentrations were in Chociwel, from 0.3 to 1.0 $mgPO_4$/L, slightly lower in Damno (0.4 to 0.7 $mgPO_4$/L) and Imielin (0.3 to 0.7 $mgPO_4$/L). The phosphate content in all samples was in the range of concentrations typical of the background (0.01-1.0 $mgPO_4$/L), and did not exceed the threshold of good groundwater quality (1.0 $mgPO_4$/L) but the PO_4 concentrations were close to these values. This may be

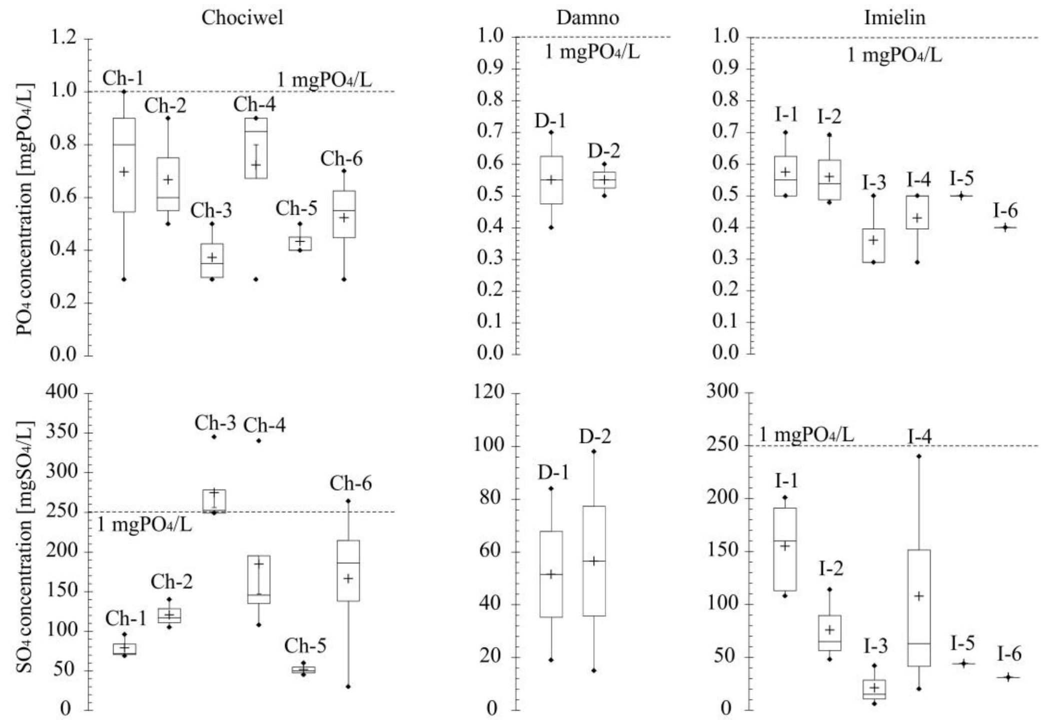

Fig. 3 Concentration of phosphates (PO_4) and sulphur (SO_4) in groundwater collected in the experimental sites

due to the inadequacy of the phosphoric fertilizer to the needs of plants. The source of phosphate in groundwater may be fertilization of crop fields. In flat regions, PO_4 transport through the soil profile plays a dominant role, which can lead to groundwater eutrophication [24], but according to WHO [25] there are no grounds to limit phosphates in water intended for human consumption.

D.Sulphur

Sulfate concentration in groundwater samples ranged from 6 to 345 $mgSO_4/L$ (Fig. 3). The highest concentrations were observed in Chociwel (30-345 $mgSO_4/L$). In Damno, SO_4 concentration had a value from 15 to 98 $mgSO_4/L$, and in Imielin – from 6 to 240 $mgSO_4/L$. The measured concentrations in most cases were higher than those typical of background values (5-60 $mgSO_4/L$). Similarly as chloride ions, sulfate ions are migrating ions used as the key indicators of pollution from anthropogenic sources to groundwater, which primarily depend on the lack of overlap sorption processes [26]. A sulfate content of less than 250 $mgSO_4/L$ is admissible for water intended for human consumption. In Chociwel, in samples taken from wells Ch-3 and Ch-4 (September), and Ch-6 (March), the sulfate concentrations exceeded the threshold values for good groundwater quality (250 $mgSO_4/L$), which most likely was caused by the oxidation of organic sulfur contained in the soil. Higher levels characteristic of the poor quality of groundwater were also reported in Imielin in wells I-1 (April) and I-4 (June).

E. Heavy metals

The zinc concentration in groundwater collected from the analyzed experimental sites was less than 0.0052 mgZn/L, copper – less than 0.021 mgCu/L, and lead – less than 0.05 mgPb/L. The results indicate that values characteristic of good quality of groundwater have not been exceeded, which are: 1 mgZn/L for zinc, 0.2 mgCu/L for copper, and 0.1 mgPb/L for lead. In the EU, the permissible concentration of copper in drinking water is 2 mgCu/L, whereas of lead – 0.01 mgPb/L. According to the "Dutch List" popular in Europe, groundwater with a content of less than 0.05 mgZn/L, 0.02 mgCu/L or 0.02 mgPb/L is considered to be clean; concentrations exceeding 0.2 mgZn/L, 0.05 mgCu/L or 0.05 mgPb/L should be indicated for detailed diagnosis, while concentrations of more than 0.8 mgZn/L, 0.2 mgCu/L or 0.2 mgPb/L are regarded as requiring pollution prevention and remediation activities.

IV. Conclusion

Analysis of groundwater samples collected from monitoring wells located in the experimental sites has shown that:

1) groundwater collected in spring (wells Ch-3 and Ch-6) and early autumn (wells Ch-3 and Ch-4) in Chociwel should be classified as water of poor quality due to the elevated concentrations of sulfate ions,

2) despite the higher concentrations of phosphates and sulfates, and based on the concentration of all tested parameters, groundwater taken from Damno can be classified as groundwater of good quality,

3) groundwater taken from monitoring wells in Imielin is characterized by lower concentration levels of the analyzed parameters in comparison to the limits for good quality of groundwater. The exception is well I-3 located in a local depression, in which a higher concentration of ammonium ions

characteristic of poor groundwater quality was measured.

In terms of the content of nitrogen compounds in the groundwater, the samples taken from Chociwel and Damno did not show a worrying state of water quality. The study shows that the applied precision nitrogen fertilization could influence the admissible concentration of nitrates in groundwater, while the inadequacy of the phosphoric fertilizer to the needs of plants could have resulted in the increased concentrations of phosphate in the analyzed groundwater samples.

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