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ORIGINAL PAPER

CONTENT OF SELECTED MACRO- AND MICROELEMENTS IN SURFACE WATER OF IN-FIELD PONDS AND IN GROUNDWATER FROM ADJACENT AGRICULTURAL AREAS*

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Abstract

Small water bodies located in agricultural areas, so-called in-field ponds, are relicts of the last glaciation. They are characterized by high biodiversity, in addition to which they are astatic and subject to strong anthropopressure due to agricultural production, leading to their eutrophication. The main factors indicating water eutrophication include phosphorus and nitrogen compounds, but of significance are also heavy metals, trace elements and other macro- and microelements contained in water. The study was conducted in two small, in-field ponds in temperate climate. The aim of the undertaken study was to analyse and assess selected macro- and microelements in surface water of two in-field ponds and in groundwater under cultivated soil adjacent to the ponds. The content of the following elements was tested in water: Mg, Ca, Fe, Mn, Na, K, Zn. Among the analyzed macro- and microelements in the studied surface water and groundwater, the highest mean values were observed for calcium and chlorides, and the content of all the elements can be presented in the following order: Ca > Cl > Mg > Na > K > Fe > Mn > Zn. The highest levels of Ca, Cl, Mg and Na were recorded in groundwater under an intensively farmed field in Stare Czarnowo and in the in-field pond located in the middle of this field. Significant seasonal changes in the content of particular macro- and microelements were observed, with frequent peaks, primarily in the summer and autumn, resulting from the mobilization of internal resources from the bottom sediment or water flora.

Keywords: surface water, groundwater, macroelements, microelements, in-field ponds, cultivated soil.

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INTRODUCTION

The last glaciation enriched the landscape of northern Poland with small depressions filled with water which formed closed water bodies, nowadays called in-field ponds. Their area does not usually exceed 1 ha and the water depth is between 1 and 3 m. Seasonal changes in the water level suggest that such ponds are astatic (Gołdyn et al. 2015). Many such ponds lie in the agricultural landscape and have a number of environmental functions: from biocenotic to physiocenotic and landscape functions. They create a specific microclimate and constitute a natural habitat for numerous species of flora and fauna (Kuczyńska-Kippen 2014). The number of vascular plant species living in in-field ponds is sometimes impressive, and in the summer reed-bed plants are abundant on a pond's surface (Symonides 2010, Wesołowski et al. 2016). In-field ponds are also important for fauna, since they regulate the biotic community of the surrounding areas. They are a site of mass breeding of entomofauna and herpetofauna and provide good breeding conditions for ichthyofauna. They also serve as habitats and water holes for field animals and game (Knutson et al. 2004). Their specific location in the agricultural landscape facilitates formation of specific protecting barriers that prevent migration of biogenic substances from agriculturally used fields, hence they act as a kind of trap for nutrients (Symonides 2010, Kuczyńska-Kippen 2014).

While having numerous environmental functions, in-field ponds are exposed to various dangers, hence their number in the agricultural environment continues to decline every year (Pieńkowski et al. 2010). Disappearance of in-field ponds results from several factors, including climate changes or the lowering of the level of groundwater which supplies them. Both mathematical and geographical studies prove the high significance of the smallest water bodies, for example owing to their role in water retention (Downing 2010). Their locatilization in an agricultural environment accelerates progressive eutrophication, which is caused by intensive agriculture, increased fertilization and the growing use of plant-protection products as well as substances stimulating the plant growth. The ecological condition of in-field ponds is determined by biogenic compounds accumulated in bottom sediments and, to a large extent, by the quality of surface water and groundwater. The main factors indicating water eutrophication include phosphorus and nitrogen compounds (Siwek et al. 2015), but of significance are also heavy metals, trace elements and other macro- and microelements contained in water, which often accumulate in bottom sediments and in living organisms (Gałczyńska et al. 2011, Karwacka et al. 2015, Kuriata-Potasznik et al. 2016).

The aim of the undertaken study was to analyse and assess selected macro- and microelements in surface waters of two in-field ponds and in groundwater under cultivated soil adjacent to the ponds.

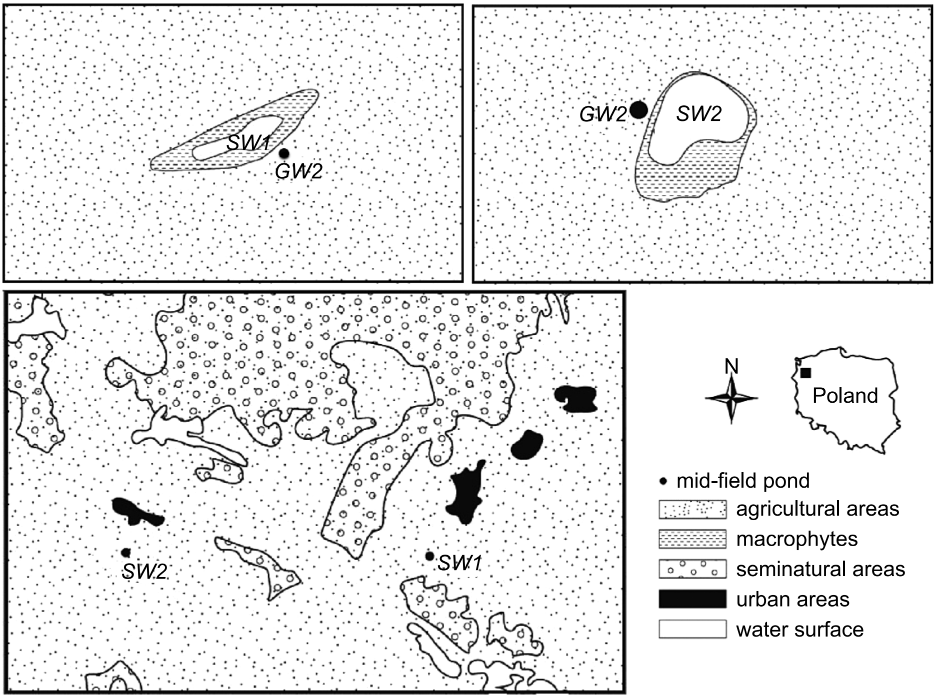


Figure 1. Map of the studied in-field ponds and land use:
SW – surface water, GW – groundwater

Study design and scope

The study was conducted in 2014-2015, in two selected in-field ponds lying in the municipality of Stare Czarnowo (Figure 1). The ponds are similar as regards environmental conditions of the drainage basin, which is entirely comprised of agricultural areas. Environmental conditions of the drainage basin were determined according to the Corine Land Cover 2006 database. Agricultural areas encompass arable lands, permanent crops, meadows and pastures as well as mixed crop zones. Semi-natural areas are forests, semi-natural ecosystems and systems of shrub plants. Urban areas are urbanised areas, industrial areas and anthropogenised green areas.

The first water body, located at 53°16′04″N 14°46′06″E, has an area of about 0.8 ha, lies in a land depression, and is constantly supplied by groundwater and rainwater as well as by runoffs from adjacent farmed soil. The surface water samples in the pond were marked with the symbol SW1. The drainage catchment of the Stare Czarnowo pond is approximately 18 ha large. The fields adjacent to the pond were located on a slope with 5% gradient in relation to the pond. To the north of the pond, a piezometer (3 m depth) for groundwater (GW1) collection was installed on arable land, 5 m from the pond. During the study crops such as winter oilseed rape (*Brassica napus* L. (partim)), winter barley (*Hordeum vulgare* L.) and triticale (*xTriti-*

cosecale Wittm. ex A. Camus), were cultivated on the whole field. The depth of the pond was about 100 cm on average, and the shores were overgrown with reed-bed plants represented by common reed (*Phragmites australis* (Cav.) Trin. ex Steud), broadleaf cattail (*Typha latifolia* L.), great manna grass (*Glyceria maxima* (Hartm.) Holmb.) and single willow trees (*Salix* L.).

The second pond was located on arable fields in the village Żelisławiec (53°16′10″N 14°39′59″E). It covers an area of 0.9 ha and is filled with surface water (SW2), which – similarly as in the first pond – was replenished with groundwater (GW2) and rainwater. A piezometer (3 m depth) was located 5 m from the pond. The field gradient was about 1%. The drainage area of the Żelisławiec pond was approximately 52 ha, 45% of which are agricultural areas. During the study, the following plants were grown in the catchment: winter wheat (*Triticum aestivum* L.) and winter oilseed rape (*Brassica napus* L. (partim)), but not in the closest proximity of the water pond (7 m). The in-field pond in Żelisławiec was overgrown with reed-bed plants: common reed and broadleaf cattail. The average water depth in this pond in 2014-2015 was about 80 cm.

Both ponds were located on the cultivated soil which belonged to Cambisols. Water samples were collected in two research periods, from April through October. Samples were taken from both ponds, at three pre-determined points, and from one shallow piezometric well each located on the adjacent agricultural areas (a few meters away from the ponds). A WHALE submersible portable pump was used to collect water, which was then transported in sealed polyethylene bottles (250 mL volume) to the Research Laboratory of the Environmental Chemistry at the Institute of Technology and Life Science in Falenty. Mg, Ca, Fe, Mn and Zn levels were determined by flame atomic absorption spectrometry at a wavelength of 248.5 nm, whereas Na and K levels were determined by an emission method with the use of a SOLAAR S atomic absorption spectrometer from Thermo Elemental. Water reaction was measured by the potentiometric method using a SevenMulti meter from Mettler Toledo, and specific electrolytic conductance was measured with a Tetragon 325 conductometric vessel.

The quality of surface water was assessed according to the *Regulation of the Minister of the Environment…* (2016), and of groundwater according to the *Regulation of the Minister of the Environment…* (2015). As for surface waters, the measurements were limited to water reaction and electrolytic conductance, since there are no limit values for uniform parts of surface waters, such as a lake or other natural water bodies.

Pooled results of chemical analyses were statistically compiled by Statistica 12.5 PL software (StatSoft Poland). A single factor analysis of variance (ANOVA) was used to determine statistically significant differences between the studied ponds and points located thereon, and to compare the content of micro- and macroelements in surface and groundwater. Additionally, standard deviation (SD) was calculated and a *post-hoc* Duncan test ($p \leq 0.01$) was used to compare mean parameters in the samples.

RESULTS AND DISCUSSION

Chemical composition of water in small in-field ponds depends on numerous factors, such as soil type and physical properties or climate conditions. The most significant, however, is how the land surrounding the water bodies is managed, which in turn determines how elements migrate in the water environment (Asare et al. 2018).

The results of theis study conducted on two in-field ponds show that the highest values of water reaction, electrolytic conductance and content of the studied elements were observed in surface water and groundwater in the locality of Stare Czarnowo (SW1 and GW1), as presented in Table 1. The differences in the content of various macro- and microelements may result from the drainage basin being used for agricultural purposes, the field gradient and biogeochemical barriers (Sharpley 1985). The pond lying in Stare Czarnowo is all surrounded by farmed fields.

The pond located in Żelisławiec is situated in an area which is less used for farming (45% of farmed fields). Moreover, there is a belt of land separating the pond from the cultivated soil, and the gradient of the adjacent arable land is smaller (1%).

Surface waters in the two in-field ponds had nearly neutral reaction (Table 1), which is typical of small water ponds located on agricultural areas (Gałczyńska et al. 2011). Water reaction values in 2014-2015 for surface waters were 7.01 (SW2) and 7.37 (SW1) – Table 1. The analyses of groundwater samples (GW1) showed slightly higher values of pH (7.11) than in surface waters (SW1), but they still corresponded to neutral reaction. The lowest pH values were observed in groundwater (GW2) – 6.38 (Table 1).

Table 1

Mean values of water pH, electrolytic conductance and the content of macro- and microelements in surface (SW) and ground water (GW) within one commune

Parameters	SW1	GW1	SW2	GW2
pH	7.37^{a}±0.28	7.11^{a}±0.28	7.01^{a}±0.30	6.38^{a}±0.57
EC (μS cm^{-1})	452^{b}±56.14	720^{c}±138.09	122^{a}±46.11	181^{a}±102.93
Cl (mg dm^{-3})	46.61^{b}±17.90	45.39^{b}±21.58	10.63^{a}±4.94	15.26^{a}±10.98
Na (mg dm^{-3})	10.04^{b}±5.61	11.65^{b}±5.28	4.25^{a}±2.10	7.49^{a}±6.19
K (mg dm^{-3})	8.04^{b}±2.70	2.72^{a}±1.19	8.72^{b}±2.44	3.68^{a}±2.06
Mg (mg dm^{-3})	10.70^{b}±2.05	15.54^{b}±4.97	1.89^{a}±1.49	3.91^{a}±3.85
Ca (mg dm^{-3})	60.20^{c}±11.14	97.91^{c}±20.49	9.68^{a}±3.59	14.76^{b}±14.26
Fe (mg dm^{-3})	0.09^{a}±0.08	0.04^{a}±0.03	0.67^{b}±0.48	1.15^{b}±1.05
Mn (mg dm^{-3})	0.02^{a}±0.02	0.03^{a}±0.04	0.05^{a}±0.07	0.65^{b}±0.40
Zn (mg dm^{-3})	0.01^{a}±0.01	0.02^{a}±0.01	0.02^{a}±0.01	0.02^{a}±0.02

The table presents mean values and standard deviations (SD). Mean values marked with identical superscripts are not significantly different at $p < 0.01$, the Duncan`s multiple range test.

The analyses of the groundwater sampled in Stare Czarnowo a few years before (2011-2012) showed slightly lower pH values, which were 6.78 on average (BRYSIEWICZ et al. 2013). No statistically significant differences were observed between the groundwater and surface water samples ($p > 0.01$). According to the Polish regulations on the quality of surface water and groundwater, the results obtained in the studied ponds and piezometric wells with regard to pH suggest good water quality (*Regulation of the Minister of the Environment 2015 and 2016*). In 2010-2012, the surface water's pH (P1) was also neutral, 7.24 on average (BRYSIEWICZ et al. 2013).

During two research periods, specific electrolytic conductance of surface waters (SW1) did not reveal significant differences and was 452 µS cm^{-1} on average. Significantly lower values, however, were obtained in the other pond SW2 – 122 µS cm^{-1}. Such low conductance could be related to changes in the floristic composition of the plant communities in the ponds, which could have caused changes in water quality, especially with regard to the intensive growth of plants in the summer (KOC et al. 2008). The values of electrolytic conductance in groundwater were higher than in the water ponds (Table 1) and with regard to GW1 they did not meet the requirements of class I quality of groundwater resources (*Regulation of the Ministry of the Environment* 2015). A statistical analysis revealed statistically significant difference ($p < 0.01$) – Table 1. Another study conducted in 2010-2012 showed lower values of electrolytic conductance in surface water and groundwater in the region of Stare Czarnowo (BRYSIEWICZ et al. 2013).

Among the analyzed mean values of macro- and microelements in the studied surface water and groundwater, the highest values were observed for calcium and chlorides, and the overall results can be presented in the following order: Ca > Cl > Mg > Na > K > Fe > Mn > Zn – Table 1.

The highest calcium levels in groundwater were observed in the village Stare Czarnowo (GW1), where they were several times higher than those observed in Żelisławiec (GW2) (Table 1). Due to the elevated values of Ca in groundwater (GW1), the studied waters were classified as representing water quality class II (Regulation of the Ministry of the Environment 2015). Low water reaction (pH) is essential for the calcium content, and the Ca content in water increases as a result of acid rains or nitrification (REPANT et al. 2017). In the surface water SW1, the calcium content was on average 60.20 mg Ca dm^{-3}, whereas in groundwater GW1 it reached 97.91 mg Ca dm^{-3}. High calcium levels were mainly observed on wetlands, where intensive water transfer is observed due to percolation (SCHOT, WASSEN 1993). Our comparison of the results from both ponds revealed statistically significant differences ($p < 0.01$). Such differences were also observed in the Stare Czarnowo pond with regard to SW1 and GW1 values (Table 1). The highest increase in calcium levels in the waters near Stare Czarnowo was observed in the summer (August) and spring (May) – Figure 2*i*. The smallest calcium loss is again observed in the summertime, and the calcium level does not decline until autumn and winter (TANDYRAK et al. 2005).

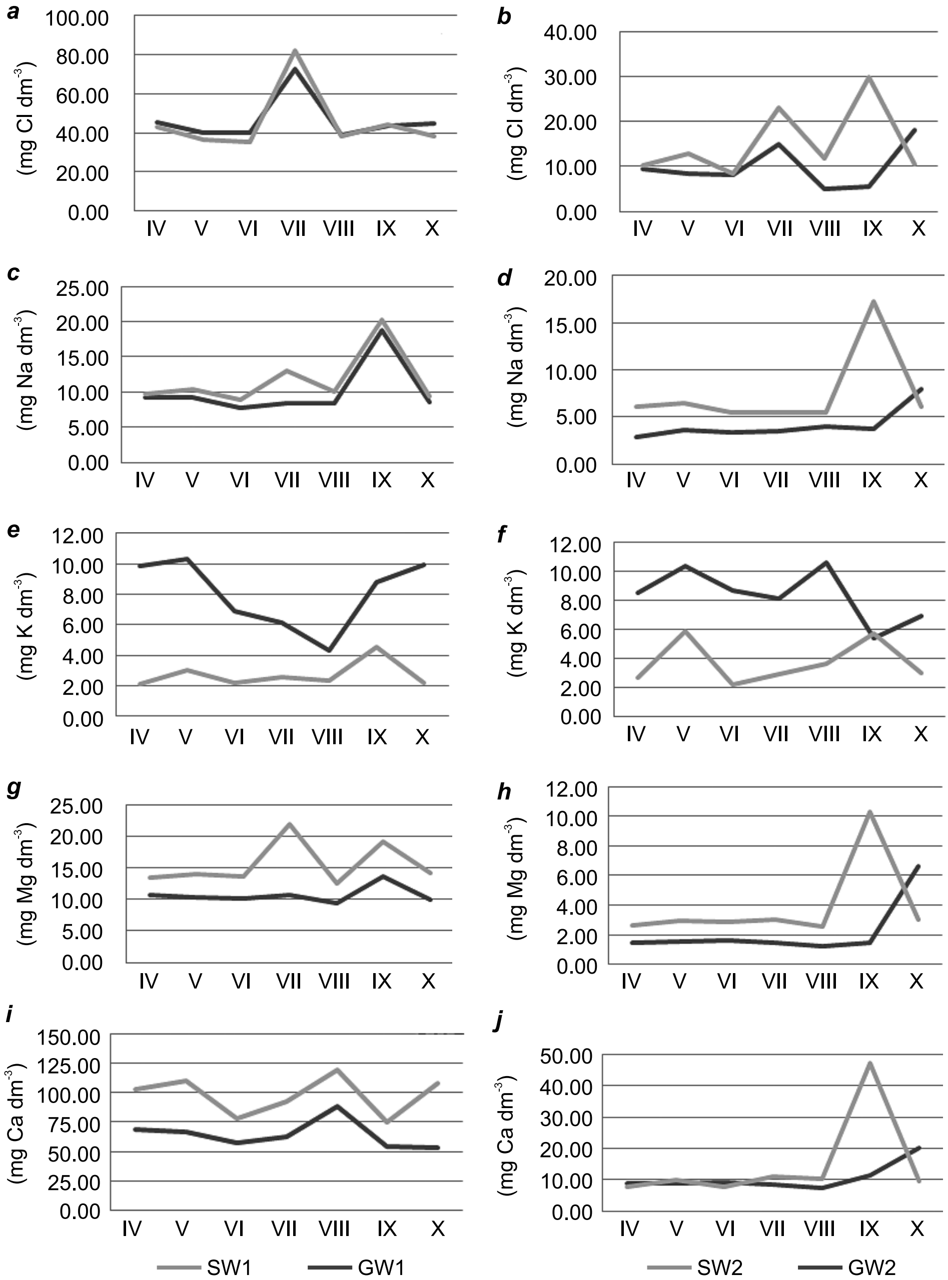
The content of chlorides in the analyzed waters was elevated, but still within the permissible limits, in the locality of Stare Czarnowo. Mean values for SW1 were 46.61 mg Cl dm^{-3}, whereas for GW1 they reached 45.39 mg Cl dm^{-3}. Significantly lower results were obtained for surface waters in the pond in Żelisławiec (SW2), namely 10.63 mg Cl dm^{-3} and 15.26 mg Cl dm^{-3} in groundwaters GW2 (Table 1). The comparison of surface water and groundwater samples between Stare Czarnowo and Żelisławiec revealed statistically significant differences ($p < 0.01$) – Table 1.

The chemical analysis of the water samples demonstrated mean magnesium levels at 10.70 mg Mg dm^{-3} for P1 and 15.54 mg Mg dm^{-3} for GW1. These waters are characterized by a relatively low magnesium content, but the values are twice as high as determined in other in-field ponds (Koc et al. 2008). In the other pond, the magnesium levels were significantly lower and equalled 1.89 mg Mg dm^{-3} (SW2) and 3.91 (GW2). The statistical analysis revealed statistically significant differences ($p < 0.01$) between the studied surface water and groundwater samples (Table 1). Comparably low magnesium levels were observed in other closed water bodies, which is typical of post-glacial areas (Koc et al. 2008).

Magnesium levels in water changed seasonally. The highest values were observed in groundwater, mainly in the summer and autumn (Figure 2*g*). This is related to the intensive magnesium absorption by plants in the spring, whereas the Mg increase in water observed in the summer and autumn is related to the activation of internal resources of the ponds (flora and bottom sediments) – Koc et al. (2008).

The in-field pond is Stare Czarnowo (SW1) was surrounded by intensively utilized arable land, which could be the cause of a higher content of calcium and magnesium, supplied to the pond together with surface runoffs. In 2014-2015 in Żelisławiec, only some (45%) of the land surrounding the studied pond was farmed. Moreover, there was a belt of land (3.5 m wide buffer zone composed of grass plants) between the arable land and the water pond. High contents of both elements studied were also observed in lakes supplied by rivers, where a specific water exchange system was created (Rafałowska, Sobczyńska 2012). The influence of river water supplying lakes (a river-lake system) can be compared to supplying in-field ponds with surface runoffs (a flow-pond system). In-field ponds are usually located in land depressions, which means that it is the flow from arable land that carries the largest amount of macro- and microelements, which can be defined as a flow-pond system.

Like chlorides, sodium levels in surface water of the pond in Stare Czarnowo were twice as high as in surface water of the pond in Żelisławiec. The mean Na content in SW1 was 10.04 mg Na dm^{-3}, and 4.25 mg Na dm^{-3} in SW2 (Table 1). The analyses of groundwater revealed higher mean concentrations: 11.65 mg Na dm^{-3} for GW1 and 7.49 mg Na dm^{-3} fpr GW2. Statistically significant differences were observed ($p < 0.01$) – Table 1. On agricul-



turally used areas, there was a positive correlation between the magnesium and sodium content in ground and surface water (Figure 2*c-d* and *g-h*).

In September, a rapid increase in the levels of chlorides, sodium, magnesium and calcium was observed in the pond in Żelisławiec, which may sug-

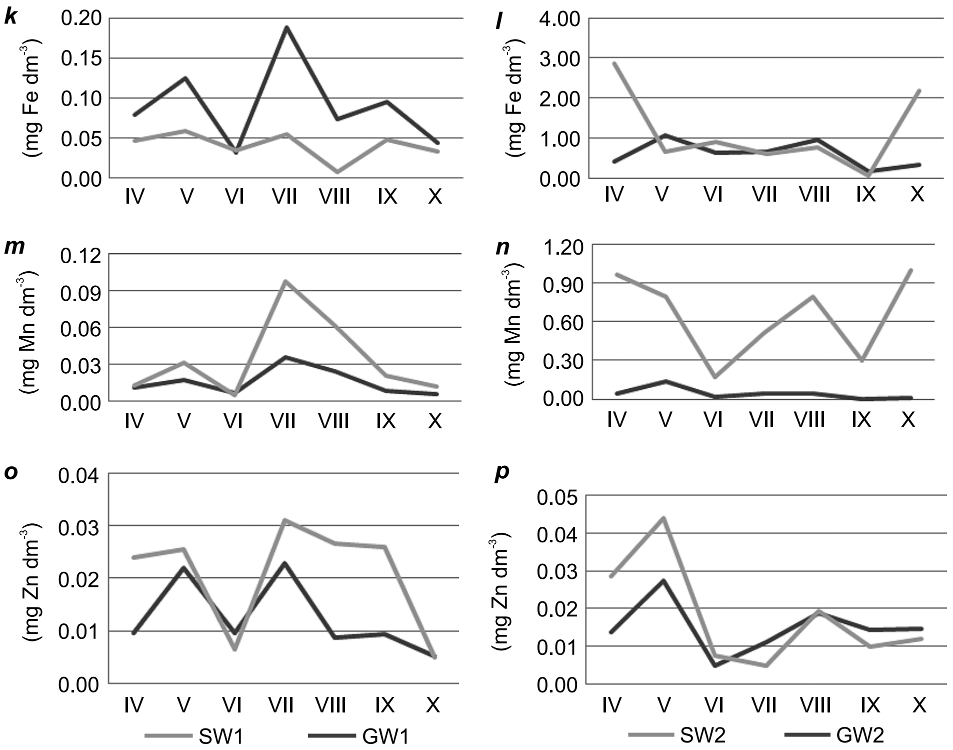


Fig. 2. Mean monthly levels of particular macro- and microelements in surface water and groundwater in Stare Czarnowo and Żelisławiec

gest internal mobilization of the pond's resources in the form of bottom sediments, a frequent event in small closed ponds in the autumn (Koc et al. 2008). This is confirmed by the results obtained from meteorological data, which indicate that the lowest average rainfall was recorded in the area of Stare Czarnowo in August, especially in 2015 (Bulletin of the National Hydrological and Meteorological Service 2015).

The potassium values obtained for surface water and groundwater were relatively low. The mean values for the two-year study were similar in both areas, i.e. 8.04 mg K dm^{-3} for SW1 and 8.72 mg K dm^{-3} for SW2. The analyses of groundwater revealed lower potassium levels and were on average 2.72 mg K dm^{-3} (GW1) and 3.68 mg K dm^{-3} (GW2) – Table 1, which means that the waters may be classified representing water quality class I (*Regulation of the Minister of the Environment* 2015). A statistical analysis revealed differences between the results from surface water and groundwater samples ($p < 0.01$) – Table 1. In the spring, an increase in the potassium content was observed, whereas in the summer, a temporary decrease in this element was noticed (Figure 2*e-f*).

The surface water and groundwater samples had different iron content. In the Stare Czarnowo pond, the iron content was low: 0.09 mg Fe dm^{-3}, whereas the content in groundwater in that site was even lower: 0.04 mg Fe dm^{-3} (Table 1). There were statistically significant differences ($p < 0.01$) between groundwater and surface water samples collected in Stare Czarnowo and in Żelisławiec (Table 1). The pond water (SW1) was characterized by high seasonal variability (Figure 2*k*), and the iron content decreased and increased three times in a year, that is in spring, summer and autumn. Similar increases were also observed in groundwater (GW1). In Żelisławiec, from May through August, the iron content was relatively stable (Figure 2*l*). The high iron content in groundwater (GW2) meant that it belonged to water quality class III (*Regulation of the Ministry of the Environment* 2015).

Surface water (SW1 and SW2) and groundwater (GW1) were characterized with a low manganese content (Table 1). In Stare Czarnowo, the content of this element was about 0.02 mg Mn dm^{-3} (SW1) and 0.03 mg Mn dm^{-3} (SW2), and in Żelisławiec it was 0.05 mg Mn dm^{-3} (SW2). An exception was the groundwater in Żelisławiec, where the mean values were over ten times higher, reaching 0.65 mg Mn dm^{-3}, which classified that water as representing class III of groundwater quality (*Regulation of the Minister of the Environment* 2015). Analysing seasonal changes in the manganese content in the water samples from Stare Czarnowo, it was observed that changes in the manganese content in groundwater and surface water (SW1 and GW1) were similar (Figure 2*m*). Such changes were not observed in the waters of Żelisławiec (Figure 2*n*). Statistically significant differences were observed between waters in Stare Czarnowo (SW1 and GW1) and surface waters in Żelisławiec (SW2) and groundwater from this area (GW2), $p < 0.01$ (Table 1).

The lowest levels of microelements were achieved in the analyses of the water zinc content (Table 1). The values were low enough (0.01 and 0.02 mg Zn dm^{-3}) to classify all samples as water quality class I (*Regulation of the Minister of the Environment* 2015). No statistically significant differences were observed (Table 1). In both sites, changes and similar zinc distribution in water were observed in groundwater and surface waters (Figure 2*o*-*p*). Zinc in water is very important because this element often accumulates in bodies of aquatic living organisms (Giardina et al. 2009). Large amounts of zinc are also present in the bottom sediment of small water bodies and concentrations of this element in particular layers decrease with the depth and age of the sediment (Szydłowski et al. 2017).

Although the two in-field ponds were supplied mainly with rainwater and groundwater, one must consider a large influence of water penetration into the ponds. This is confirmed by results from studies conducted in particular seasons when changes in the content of macro- and microelements are visible in groundwater and surface water (Figre 2).

Climate change, droughts, intensification of agriculture and, especially, high quantities of nutrients flowing to the ponds deteriorate their poor condition, accelerate eutrophication and contribute to gradual disappearance (Pieńkowski et al. 2010). For years, there have been calls for the inclusion of a small water body construction programme in the regional land-use planning, which would increase water retention, essential in agricultural areas (Starczewski, Czarnocki 2009). It is worth following the example of the Scandinavian countries, where after many years the role of small water ponds has been appreciated and such water bodies are now restored (Strand, Weisner 2013). Those examples should make us strive towards the preservation of these precious ecosystems in the agricultural environment while they are still present, since their reconstruction will entail huge costs.

CONCLUSIONS

1. The analyses of surface water and groundwater samples revealed high differences between particular macro- and microelements, which was due to the drainage basin used for agricultural purposes, the field gradient and biogeochemical barriers.

2. Significant seasonal changes in the content of particular macro- and microelements were observed with frequent increases, primarily in the summer and autumn, which could have resulted from the mobilisation of internal resources from the bottom sediment or water flora.

3. The in-field pond in Stare Czarnowo bordered with a crop field of a 5% gradient which was intensively farmed, and these circumstances contributed to a higher load of macro- and microelements from surface runoffs.

4. A comparison of changes in the content of particular elements demonstrated similarities in increases and decreases of their content, which could suggest a high degree of penetration of groundwater into in-field ponds.

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