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Monthly changes in physicochemical parameters of the groundwater in Nida valley, Poland (case study)

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Abstract: The groundwater of the Nida valley was investigated to assess the quality of water source and monthly variations of the physicochemical parameters. A total of 70 water samples were collected from 7 sampling sites during a 10 months period from June 2021 to March 2022. Sampling frequency was once per month. The parameters such as temperature (*T*), electrical conductivity (*EC*), dissolved oxygen (DO), pH, total dissolved solids (TDS) were measured *in-situ* by using handheld device. Meanwhile, total nitrogen (TN), total phosphorus (TP), chloride (Cl^-), sulphate (SO_4^{2-}), manganese (Mn), iron (Fe), zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu), chemical oxygen demand (*COD*) were analysed in the laboratory. According to the classification of Ministry of Marine Economy and Inland Navigation in Poland (2019), some investigated parameters are classified as unsatisfactory quality waters (class 4) and poor-quality waters (class 5) for a few specific months. Such as, TP concentrations obtained in June and January are classified as class 4, SO_4^{2-} concentrations corresponded to classes 4 and 5 in June, July and August, and Mn concentrations (except in January) are settled in class 5. The high values of Fe in November are arranged in class 5 and in June, July to September and March are classified in class 4. Statistical methods were used as: Shapiro–Wilk test ($\alpha = 0.05$), ANOVA test and post-hoc Tukey test ($\alpha = 0.05$), Kruskal–Wallis test and Wilcoxon (Mann–Whitney) rank sum test ($\alpha = 0.05$) estimated the significant differences in sampling months. Pearson correlation analysis ($\alpha = 0.01$ and 0.05), principal component analysis (PCA) and cluster analysis showed correlation between the parameters and sampling months.

Keywords: groundwater, Nida valley, physicochemical water property, statistical method, water quality classification

INTRODUCTION

In general, groundwater provides 50% of drinking water and 38% for irrigation [Siebert *et al.* 2010]. Additionally, it provides water for rivers, streams, ponds and oceans, contributing to stabilising the flow of many rivers, helping to fix the upper layers of soil and rock, avoiding landslides and subsidence.

The assessment of groundwater resources is based on two important factors: its quality as well as its availability. The physicochemical properties of water are essential requirements that must be considered before being used for different human purposes. Groundwater pollution can be one of natural and anthropogenic causes. Examples of natural sources such as the dissolution of available minerals in the soil and anthropogenic sources such as various human activities, urbanisation, intensive irrigated agriculture, disposing of untreated wastewater in rivers and land [Amadi *et al.* 2010; Kowalik *et al.* 2014; Sojka *et al.* 2010; Voudouris *et al.* 2018]. For natural landscape areas that are less affected by humans, groundwater pollution is mainly due to the specific properties of the soil (weathering of the parent rock), soil environmental conditions and underground flows. It has been shown that groundwater pollution is a major cause of various diseases and other health related issues [Fetter *et al.* 1993]. Therefore, groundwater protection requires appropriate monitoring and management and it should be a top priority because pollutant treatment and quality restoration in groundwater cannot be achieved, once it was contaminated [AL-HADITHI 2012; AZIMOV *et al.* 2022].

Natural groundwater fluctuations are the result of changes in hydrometeorological factors and topographic as well as hydrogeological features [GIESE *et al.* 2020; RINDERER *et al.* 2019]. The dominant hydrometeorological feature of cold humid climates is heavy precipitation in winter, which is stored as ice during cold months and released as meltwater in spring [CLILVERD *et al.* 2011; JASECHKO *et al.* 2017]. Snow melt is the main source of annual groundwater recharge [JASECHKO *et al.* 2017; KLØVE *et al.* 2017]. In addition, increasing rainfall will intensify groundwater recharge [JYRKAMA, SYKES 2007; KOVALEVSKII 2007; MEIXNER *et al.* 2016]. Any of these impacts could increase pressure on vital ecosystems that depend on groundwater [JYVÄSJÄRVI *et al.* 2015; TAYLOR *et al.* 2013]. Adjustments to changes in water availability in the future depend on the rate of change and their capacity to adapt [KIRKINEN *et al.* 2005; KLØVE *et al.* 2017]. As a result, annual fluctuations in groundwater can have serious impacts on both the environment and society.

The object of interest has been located in the lowland river valley. The measurements section lays in Poland (Europe) in the middle run of the Nida River, a left tributary of the Vistula. Through the process of rural society development, the flow of the Nida has been changed many times for the purpose of regulating flow and reducing flooding in valley, the flow has been artificially shortened in many sections. Some river branches have disappeared, leading to a change in the ecological function of some areas [ŁAJCZAK 2004]. We hypothesise that despite some significant impacts, the groundwater in this area is still of good quality. However, it doesn't stay uniform and varies from month to month depending on natural factors such as air temperature, precipitation, and groundwater flow in the area. Hence, the current study was performed to clarify this issue, the information obtained from this study can provide a reference for future studies in the Nida valley as well as other areas of the similar river basins.

MATERIALS AND METHODS

STUDY AREA

The lower Nida valley lies largely within the Nadnidziański Landscape Park and entirely within an ecological corridor consisting of lowland plains, wetlands, and flooded forests. The ground is mostly composed of sands with the thin layer of muds on the top. Flowing through the central part of Poland, the Nida had created a unique multichannel system called "an inland delta". In the middle of it runs close to the town of Pińczów [STRUŻYŃSKI *et al.* 2015].

The study area stretches from the Nida to the Smuga branch located between the boundaries of the Pińczów and Kije communes in the Pińczów district (Fig. 1). This is where the positive and negative effects of previous regulation and drainage measures to limit flood risk are located. One of the negative effects is a permanent increase in the depth of the groundwater table in the valley bottom and the incision of the river channels [ŻELAZO 1993].

The entire width of the Nida floodplain is regularly flooded during spring floods and frequently in summer, and the duration of inundation is two and even five months a year. The width of the floodplain ranges from 0.3 to 5.0 km and greatest along the river sections in the vicinity of Umianowice. The floodplains along the interconnected Nida River act as a natural accumulation

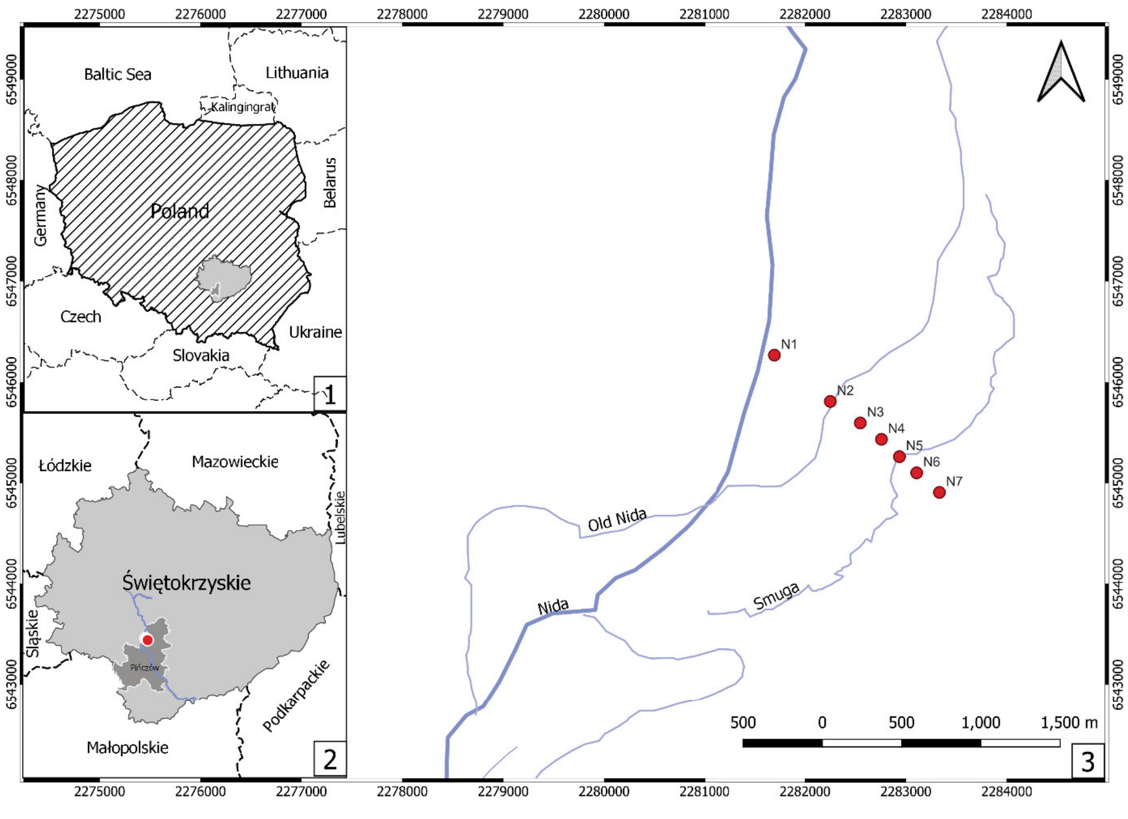


Fig. 1. Map of study area and sampling sites in the Nida valley; source: own elaboration

of water and sediment, thereby reducing the risk of further flooding along the river [ŁAJCZAK 2004].

Between the early 1960s and the mid-1990s, the Nida was shortened due to flow regulation that took place along the river to the vicinity of Kowala below Pińczów. Rivers further to the mouth of the river still keep their natural flow. In 1970, the Nida near Pińczów was directed to a new artificial base. In the early 1990s, the river network in the floodplain area near Umianowice underwent drastic changes, where a new artificial channel was formed, and large areas were drained with the network. The channel network is up to 2 m deep, while filling multiple backup rivers at the same time. As a result, this part of the Nida valley, which is naturally most valuable, has not only been almost completely drained (remaining only fragments of old marshes and waters), it has almost can no longer perform its basic function, where water and sediment accumulate. The other two successive sections of the Nida (near Pińczów and above Wiślica) were decommissioned at least in the early 20th century [ŁAJCZAK 2004].

SELECTION OF SAMPLING POINTS

The sampling points selected at 7 locations are wells 2 m deep and 10 cm in diameter, drilled in the ground at a cross section of every 150–200 m. These wells stabilised by plastic pipes have a function of collection points for groundwater samples. The sampling sites were arranged across the Nida valley throughout the Nadnidziański Landscape Park, starting in the Nida regulated channel, running through the Smuga Umianowicka branch, ending at the floodplain area (Fig. 1) located 1365 m away from the main channel of the river. The locations of the sampling points are described in Table 1.

SAMPLE COLLECTION

A total of 70 water samples were collected from 7 sampling sites during a 10 months period from June 2021 to March 2022. Sampling frequency was once per month. Water samples were collected using a vertical tube sampler with a check valve. Water samples were kept in 300 cm^3 sampling bottles. They were transported to the laboratory within the same day and stored in the refrigerator at 4°C.

FIELD MEASUREMENT

The physical parameters such as temperature (*T*), dissolved oxygen (DO), electric conductivity (*EC*), pH, total dissolved solids (TDS) were measured *in-situ* during sample collection. *T* and DO were measured by oxygen meter (CO-411), *EC*, pH, and TDS – using conductivity meter (CC-102), pH meter (CP-104) and dissolved substances meter (TDS-3) respectively. The devices were calibrated according to manufacturer's recommendations to ensure the accuracy of the reading.

LABORATORY ANALYSIS

The chemical parameters such as total nitrogen (TN), total phosphorus (TP), chloride (Cl^-), sulphate (SO_4^{2-}), manganese (Mn), iron (Fe), zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu) and chemical oxygen demand (*COD*) were measured in the laboratory according to the standard methods recommended by American Public Health Association [APHA 1998] and Environmental Protection Agency [EPA 1983]. Amounts of TN and TP were determined via flow analysis method using FiaCompact MLE flow analyser with mineraliser, Cl^- was measured via flow analysis method by FiaSTAR flow analyser, SO_4^{2-} was determined via turbidimetric method. Content of Fe, Mn and Zn was measured by ASA atomic absorption spectrometry method using Unicam Solar atomic absorption spectrophotometer at wavelength 248.3 nm, 249.5 nm and 213.9 nm respectively, Cd, Pb and Cu were determined via colorimetric method by EcaFlow colorimetric analyser. Chemical oxygen demand (COD) was measured by titration method with potassium permanganate. Limit of detection (*LOD*) and limit of quantitation (*LOQ*) for the parameters were showed in Table 2.

DATA AND STATISTICAL ANALYSIS

Monthly data on physicochemical properties of groundwater are classified according to the regulations of Ministry of Marine Economy and Inland Navigation in Poland in 2019 [Rozporządzenie… 2019]. Details are shown in Table 3.

Table 1. Coordinates of sampling points

Sampling point	N1	N2	N3	N4	N5	N6	N7
Longitude	20.49683	20.50180	20.50447	20.50636	20.50796	20.50949	20.51152
Latitude	50.57392	50.57130	50.57008	50.56916	50.56818	50.56726	50.56616

Source: own elaboration.

Table 2. Limit of detection (*LOD*) and limit of quantitation (*LOQ*) for the parameters

Parameter	Measurement unit	*LOD*	*LOQ*
TN	$mg \cdot dm^{-3}$	0.05	0.05
TP	$mg \cdot dm^{-3}$	0.005	0.01
Cu	$\mu g \cdot dm^{-3}$	0.5	1.00
Pb	$\mu g \cdot dm^{-3}$	0.5	1.00
Cd	$\mu g \cdot dm^{-3}$	0.5	1.00
Cl^-	$mg \cdot dm^{-3}$	0.1	1.00
Fe	$mg \cdot dm^{-3}$	0.027	0.0743
Mn	$mg \cdot dm^{-3}$	0.009	0.027
Zn	$mg \cdot dm^{-3}$	0.0065	0.0198

Source: own elaboration.

Table 3. Classification of groundwater quality

Parameter	Classification of groundwater quality [Rozporządzenie … 2019]				
	I	II	III	IV	V
TP ($mg \cdot dm^{-3}$)	0.5	0.5	1	5	>5
TN ($mg \cdot dm^{-3}$)	10	25	50	100	>100
Cl^- ($mg \cdot dm^{-3}$)	60	150	250	500	>500
SO_4^{2-} ($mg \cdot dm^{-3}$)	60	250	250	500	500
Mn ($mg \cdot dm^{-3}$)	0.05	0.4	1	1	>1
Fe ($mg \cdot dm^{-3}$)	0.2	1	5	10	>10
Zn ($mg \cdot dm^{-3}$)	0.05	0.5	1	2	>2
Cd ($mg \cdot dm^{-3}$)	0.001	0.003	0.005	0.01	>0.01
Pb ($mg \cdot dm^{-3}$)	0.01	0.025	0.1	0.1	>0.1
Cu ($mg \cdot dm^{-3}$)	0.01	0.05	0.2	0.5	>0.5
COD (mg $O_2 \cdot dm^{-3}$)	–	–	–	–	–
T (°C)	<10	12	16	25	>25
pH	6.5–9.5			<6.5 or >9.5	
EC ($\mu S \cdot cm^{-1}$)	700	2500	2500	3000	>3000
DO (mg $O_2 \cdot dm^{-3}$)	>1	0,5–1	<0.5	<0,5	<0.5
TDS (ppm)	–	–	–	–	–

Explanations: class I – very good quality waters, in which the values of physicochemical elements: a) they are formed only as a result of natural processes in groundwater and fall within the hydrogeochemical background, b) do not indicate the impact of human activities; class II – good quality waters in which: a) the values of some physicochemical elements are increased as a result of natural processes in groundwater, b) the values of the physicochemical elements do not indicate the influence of human activity or the influence is very high weak; class III – satisfactory quality waters, in which the values of physicochemical elements are increased as a result of: a) natural groundwater processes or b) weak impact of human activities; class IV – unsatisfactory quality waters, in which the values of physicochemical elements: a) they are increased as a result of natural processes in groundwater, b) show the marked impact of human activities; class V – poor quality waters, in which the values of physicochemical elements indicate a significant influence of human activity.
Source: own study and Rozporządzenie … [2019].

Shapiro–Wilk test ($\alpha = 0.05$) was used to check whether the variables were in accordance with normal distribution. In order to estimate the significance differences between samples taken in different time, non-parametric analysis (Kruskal–Wallis test and Wilcoxon (Mann–Whitney) rank sum test at $\alpha = 0.05$) or parametric analysis (ANOVA test and post-hoc Tukey test at $\alpha = 0.05$) was conducted. Besides, the physicochemical parameters were analysed by calculating Pearson's correlation coefficient (r) value. The correlation matrix was constructed by calculating the coefficients of different pairs of parameters and correlation for significance was determined using r-value and the level significance (p) at 0.01 and 0.05 (2-tailed analysis). The principal component analysis (PCA) was used to compare the parameters between the monthly taken samples and identify the parameters that influence each one. Cluster analysis was employed for the normalised data with Ward's method, using squared Euclidean distances as a measure of similarity. The hierarchical cluster analysis was used to identify the similarity between different sampling months. Precipitation and air temperature monitoring data in the study area were collected from website (Climate-Data.org) to find out the relationship between clusters and observed data. Details of monthly changes in precipitation and air temperature are presented in Figure 2.

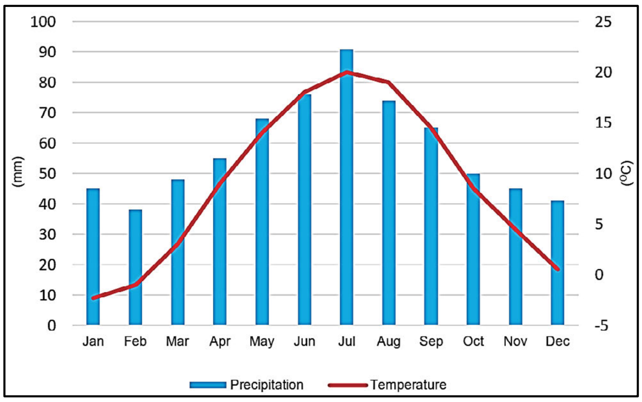


Fig. 2. Annual mean values of temperature and precipitation in the study area; source: Climate-Data.org

The analysis was performed in the R program (version 4.1.2) and applied to present statistical analysis as mean values, standard deviation, minimum and maximum value with focus to the monthly fluctuation of physicochemical parameters.

RESULTS AND DISCUSSION

PHYSICAL PARAMETERS

The physical parameters, such as *T*, pH, *EC*, DO, TDS were presented in Figure 3. Minimum and maximum values are shown with whiskers that represents lowest and highest value. Differences between sampling months are shown by median, according to Kruskal–Wallis test and Wilcoxon (Mann–Whitney) rank sum test or by mean according to ANOVA test and Post-hoc Tukey test.

Temperature of water is a significant element as it controls almost physicochemical and biological reactions. Any unexpected variation in this parameter causes a disruption in the balance of the water ecosystem and mainly influences climatic changes [Beyaitan Bantin *et al.* 2020]. Water temperature have an impact on the acceptability of a number of other inorganic components and chemical pollutants that may affect taste. High water temperature improves the growth of microorganisms and may increase problems related to taste, odour, colour and corrosion [WHO 2017]. In this study, the Kruskal–Wallis test (chi-squared = 60.417, $df = 9$, $p = 1.114e{-}9$) showed that there is statistical difference between the monthly temperature values. The Wilcoxon test demonstrated significant difference between June and October ($p = 3.125e{-}2$), June and November–March with the same $p = 1.563e{-}2$, July, August, and October ($p = 3.125e{-}2$), November ($p = 2.225e{-}2$), December–March ($p = 1.563e{-}2$), August and October–February ($p = 3.125e{-}2$), March ($p = 3.552e{-}2$), September and October ($p = 3.501e{-}2$), November–March ($p = 3.125e{-}2$), October and November ($p = 3.552e{-}2$), December–February ($p = 3.125e{-}2$), November and December ($p = 2.225e{-}2$), January and February ($p = 1.563e{-}2$), March ($p = 3.125e{-}2$), December and January ($p = 2.225e{-}2$),

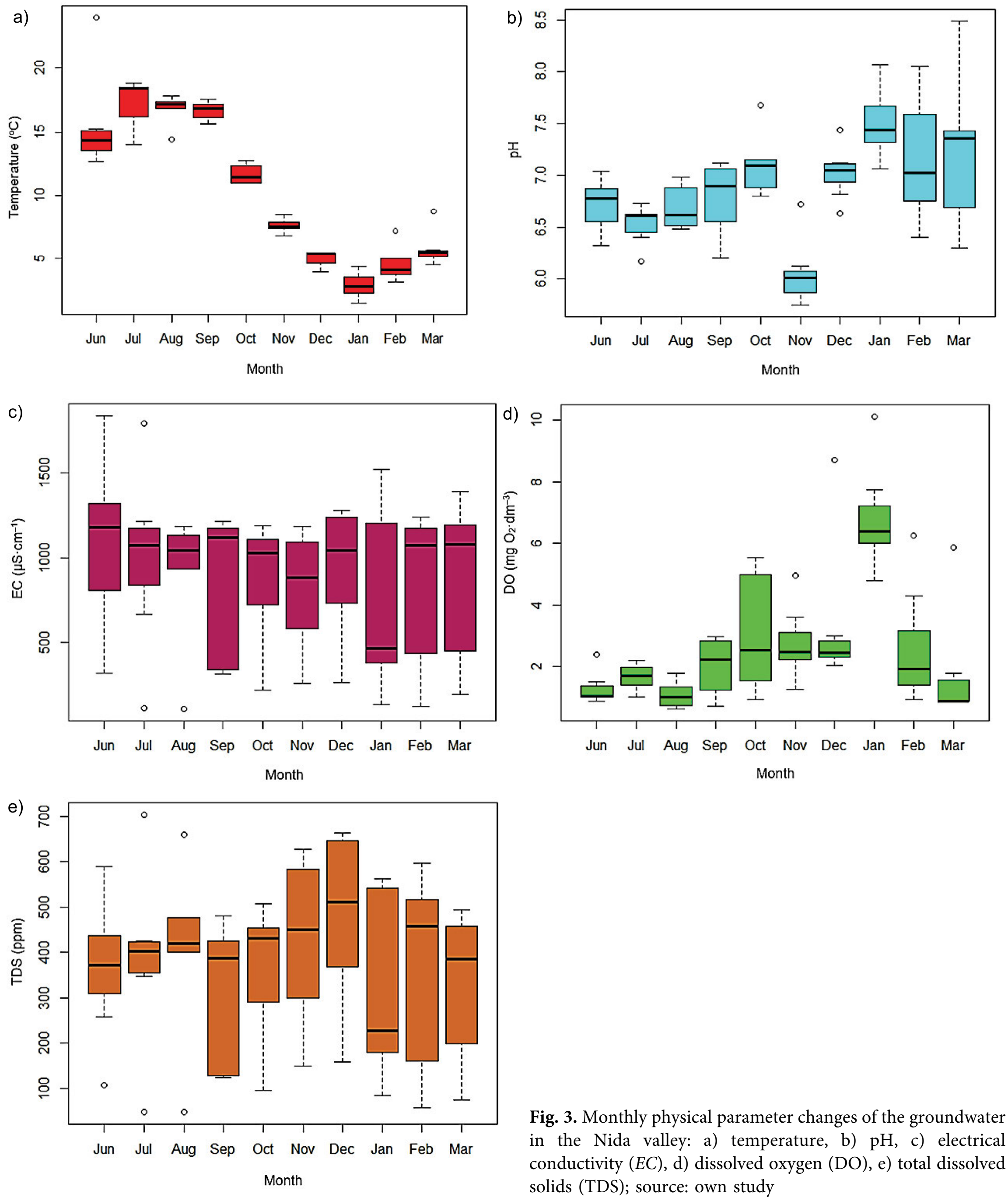


Fig. 3. Monthly physical parameter changes of the groundwater in the Nida valley: a) temperature, b) pH, c) electrical conductivity (*EC*), d) dissolved oxygen (DO), e) total dissolved solids (TDS); source: own study

January and February (p = 3.429e–2), March (p = 2.225e–2), February and March (p = 1.563 e–2) – Figure 3a. The mean temperature obtained in the study area ranged from 2.9 to 17.2°C, the highest temperature recorded in July and the lowest in January. Mean temperature value in June (15.4°C) is classified in class 3 (>12°C) as satisfactory quality waters. In July (17.2°C), August (16.8°C) and September (16.7°C) are in class 4 (>16°C) as unsatisfactory quality water and the other months are in class 1 and 2 (<12°C) as very good and good quality waters specified in Rozporządzenie … [2019] (Tab. 3). Water temperature changes with the ambient temperature, which is strongly influenced by seasonal changes. That explains the high rise in water temperature in the months of June to September.

Value of pH is considered as a parameter of overall productivity that causes habitat diversity. Most of the biological processes and biochemical reactions depend on pH [Minns 1989]. The ANOVA test (F (9, 57) = 7.229, p = 6.4e–7) for pH variable showed there is statistical difference between the monthly pH values and the post-hoc Tukey test presented the significant difference between January and August (p = 1.82e–2), June (p = 1.87e–2), July (p = 1.171e–3), November and December (p = 1.224e–3), February (p =1.434e–4), January (p = 4e–7), March (p = 8.33e–5), October (p = 6.206e–4) – Figure 3b. Mean pH value ranged from 6.1 to 7.5, which indicated that the water was slightly acidic. The highest pH was measured in January and the lowest in November. Most of the mean pH values in all monthly samples were within the permissible limits 6.5–9.5 for satisfactory quality waters acc. to Rozporządzenie … [2019] except November (pH < 6.5) classified as unsatisfactory quality water (Tab. 3). Mean pH value was slightly lower in November, but it was fairly consistent throughout the other months. The pH values remained around 7. Therefore, pH did not serve as a limiting factor in the assessment of groundwater quality except in November. Due to the lack of oxygen in the environment, the pH in groundwater is often found to be acidic [Praparna, Shashikant 2002], which were basically appropriate to the values found in this study. Slightly acidic nature may result from carbonic acid deposit formed via reaction of carbon dioxide with rain water [Tiwari *et al.* 2015]. This may be transported from soil surface level to form deposits in the groundwater via some chemical processes over a period of time.

Electrical conductivity (*EC*) is directly related to TDS as it measures ionic content of water sample which determines its ability an electric current. As ionic concentration of water sample increases, the *EC* strength also increases [Popoola *et al.* 2019]. The *EC* values are controlled by various hydrochemical processes such as cycling salting, water–rock interaction and anthropogenic pollution [El Maghraby *et al.* 2013]. It provides information on the degree of mineralisation of the water, the variations according to the concentration of dissolved salts and it is often influenced by temperature which acts on the dissolution of salts in water [Benrabah *et al.* 2016]. The ANOVA test showed F (9, 57) = 0.326, p = 0.963 and the Kruskal–Wallis test showed chi-squared = 3.5396, df = 9, p = 0.939. Thus, there were no statistical differences between the *EC* value in months. Mean *EC* measured range from 755 to 1084.6 $\mu S \cdot cm^{-1}$, the highest value in June and the lowest in January – Figure 3c. Values of *EC* observed in all monthly sample corresponded to class 2 (>700 $\mu S \cdot cm^{-1}$), which is defined as good quality waters in Rozporządzenie … [2019] (Tab. 3). The *EC* value exhibited could be attributed to being located in an area that is frequently flooded, forming an anaerobic environment, enabling microorganisms to degrade minerals and accumulate in the groundwater for long periods of time. It is a result of natural processes in groundwater and do not indicate the influence of human activity [Rozporządzenie … 2019].

Dissolved oxygen (DO) is an important parameter in water quality assessment. In groundwater, the DO value is usually much lower than in surface water and it is formed mainly by the penetration of surface water into the underground stream carrying free oxygen. This parameter depends on three main factors: temperature, salinity and pressure; it decreases with increasing temperature, increasing salinity, and DO increases with increasing pressure [Jantzen 1978]. In addition, DO is influenced by the source, treatment and chemical or biological processes taking place in the distribution system [WHO 2017]. The Kruskal–Wallis test (chi-squared = 34.605, df = 9, p = 6.993e–5) showed there is statistical difference between the DO values in months. The Wilcoxon test presented the significant difference between June and November to January (p = 1.563e–2), July and October, December and January (p = 1.563e–2), August and December, January (p = 3.125e–2), September and January (p = 3.125e–2), October and March (p = 3.125e–2), November and January (p = 1.563e–2), December and January, March (p =1.563e–2), January and February, March (p = 1.563e–2) – Figure 3d. Mean DO value ranged from 1.1 to 6.8 mg $O_2 \cdot dm^{-3}$, the highest value in January and opposite trend of the lowest air temperature in January. DO value in all monthly samples is settled in class 1 (>1 mg $O_2 \cdot dm^{-3}$) in Rozporządzenie … [2019], which defines as very good quality waters (Tab. 3). This result is consistent in nature because of groundwater had minimum contact with air [Subhan *et al.* 2008]. In this study, the DO value was higher in two sampling locations N1 and N5, which are closer to the Nida River and Smuga branch than the other measured locations (Fig. 1). Therefore, the ability to dissolve oxygen into water due to the interaction of surface water and groundwater is significantly increased.

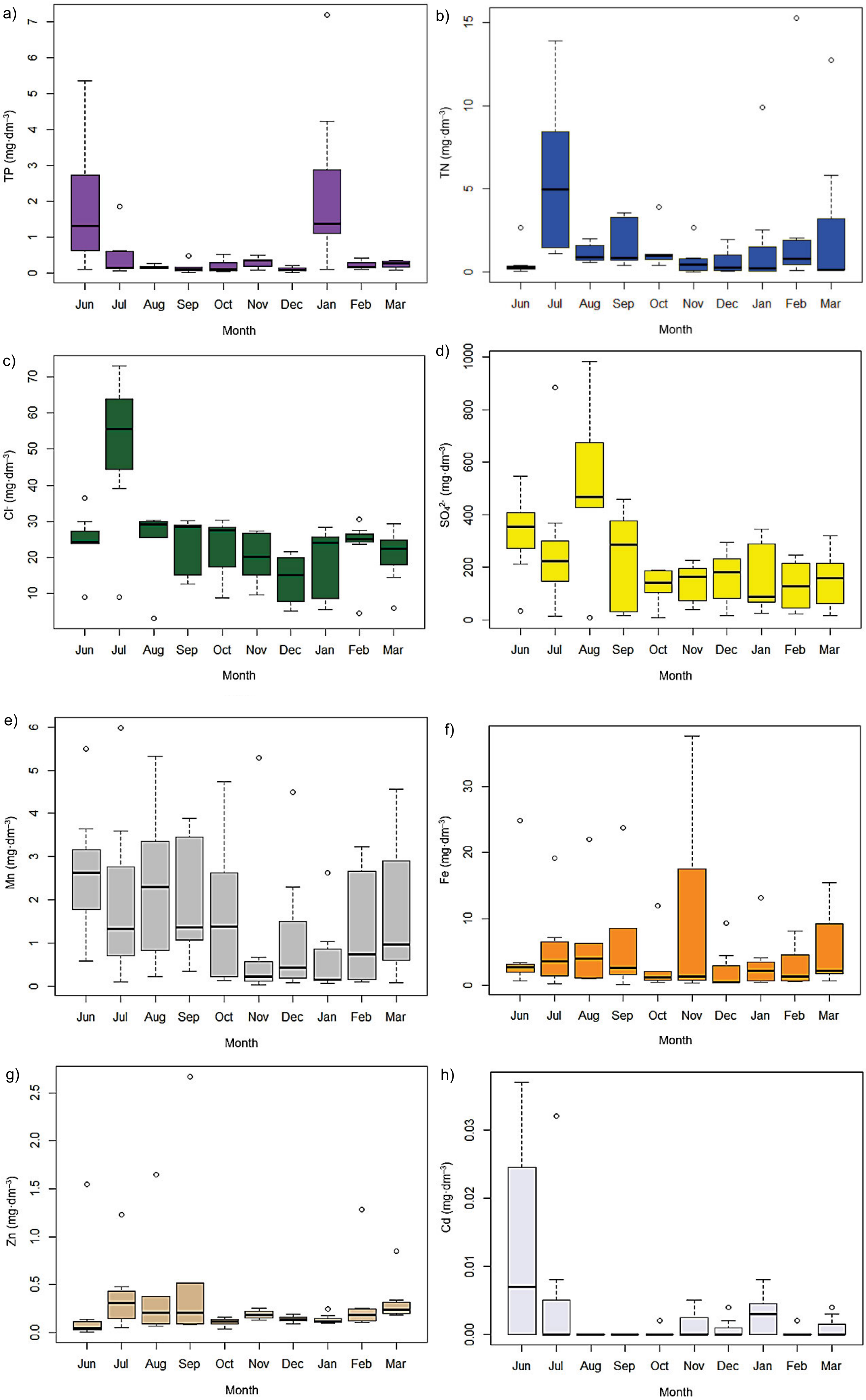
Total dissolved solids (TDS) comprises inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates) and small amounts of organic matter that are dissolved in water. This parameter in groundwater originates from natural sources, sewage, urban runoff and industrial wastewater. Salts used for road de-icing in some countries may also contribute to the TDS content of water. Concentrations of TDS in water vary considerably in different geological regions owing to differences in the solubilities of minerals [WHO 2017]. Values of TDS tend to be higher in arid/desert areas than in wet areas that receive abundant rainfall [Uhl *et al.* 2009]. In this study, mean TDS ranged from 322.3 to 480.6 ppm. Rozporządzenie … [2019] does not specify TDS value. It is considered an indication of saline water which may be attributed to the presence of natural solute via dissolution of soils and weathering [Boyd 1999]. The variation of TDS obtained was similar to that of *EC*. There were no statistical differences between the TDS values measured in separate months.

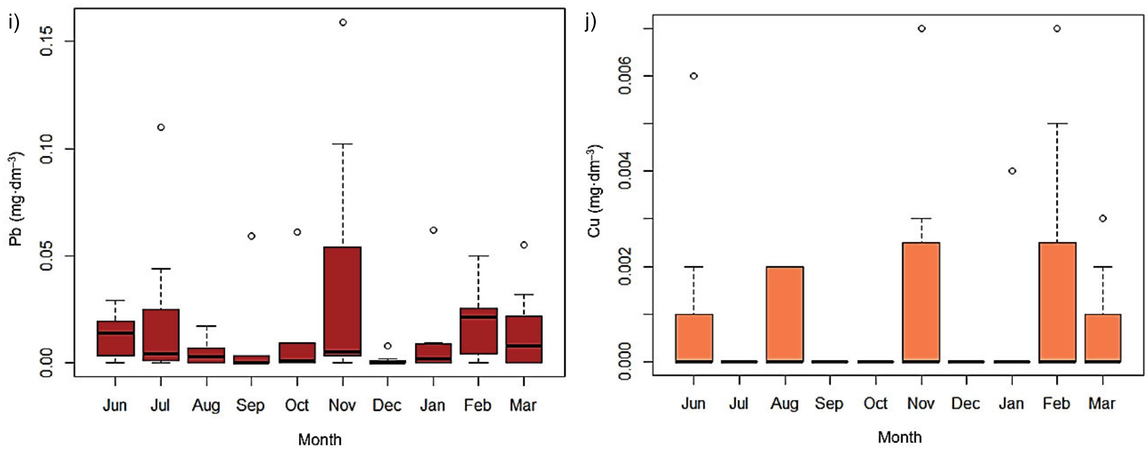
CHEMICAL PARAMETERS

The chemical parameters (TP, TN, Cl^-, SO_4^{2-}, Mn, Fe, Zn, Pb, Cd, Cu, *COD*) are presented at Figure 4.

Total phosphorus (TP) measures all the forms of phosphorus (organic phosphate and inorganic phosphate). Organic phosphate is bound to plant or animal tissue and inorganic phosphate is not associated with organic material. Types of inorganic phosphate include mainly orthophosphate [Dong *et al.* 2019]. The main source of phosphates in groundwater can be minerals in parent materials or from pollution caused by fertiliser, wastewater, industrial waste, and anthropogenic processes [Krapac *et al.* 2002; Zanini *et al.* 1998]. In this study, the Kruskal–Wallis test (chi-squared = 23.87, df = 9, p = 4.512e–3) showed that there is statistical difference between the TP values in months. The Wilcoxon test described the significant difference between June and October (p = 3.125e–2), December (p = 1.563e–2), December and January, February (p = 3.125e–2), March (p = 1.563e–2), January and February, March (p = 3.125e–2) – Figure 4a. Mean TP value of samples ranged from 0.1 to 2.4 $mg \cdot dm^{-3}$. The high values obtained in June (1.9 $mg \cdot dm^{-3}$) and January (2.4 $mg \cdot dm^{-3}$) are classified as class 4 (>1 $mg \cdot dm^{-3}$), which is considered an unsatisfactory quality waters specified in Rozporządzenie … [2019]. However, the remaining months are recorded with low and fairly uniform values. Values of TP were in class 1 and class 2 (<0.5 $mg \cdot dm^{-3}$) for good and very good quality waters (Tab. 3). The decrease in phosphate concentration in groundwater may be due to strong soil adsorption of phosphate ions, while the increase in phosphate ion concentration may be due to agricultural activities [Seiler *et al.* 1988].

Total nitrogen (TN) include nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3) and organically bonded nitrogen. Extended concentration of TN in groundwater usually occurs as a result of leakage from wastewater as well as from fertilisers application and erosion of natural deposits [Bob *et al.* 2015]. The concentration of


a)
TP (mg·dm⁻³)
0 1 2 3 4 5 6 7
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
b)
TN (mg·dm⁻³)
0 5 10 15
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
c)
Cl⁻ (mg·dm⁻³)
10 20 30 40 50 60 70
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
d)
SO₄²⁻ (mg·dm⁻³)
0 200 400 600 800 1000
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
e)
Mn (mg·dm⁻³)
0 1 2 3 4 5 6
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
f)
Fe (mg·dm⁻³)
0 10 20 30
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
g)
Zn (mg·dm⁻³)
0.0 0.5 1.0 1.5 2.0 2.5
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month
h)
Cd (mg·dm⁻³)
0.00 0.01 0.02 0.03
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar
Month



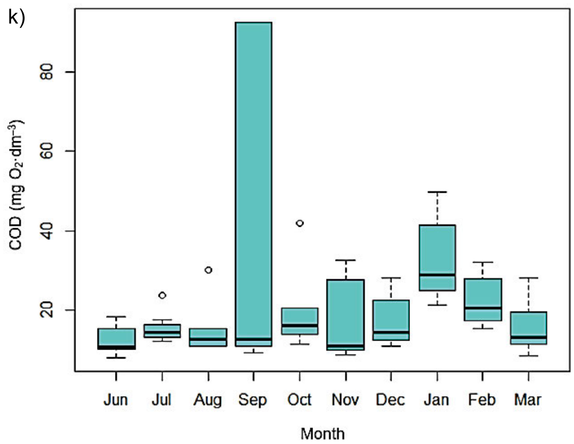


Fig. 4. Monthly chemical parameter changes of the groundwater in the Nida valley: a) total phosphorus (TP), b) total nitrogen (TN), c) chloride (Cl^-), d) sulphate (SO_4^{2-}), e) manganese (Mn), f) iron (Fe), g) zinc (Zn), h) cadmium (Cd), i) lead (Pb), j) copper (Cu), k) chemical oxygen demand (*COD*); source: own study

nitrate present in water originates from agricultural wastes and wastewater pollution. The rapid decomposition of organic matter increases the nitrate content. When organic matter breaks down into water, it forms complex proteins, which are converted to nitrogenous organic matter and finally to nitrate by the action of bacteria [Soceanu *et al.* 2021]. The fact that mean TN concentration in these groundwater samples ranged from 0.6 to 5.7 mg·dm^{-3}. These values are lower than the permissible limits (10 mg·dm^{-3}) for very good quality waters and classified as class 1 [Rozporządzenie … 2019]. It further supports the conclusion made earlier that no significant contamination of the groundwater in the study area had occurred by leakage of wastewater from different sources. The highest TN value measured in July and the lowest value in June. The Kruskal–Wallis test (chi-squared = 18.623, df = 9, p = 2.86e–2) presented there is statistical difference between the monthly TN values and the Wilcoxon test delivered the significant difference between June and July (p = 1.563e–2), August (p = 3.125e–2), September (p = 3.125e–2), October (p = 3.125e–2), February (p = 3.125e–2), July and October (p = 3.125e–2), November (p = 1.563e–2), December (p = 1.563e–2), August and November (p = 3.125e–2), December (p = 3.552e–2) – Figure 4b.

Concentration of chloride (Cl^-) varies from types of water and has been found to exist naturally in the form of sodium and potassium salts. It is a stable water component whose concentration is uninterrupted by both biological and physicochemical processes [Popoola *et al.* 2019]. The Kruskal–Wallis test (chi-squared = 21.191, df = 9, p = 1.183e–2) performed there is statistical difference between the Cl^- value in months. The Wilcoxon test showed the significant difference between June and December (p = 1.563e–2), July and August, October, November (p = 3.125e–2), December and March (p = 1.563e–2), October and December (p = 3.125e–2), November and December (p = 3.125e–2), December and February (p = 3.125e–2) – Figure 4c. The mean Cl^- value investigated range from 13.9 to 50.6 mg·dm^{-3}. The highest value in July and the lowest in December. In addition, there were no significant unusual fluctuations in the remaining months. All measured concentrations were below the permissible limit value of 60 mg·dm^{-3}, which is arranged as class 1 (very good quality waters) specified in Rozporządzenie … [2019] – Table 3. The presence of Cl^- could be due to chloride-containing soils and rocks undergoing leaching which later got in contact with groundwater for all examined locations [Aremu *et al.* 2011]. Because Cl^- exists in urine as well as in maintenance products [Benrabah *et al.* 2016], municipal wastewater discharged by residents near the examined locations is often rich in Cl^-, which can enter into groundwater through leaching and accumulation [Gorde, Jadhav 2013].

Sulphates (SO_4^{2-}) occur naturally in numerous minerals and the highest levels usually occur in groundwater from natural sources, including barite ($BaSO_4$), epsomite ($MgSO_4{\cdot}7H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) [Greenwood, Earnshaw 1984]. Sulphates are oxidation results of their ores and H_2S by some bacteria activities such as chlorothiobacteria and rhodothiobacteria [Popoola *et al.* 2019]. The presence of sulphate in unpolluted waters invokes the presence of gypsum with a concentration varying between 0 and 58 mg·dm^{-3} [Chapman (ed.) 1996]. However, accumulation of sulphate in water may lead to increase in water pH causing acidosis [Asamoah, Amorin 2011]. In this study, the ANOVA test (F (9, 57) = 3.131, p = 3.94e-03) showed there is statistical difference between the SO_4^{2-} value in months and the post-hoc Tukey test showed significant difference between the SO_4^{2-} value in December and August (p = 2.13e–2), January and August (p = 2.75e–2), March and August (p = 1.58e–2), November and August (p = 1.1e–2), October and August (p = 1.28e–2) – Figure 4d. Mean sulphates of the study area varied from 129.6 to 504.5 mg·dm^{-3}. High sulphate concentrations are mainly in June (328 mg·dm^{-3}), July (288 mg·dm^{-3}) and August (504.53 mg·dm^{-3}). Concentrations of SO_4^{2-} in these months belonged in classes 4 and 5 (>250 mg·dm^{-3}) as unsatisfactory quality and poor-quality waters acc. to Rozporządzenie … [2019]. The presence of high levels of sulphate is due to the strong activity of sulphur-degrading bacteria groups that increase the ability to oxidise sulphur-containing ores when the ambient temperature is increased. Sulphate values are arranged as classes 2 and 3 for good quality and satisfactory quality waters in the rest of months.

Manganese (Mn) usually occur with iron and it is also an abundant metal. Manganese is naturally occurring in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions [WHO 2017]. In general, sources of Mn in groundwater are minerals, which contain Mn. The parent rock is weathered and moves Mn into the water. This chemical element is used for a variety of purposes and thus can enter the water in different ways [Deshpande, Aher 2012]. It was used in chemical industry as the additives. It was also used in agriculture, so manganese can also be released from fertilisers and from animal feed [Al-Hadithi 2012]. The ANOVA test showed F (9, 57) = 0.951, p = 0.49 and the Kruskal–Wallis test showed chi-squared = 13.607, df = 9, p = 0.137. Thus, there were no statistical differences between the Mn value in months. The mean Mn recorded for all samples ranged from 0.7 to 2.7 mg·dm^{-3}. Except for January, all other months showed very high Mn values from 1 to 2.4 mg·dm^{-3}. These Mn values are classified in class 5 (>1 mg·dm^{-3}) for poor quality waters specified in Rozporządzenie … [2019] (Tab. 3), in which the values of Mn indicate a significant influence of human activity. However, the high Mn concentration in this study due to natural sources.

Iron (Fe) is one of the most abundant metals in Earth's crust. It is found in natural waters at levels ranging from 0.5 to 50 mg·dm^{-3}. The iron content in water depends on the pH and alkalinity of the water. Value of pH (6.8–7.3 range), hardness and alkalinity (at least 40 mg·dm^{-3}, as calcium carbonate) is ideal for controlling iron corrosion [WHO 2017]. The ANOVA test showed F (9, 57) = 0.669, p = 0.733 and the Kruskal–Wallis test showed chi-squared = 6.4791, df = 9, p = 0.6912. Thus, there were no statistical differences between the monthly Fe values. The mean Fe concentration for all the sample ranged from 2.4 to 10.8 mg·dm^{-3}. The highest value is in November (10.8 mg·dm^{-3}) classified in class 5 (>10 mg·dm^{-3}) as poor quality waters and in June (5.5 mg·dm^{-3}), July (5.5 mg· dm^{-3}), August (6.4 mg·dm^{-3}), September (6.5 mg·dm^{-3}) and March (5.7 mg·dm^{-3}) are arranged in class 4 (>5 mg·dm^{-3}) as unsatisfactory quality waters acc. to Rozporządzenie … [2019]. Value of Fe in the rest of months is settled in class 3 (satisfactory quality waters) – Table 3. The investigated Fe concentration higher the permissible limit could be connected to weathering of minerals and rocks of iron in the soil for the examined locations and dissolution of iron natural deposits into groundwater via leaching [Popoola *et al.* 2019]. This result is quite similar to the occurrence of high Mn content and it is interpreted similarly also support for this conclusion.

Zinc (Zn) is found naturally at low concentrations in rocks and soils principally as sulphide ores (ZnS) and carbonates ($ZnCO_3$). Research has recorded approximately 0.05 g of Zn to be present naturally in 1 kg of the Earth's crust [Dohare *et al.* 2014]. Most Zn is introduced into water by artificial pathways such as byproducts of steel production or coal-fired power station or from burning of waste materials, from fertiliser that may leach into groundwater [Behailu *et al.* 2017]. The solubility of Zn in water is a function of pH and total inorganic carbon concentrations. The solubility of basic Zn carbonate decreases with increase in pH and concentrations of carbonate species. For low-alkalinity waters, an increase of pH to 8.5 should be sufficient to control the dissolution of Zn [WHO 2017]. The Kruskal–Wallis test (chi-squared = 17.734, df = 9, p = 3.84e–2) showed there is statistical difference between the Zn value in months and the Wilcoxon test delivered the significant difference between the Zn value in June and August, September (p = 3.125e–2), October and November, March (p = 3.125e–2), December and March (p = 1.56e–2), January and February (p = 3.125e–2), March (p = 1.56e–2) – Figure 4g. The mean Zn value ranged from 0.1 to 0.6 mg·dm^{-3}. No abnormalities were noted during the months. All examined samples revealed Zn concentration corresponded to classes 2 and 3 (good quality and satisfactory quality waters) specified in Rozporządzenie … [2019] – Table 3. This could be that the Zn in its natural mineral form (sphalerite) dissolved into groundwater via leaching in all examined locations [Broadly *et al.* 2007]. The values of Zn are increased as a result of natural processes in groundwater, and do not indicate the influence of human activity or the influence is very weak [Rozporządzenie … 2019].

Cadmium (Cd) exists as natural ores in rocks and soils, and Zn refining by-product [Wang *et al.* 2006]. The presence of cadmium in groundwater occurred via leaching when in contact with soil contaminated with discharges from mining, paints, electroplating, petrochemical, plastics and fertiliser industries [De Zuane 1996]. The ANOVA test (F (9, 57) = 2.864, p = 7.39e–3) presented that there is statistical difference between the Cd value in months and the post-hoc Tukey test showed significant difference between the Cd value in June and August (p = 1.65e–2), December (p = 2.186e–2), June and March (p = 2.456e–2), November (p = 3.46e–2), October (p = 2.157e–2), September (p = 1.65e–2) – Figure 4h. The mean value of Cd observed range from 0 to 0.01 mg·dm^{-3}. No presence of Cd was detected in August, September, October, and February. High value was found in June (0.01 mg·dm^{-3}) and this value is classified in class 5 as poor quality waters specified in Rozporządzenie … [2019]. In the other months, Cd value observed in class 1 (very good quality waters) – Table 3. The anomaly obtained in June can be explained by the unusual intrusion of Cd into groundwater originating from natural processes or brought about by human activities. This element was absorbed into the soil reducing the concentration in the water when the groundwater level was descended. In contrast, the release of Cd increases the concentration of Cd in the water as the water level rises.

In the past, lead (Pb) was mainly used in the manufacture of lead-acid batteries, solders and alloys, rust inhibitors and lubricants in gasoline (tetramethyl lead). To date, their use for these purposes in many countries is being phased out. This has reduced lead in the air and soil and reduced accumulation in groundwater. Lead is found in groundwater mainly through the dissolution of lead-containing minerals: galena (PbS), cerussite ($PbCO_3$), anglesite ($PbSO_4$) [WHO 2004]. The amount of lead dissolved in water depends on a number of factors, including pH, temperature, water hardness, and standing time of the water. The solubility of lead salts increases markedly as the pH increases above or decreases below 8.3 because of the substantial decrease in the equilibrium carbonate concentration [WHO 2017]. The ANOVA test showed F (9, 57) = 0.914, p = 0.52 and the Kruskal–Wallis test showed chi-squared = 9.5103, df = 9, p = 0.3916. Thus, there were no statistical differences between the monthly Pb values. The mean Pb obtained range from 0.001 to 0.040 mg·dm^{-3}. Low value of Pb concentration was recorded in August (0.005 mg·dm^{-3}) and December (0.001 mg·dm^{-3}). They are settled in class 1 (<0.01 mg·dm^{-3}) as very good quality waters acc. to Rozporządzenie … [2019]. In the other months, categorise of Pb concentrations are in class 2 (<0.025 mg·dm^{-3}) as good quality waters (Tab. 3). The major cause of increasing lead concentrations in water samples as a result of natural processes in groundwater. It could be from leaching of natural deposits of lead ores in the soil into the groundwater and there is no uniformity between months [Imam 2012] and these values do not indicate the influence of human activity or the influence is very high weak [Rozporządzenie … 2019].

The main sources of copper (Cu) accumulation in water bodies can be traced back to the various activities such as agricultural production, solid waste disposal, and the use of batteries and chemicals for consumer products [WHO 2004]. Similar to lead, copper can enter water by dissolving corrosion products and naturally occurring basic copper carbonates. Solubility is mainly a function of pH and total inorganic carbon. Solubility decreases with increasing pH, but increases with increasing concentration of carbonate species. Water with a pH below 6.5 and a hardness below 60 mg of calcium carbonate per liter increases copper solubility [WHO 2017]. The ANOVA test showed F (9, 57) = 1.174, p = 0.329 and the Kruskal–Wallis test showed chi-squared = 10.971, df = 9, p = 0.2777. Thus, there were no statistical differences between the Cu values in months. The mean Cu values received for whole samples ranged from 0 to 0.001 mg·dm^{-3}. All values obtained were below the permissible limit of 0.01 mg·dm^{-3} for class 1 (very good quality waters) according to Rozporządzenie … [2019]. Many months did not detect the presence of Cu (July, September, October, December). This result shows that groundwater in the surveyed area is hardly affected by production activities.

Chemical oxygen demand (*COD*) measures oxygen requirement for organic matter chemical oxidation to take place via assistance of strong chemical oxidant. The present of *COD* in groundwater always is found [Sumant *et al.* 2015]. In addition, the increase in *COD* value is also due to natural processes in groundwater such as weathering, washing away the parent rock or the process of intruding organic substances of natural origin from surface water. The Kruskal–Wallis test (chi-squared = 19.179, df = 9, p = 2.372e–2) performed there is statistical differences between the *COD* value in months. The Wilcoxon test showed the significant difference between June and October (p = 3.125e–2), December to February (p = 1.563e–2), July and January, February (p = 1.563e–2), August and January (p = 3.125e–2), November and January (p = 1.563e–2), December and January, February (p = 1.563e–2), January and February, March (p = 1.563e–2), February and March (p = 1.563e–2) – Figure 4k. The mean value of *COD* was 12.6 –38.4 mg O_2·dm^{-3}. The highest value of *COD* was obtained in September and lowest in June. The increase in *COD* concentration may be due to the decomposition of organic matter of plant and animal origin and the intrusion of underground flows carrying amounts of organic matter into the observation site. The Rozporządzenie … [2019] does not prescribe for the water quality classification for *COD* values.

PEARSON'S CORRELATION ANALYSIS

Correlation matrix (Tab. 4) shows the correlation coefficients (r) of all studied parameters, with their significance level (p value). Negative correlations were found in 56 cases and positive correlation were 49 cases. Not significant correlation had TP and *COD* with other parameters. Strong positively were TN correlated with Cl^- (r = 0.91, p < 0.01) and Mn correlated with T (r = 0.9, p < 0.01). Strong negative correlations were presented between SO_4^{2-} and DO (r = –0.84, p < 0.01), T and DO (r = –0.85, p < 0.01). Besides, significant positive correlations between SO_4^{2-} and Mn (r = 0.75, 0.01 < p < 0.05), SO_4^{2-} and *EC* (r = 0.81, 0.01 < p < 0.05), Fe and Pb (r = 0.77, 0.01 < p < 0.05), Fe and Cu (r = 0.72, 0.01 < p < 0.05), Zn and T (r = 0.76, 0.01 < p < 0.05), Cd and *EC* (r = 0.72, 0.01 < p < 0.05) were showed. Negative correlations were found between Pb and pH (r = –0.71, 0.01 < p < 0.05), *EC* and DO (r = –0.72, 0.01 < p < 0.05). The results of this study indicated that TN and Cl^-, Mn and T, Mn and DO, Fe and pH, T and DO were strongly correlated. SO_4^{2-} and Mn, Mn and *EC*, Fe and Pb, Fe and Cu, Zn and T, Cd and *EC*, Pb and pH, *EC* and DO were correlated.

The positive correlations between Mn, Zn, SO_4^{2-} and T explained the formation of sulphates from the ores when the groups of sulphur-degrading bacteria are more active under increasing ambient temperature [Popoola *et al.* 2019]. The positive correlations between Mn, Cd and *EC* probably due to the geological weathering conditions at examined locations acquiring high concentrations of the dissolved minerals increases *EC* value [Costello *et al.* 1984]. The negative correlation of the pairs *EC* and DO, Mn and DO were explained the decrease oxygen solubility as *EC* increase and *EC* increase is caused by Mn concentration increase [Allan 1995]. The negative correlation of Fe, Pb and pH demonstrated that the solubility of Fe and Pb increases in low pH environment [WHO 2017]. The negative correlation between T and DO is evidence that the DO content in water is also affected by water temperature [WHO 2004]. Concentration of DO in water is inversely proportional to water temperature [Hynes 1960]. The positive correlations between pairs of metals showed similar behaviour of metals Fe, Pb and Cu in the water and could suggest the possibility of their general origination [Soceanu *et al.* 2021]. Pearson's correlation analysis has been widely used in assessing the relationship between groundwater quality parameters and has been shown by Bendida *et al.* [2021], and Somia *et al.* [2022].

PRINCIPAL COMPONENT ANALYSIS (PCA)

Statistically, four factors were extracted that explained 83.5% of total variance and were showed at PCA-biplot: 33.4% for Dim1 and 17.8% for Dim2 (Fig. 5a), 14.3% for Dim3 and 12.4% for Dim4 (Fig. 5b).

Table 4. Correlation matrix of the groundwater parameters

Parameter	TP	TN	Cl^-	SO_4^{2-}	Mn	Fe	Zn	Cd	Pb	Cu	*COD*	*T*	pH	*EC*	DO
TP	1														
TN	−0.02	1													
Cl^-	−0.10	0.91**	1												
SO_4^{2-}	−0.02	0.10	0.32	1											
Mn	−0.11	0.12	0.45	0.75*	1										
Fe	−0.21	−0.07	0.13	0.16	0.05	1									
Zn	−0.29	0.28	0.40	0.58	0.54	0.35	1								
Cd	0.63	0.13	0.32	0.22	0.47	−0.01	−0.06	1							
Pb	−0.04	0.24	0.31	−0.31	−0.25	0.77*	−0.09	0.12	1						
Cu	0.31	−0.43	−0.25	0.07	−0.08	0.72*	−0.21	0.32	0.60	1					
COD	0.15	−0.01	−0.24	−0.31	−0.41	−0.06	0.33	−0.42	−0.13	−0.29	1				
T	−0.29	0.35	0.64	0.69	0.90**	0.25	0.76*	0.25	−0.03	−0.16	−0.19	1			
pH	0.44	−0.08	−0.34	−0.21	−0.26	−0.87**	−0.31	−0.11	−0.71*	−0.54	0.43	−0.41	1		
EC	−0.01	0.18	0.45	0.45	0.81*	−0.12	0.23	0.72*	−0.18	−0.09	−0.62	0.63	−0.25	1	
DO	0.52	−0.07	−0.43	−0.60	−0.84**	−0.38	−0.56	−0.23	−0.05	−0.05	0.52	−0.85**	0.67	−0.72*	1

Explanations: TP = total phosphorus, TN = total nitrogen, *COD* = chemical oxygen demand, *T* = temperature, *EC* = electrical conductivity, DO = dissolved oxygen, * correlation is significant at the 0.05 level, ** correlation is significant at the 0.01 level.
Source: own study.

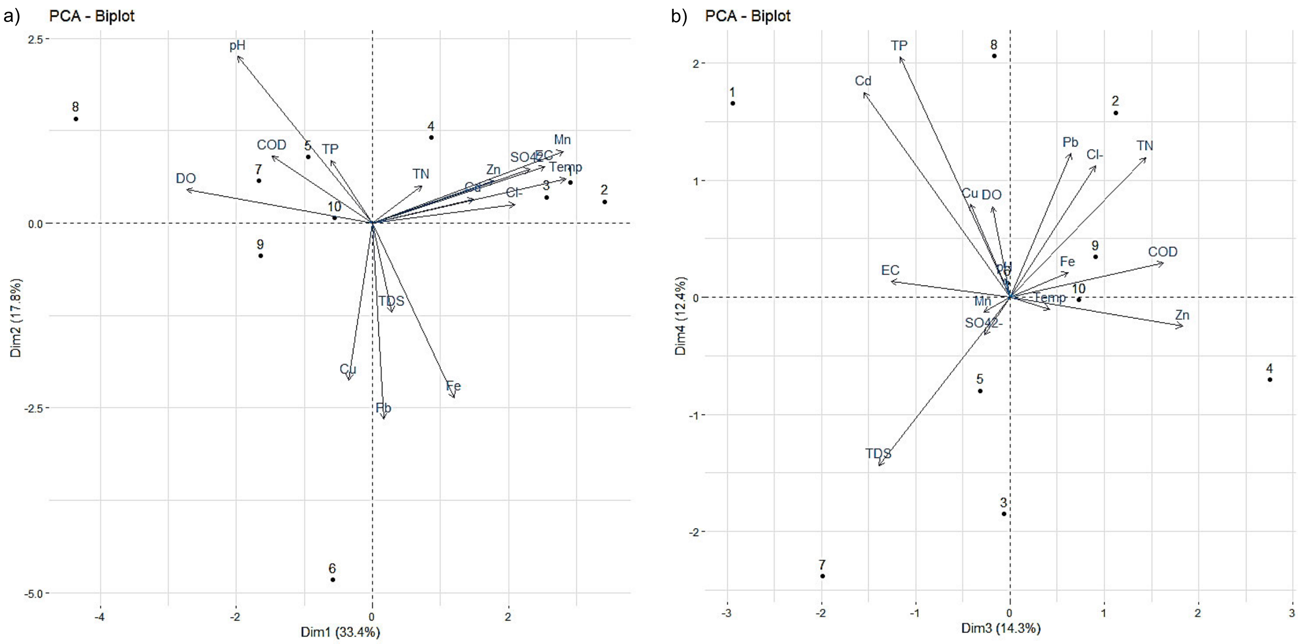


Fig. 5 Biplot – resulting from the principal component analysis: a) Dim1, Dim2, b) Dim3, Dim4; source: own study

Dim1 showed positive loading with Mn, *T*, Zn, *EC*, SO_4^{2-}, Cl^-, Cd, TN, TDS, Pb, Fe and negative loading with Cu, TP, pH, *COD*, and DO. Therein, the variable *T* showed strongest positive loading, however DO showed strongest negative loading with other variables. Thus, with the increase of *T*, the other parameters will increase and when DO decrease lead to the increase of other variables. Moreover, Dim1 presented a strong dissimilarity was observed between January (point No. 8) with other months and strong similarity between June (point No. 1), July (point No. 2) and August (point No. 3). On the basis of the biplots, it was possible to conclude that January was unique due to the highest pH, DO and TP, and the lowest *T* and Mn in the studied water sample.

Dim2 demonstrated positive loading with Mn, *T*, Zn, *EC*, SO_4^{2-}, Cl^-, Cd, TN, TP, pH, *COD*, DO and negative loading with TDS, Pb, Cu, and Fe. The pH variation showed the strongest positive loading. That mean, the increase of pH, the other parameters will increase. Dim2 also performed a strong dissimilarity was obtained between November (point No. 6) with other months due to high content of TDS, Fe, Cu, Pb and low of pH value.

Dim3 described negative loading with *COD*, *T*, Zn, Fe, TN, Cl^{-}, Pb, and positive loading with TP, Cd, Cu, pH, EC, Mn, SO_4^{2-}, TDS, and DO. The strongest negative loading was recorded of Zn variation with others. That mean, the decrease of Zn, the other parameters will increase. Dim3 showed a strong dissimilarity was investigated between June (point No. 1) with September (point No. 4). Therein, June is characterised by high content of Cd, *EC* and September is characterised by high *COD*, content of Zn and low content of TDS.

Dim4 presented negative loading with TDS, SO_4^{2-}, Mn, *T,* Zn and positive loading with TP, Cd, Cu, pH, TN, Fe, *EC*, Pb, *COD*, DO, Cl^{-}. The strongest negative loading was recorded of TDS variation and strongest positive loading of TP variation with others. That mean, the decrease of TDS, the other parameters will increase and the increase of TP, the other parameters will increase. Dim4 showed a strong dissimilarity was recorded between December (point No. 7) and January (point No. 8). Therein, December is described by high content of TDS and low content of TP. However, January is described by high content of TP and low content of TDS.

The relationship between groundwater quality parameters and their dependent variables also analysed by PCA method has been reported by El Qryefy *et al.* [2021], and Somia *et al.* [2022].

CLUSTER ANALYSIS

The dendrogram (Fig. 6) presented the correlation between sampling months for 10 months (from June 2021 to March 2022). Ward's association method and squared Euclidean distance were used and showed 2 statistically significant clusters. The first cluster covers three months (June–August). These months presented relatively higher concentrations of all parameters. This result also was presented on biplot through PCA. These months are within the hottest seasons, the average temperature and average precipitation are highest in year (Fig. 2). The second cluster contains the sampling months of September–March. During these sampling months, relatively lower concentrations of water quality parameters were recorded. The main feature of these months is that the average temperature and rainfall are lower than other months. The correlation between the groundwater quality in sampling months were also noted by Vidhya *et al.* [2018], Xin *et al.* [2020], and Zacchaeus *et al.* [2020].

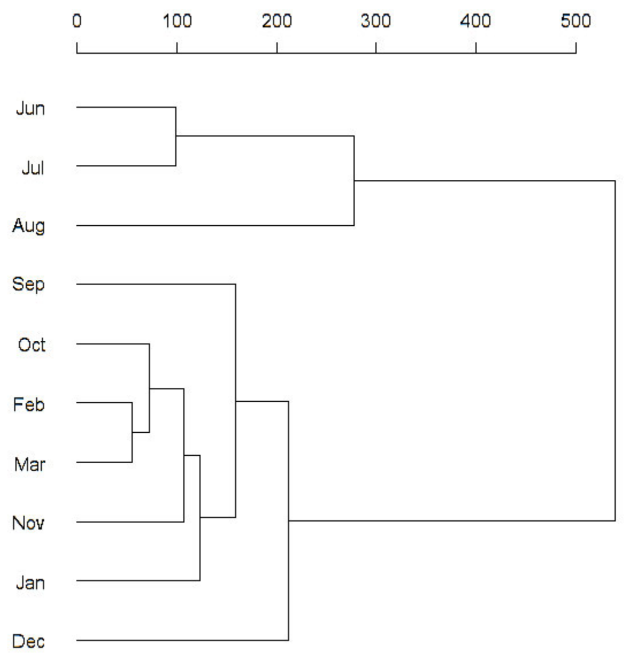


Fig. 6. Cluster analysis dendrogram of sampling months; source: own study

CONCLUSIONS

This study presents detailed information about the quality status of groundwater samples at the Nida valley, Poland. Groundwater samples were analysed for the physical parameters and the chemical parameters. The parameters were classified in order to assess water quality by Polish law.

In general, the quality of groundwater in the study area is good and satisfactory quality waters. Most of the parameters are classified into classes 1, 2 and 3. Except for a few specific parameters in a few months are classified into classes 4 and 5 as unsatisfactory and poor quality waters. As follows: *T* values in July, August and September are in class 4, pH values in November are in class 4. The high TP values obtained in June and January are classified as class 4. The high sulphate concentrations are mainly in June, July and August. Water quality in these months corresponded to classes 4 and 5. Except for water in January, in all other months, Mn values were very high. These Mn values are classified in class 5. The highest Fe value in November is classified in class 5 and in June, July, August, September and March are arranged in class 4. High value Cd was found in June and these values are classified in class 5.

Shapiro–Wilk test (α = 0.05), Kruskal–Wallis test and Wilcoxon (Mann–Whitney) rank sum test (α = 0.05), ANOVA test and post-hoc Tukey test (α = 0.05) showed the significant difference between months for *T*, DO, pH, TN, TP, Cl^{-}, SO_4^{2-}, Zn, Cd and *COD*. Pearson correlation coefficient analysis (α = 0.01 and 0.05) performed a very strong correlation was found between TN and Cl^{-}, Mn and *T*, Mn and DO, Fe and pH, *T* and DO in this study. Principal component analysis (PCA) presented the associations of parameters and month and described a strong dissimilarity between January (the highest of pH, DO and TP, and the lowest of *T* and Mn) and November (the highest of TDS, Fe, Cu, Pb and the lowest of pH) with other months. Cluster analysis presented the correlation between sampling water in months for 10 months and showed two statistically significant clusters.

The obtained results are consistent and reliable. This study is still being conducted, the data will be supplemented and completed within 2 years. They can be used as reference data for groundwater studies in the Nida valley.

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