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ORIGINAL PAPER

GROUNDWATER CHEMISTRY AND HYDROGEOCHEMICAL PROCESSES IN A SOIL CATENA OF THE POZNAŃ LAKELAND, CENTRAL POLAND

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Abstract

An attempt has been made to identify the chemical processes that control the hydrochemistry of groundwater in the catena of Retisols/Luvisols and Gleysols/Phaeozems within the Opalenica Plain, central Poland. Groundwater samples were collected from 6 representative piezometers. The quantity of dissolved components in groundwater was connected with the location of piezometers in the relief studied and the properties of the soil's parent materials. The groundwater of soil located higher in the soil catena was characterised by smaller concentrations of the components when compared with the composition of water from the lowest sites on the slope. The dominant hydrochemical facies are Ca,Mg–HCO_3,SO_4, Ca,Mg-mixed or Ca,Mg–HCO_3 types in the groundwater from the higher part of the slope and Mg–HCO_3,SO_4 and Mg–HCO_3 types in the water from the lower part of the catena. The chemistry of groundwater is the product of the weathering of carbonate minerals and silicate. The Ca^{2+}/alkalinity molar ratio in the groundwater samples from piezometers located higher in the soil catena indicate that the weathering of both calcite and dolomite can occur there, while only dolomite weathering takes place in the groundwater of the catena pediment. The Ca^{2+}/Mg^{2+} molar ratio in the water samples from the footslope shows an excess of magnesium over calcium, which could be a result of water interacting with Mg-rich silicate minerals, as an additional process to dissolution of dolomite. Furthermore, data for a few water samples from the footslope cover the evaporation zone of the Gibbs plot. This suggests that while contamination could affect the amount of dissolved components, evaporation can modify the groundwater chemistry of footslope. Cluster analysis grouped groundwater samples into two groups with similar characteristics, indicating the influence of the location of a piezometer in the soil catena on the groundwater chemistry.

Keyword: groundwater chemistry, soil catena, Retisols/Luvisols, Gleysols/Phaeozems.

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INTRODUCTION

Many factors and processes contribute to the chemical composition of groundwater. At each site, groundwater has unique chemical composition owing to numerous geochemical reactions that take place along the direction of water flow (Hem 1991, Rao et al. 2012). These geochemical interactions in the soil/rock-groundwater system need to be understood so as to assess the distribution of major ions in a given region (Reddy et al. 2010, Reddy, Kumar 2010, Raju et al. 2011). Moreover, detailed knowledge of geochemical processes that regulate the chemical composition of groundwater is necessary in order to address groundwater-related issues (Subramani et al. 2010).

Diagnosis of the temporal and spatial variability of various ions in groundwater helps to identify the major processes controlling its chemical composition (Laluraj, Gopinath 2006, Rao 2006, Kozłowski et al. 2012, Kozłowski, Komisarek 2013). Hence, it is vital to study and understand various hydrogeochemical characteristics of groundwater in a particular area (Sikdar et al. 2001, Elango et al. 2003, Apadaca et al. 2007). Many diverse graphic and indicator methods have been designed in recent years to assess the groundwater chemistry and to identify the processes that control the chemical composition of water (Elango et al. 2003, Kumar et al. 2006, Rao 2006, Rao et al. 2012, Apadaca et al. 2007). Subramani et al. (2010), Senthilkumar and Elango (2013) and Reddy and Kumar (2010) have concluded that mainly the weathering of carbonate and silicate minerals and ion exchange reaction, followed by evapotranspiration process, control the major ionic distribution in groundwater.

The principal objective of this study was to recognise factors and processes governing the chemical composition of groundwater in a soil catena of an undulating ground moraine of the Poznań Lakeland.

MATERIAL AND METHODS

Study area

The study was carried out in a cultivated catchment area of the Przybroda Experimental Station located in the north-central part of the Poznań Lakeland (western part of Poland) within the Szamotuly Plain (Figure 1). The study area is between north longitudes 52°30′16″-52°30′52″ and east latitudes 16°39′35″-16°39′53″. This area is part of an undulating ground moraine of the Poznań Phase of Baltic Glaciation. In this area, the Retisols/ Luvisols and the Phaeozems/Gleysols create soil sequences along slopes called a catena (Figure 1). The mean annual precipitation of the Poznań Lakeland is 597 mm, mean annual real evapotranspiration is 495 mm and the average annual temperature is 8°C (Figure 2). The *meteorological data*

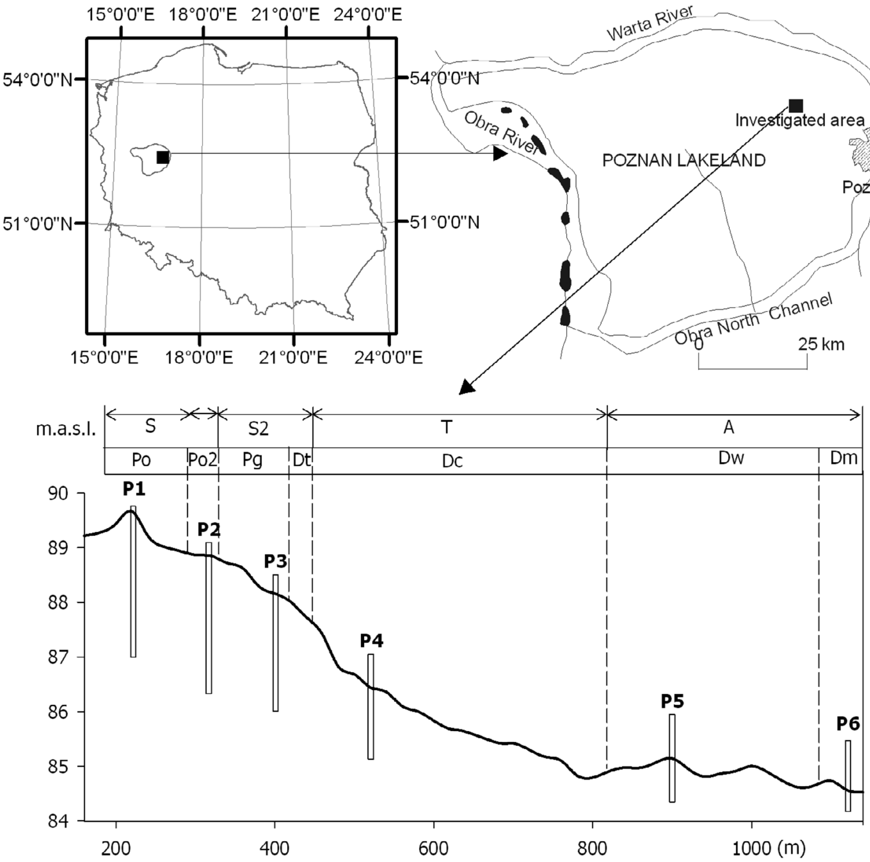

Fig. 1. Location of the investigated area and distribution of piezometers in the soil catena: S – summit, S2 – shoulder, T – pediment, A – footslope, Po – Eutric Albic Retisols (Loamic, Aric, Cutanic, Ochric), Po2 – Albic Luvisols (Loamic, Aric, Cutanic, Ochric), Pg – Gleyic Luvisols (Loamic, Aric, Cutanic), Dt – Luvic Gleyic Phaozems (Loamic, Aric), Dc – Cambic Gleyic Endocalcic Phaozems (Loamic, Aric), Dw – Calcic Mollic Gleysols (Loamic, Aric, Drainic), Dm – Calcaric Mollic Gleysols (Loamic, Aric, Drainic, Humic)

indicate that the amount of water that can infiltrate and percolate through the unsaturated soil zone and supply groundwater is 100 mm. SZAFRAŃSKI (1998) concluded that soils of the lower part of the catena receive 15% more water than soils of the higher part of the slope as a result of the lateral soil water flow. The downslope lateral water flow could substantially modify the chemical composition of the groundwater in the lower part of the catena.

At the beginning of the study, the soil cover variability in the catchment area was determined. Then, the locations of representative pedons (6 pedons) were selected (Figure 1). These pedons were instrumented with piezometers constructed of 80 mm polyvinyl chloride (PCV) pipe. The piezometers were installed using a hand auger and sealed with a shield tube at the ground

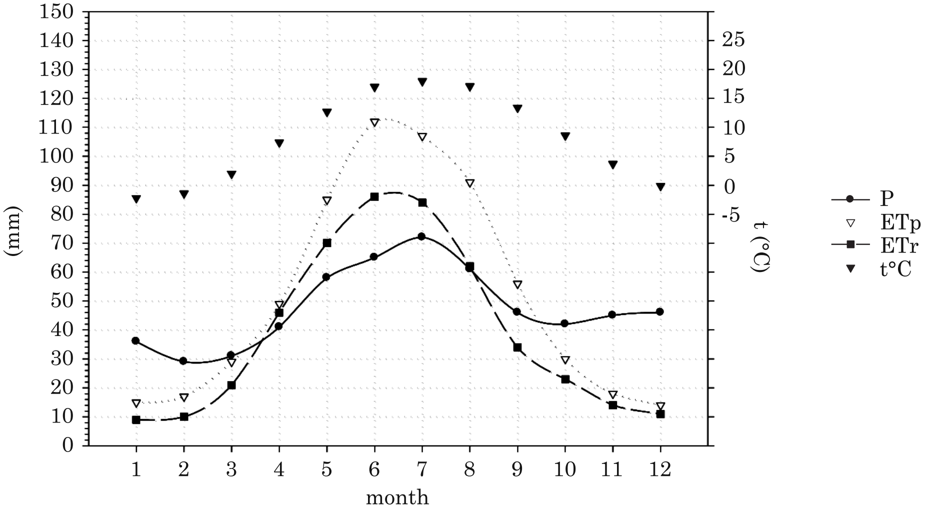

Fig. 2. The precipitation (P), potential evapotranspiration (ETp), real evapotranspiration (ETr) and average temperature (t°C) for the Poznań Lakeland

surface to prevent surface water infiltration along the side of the piezometer and rainfall from entering.

Groundwater sampling and analysis

Samples of groundwater from the 6 representative piezometers located over the catena were collected every two or four weeks from 2002 to 2014. The samples were collected into pre-cleaned 1-dm^3 polyethylene bottles, after removing stagnant water from the piezometer. In the field, using digital instruments, EC (electrical conductivity), temperatures and pH were measured. The water samples were analysed for various chemical parameters. Calcium, magnesium, potassium and sodium were analysed using AAS methods; phosphate was assessed with a UV/visible spectrophotometer; alkalinity (HCO_3^-+CO_3^{2-}) by the titration technique; chloride (Cl) was determined by titrating against $AgNO_3$ standard solution and sulphate as barium sulphate using the gravimetric method. The total dissolved solids (TDS) were calculated according to the methods described by HEM (1991).

To understand the chemical characteristics of groundwater in the studied soil catena, the analytical results of the chemical composition of water samples were plotted in a piper trilinear diagram (PIPER 1944). There is no single widely accepted method for classification of water types according to their major ion composition. In this study, the UPCHURCH (1992) and the FRAZEE (1982) classifications of chemical water types were used, in the absence of one generally accepted method for identification of hydrochemical water types. Also, the Gibbs plot was used to identify the mechanisms that control the groundwater chemistry of a soil catena (GIBBS 1970).

In the present study, agglomerative hierarchical cluster analysis (CA) was carried out using the Ward's method and the Euclidean distance, as a measure of proximity, for the grouping of sampled groundwaters. For this statistical analysis, all variables were log-transformed and more closely corresponded to normally distributed data. Subsequently, the data were standardised. Hydrochemical results of the groundwater chemical composition were statistically analysed using the software Statistica ver. 10 (StatSoft 2011).

RESULTS AND DISCUSSION

Groundwater level and general hydrochemistry

In soil of the slope summit and shoulder, the average groundwater table depths were 330, 315 and 258 cm below surface level, respectively for P1, P2 and P3, whereas in Phaeozems and Gleysols of the slope summit and shoulder they were 215 (P4), 134 (P5) and 118 (P6) cm below surface level (Table 1).

Table 1

The average values of chemical composition analyses of groundwater

Piezometer number	EC (μS cm^{-1})	pH	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	K^+	Na^+	GL (cm b.s.l.)
			(meq dm^{-3})							
P1	2.07	7.46	8.25	3.27	2.73	3.90	4.11	0.07	0.99	330
P2	2.26	7.46	6.32	3.95	3.03	5.48	3.62	0.06	1.23	315
P3	1.95	7.54	5.34	2.71	3.01	5.50	2.72	0.03	0.70	258
P4	1.73	7.55	5.39	3.25	2.42	4.25	3.16	0.02	0.75	215
P5	2.51	7.78	9.26	5.62	2.05	2.35	9.85	0.14	3.12	134
P6	2.94	7.49	14.76	5.10	2.74	3.85	9.57	0.15	2.21	118

* GL – the average groundwater level

In groundwater of Retisols and Luvisols (P1-P3), the mean value of the EC ranged from 1.95 to 2.26 dS m^{-1}, while in Gleysol's water at the footslope (P5 and P6) these values were much higher and ranged from 2.51 to 2.93 dS m^{-1} (Table 1). The values of groundwater pH ranged from 7.45 (P1) to 7.78 (P5). The average calcium content was from 2.35 (P5) to 5.50 (P3) meq dm^{-3}, whereas the content of Mg^{2+} in the groundwater of Gleysols (P5 and P6) was from two to three times higher (9.85 and 9.57 meq dm^{-3}) than the content of Mg^{2+} in groundwater of the remaining soils (from 2.72 meq dm^{-3} for P3 to 4.11 meq dm^{-3} for P1). The highest concentrations of potassium were recorded in the water from the P5 and P6, in which the average contents were 0.14 and 0.15 meq dm^{-3}, respectively. In the remaining grounwaters, the average concentrations of this ion ranged from 0.02 (P4) to

0.07 (P1) meq dm^{-3}. The average amounts of Na$^+$ in the water from the P1, P2, P3 and P4 were 0.99, 1.23, 0.70 and 0.75 meq dm^{-3}, respectively. Clearly, the highest contents of sodium were observed in groundwaters P5 and P6 (3.12 and 2.21 meq dm^{-3}, respectively) in comparison to the sodium contents in the other water samples (P1-P4). The differences are related to the chemical composition of the soils.

Hydrogeochemical processes

Chemical groundwater types

In the groundwater samples from P1 soil, the principal hydrochemical types are Ca,Mg–HCO_3(38%) and Ca,Mg–HCO_3,SO_4(38%), in the samples from P2 piezometer - Ca,Mg-mixed (53%) and Ca,Mg–HCO_3,SO_4(20%), in the samples from P3 piezometer - Ca-mixed (34%) and Ca,Mg-mixed (28%), and in P4 piezometer - Ca,Mg–HCO_3,SO_4(35%) and Ca,Mg-mixed (29%) – Figure 3.

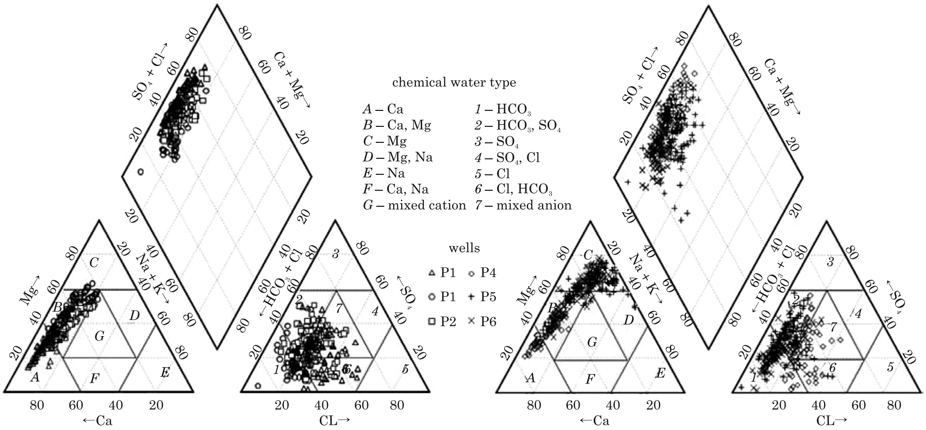

Fig. 3. Piper trilinear diagram indicating the groundwater type

Magnesium predominated over other cations in the majority of the *water* samples from P5 and P6 piezometers, and therefore about 70% of samples are characterised by Mg–HCO_3,SO_4 and Mg–HCO_3 hydrochemical facies.

The Gibbs plot shows that most of the data points lie in the rock dominance area, which indicates that interactions between aquifer rocks and water are the dominat factors influencing the groundwater chemistry of this area (Figure 4). Also, evaporation can influence the amount of dissolved components in some groundwater samples of the footslope (P5 and P6 piezometers). This observation suggests that dissolution of carbonate and silicate minerals is mostly controlled by the groundwater chemistry in the study area. However, the data for a few water samples covering the evaporation zone suggest that contaminants could affect the amount of dissolved components (Gibbs 1970).

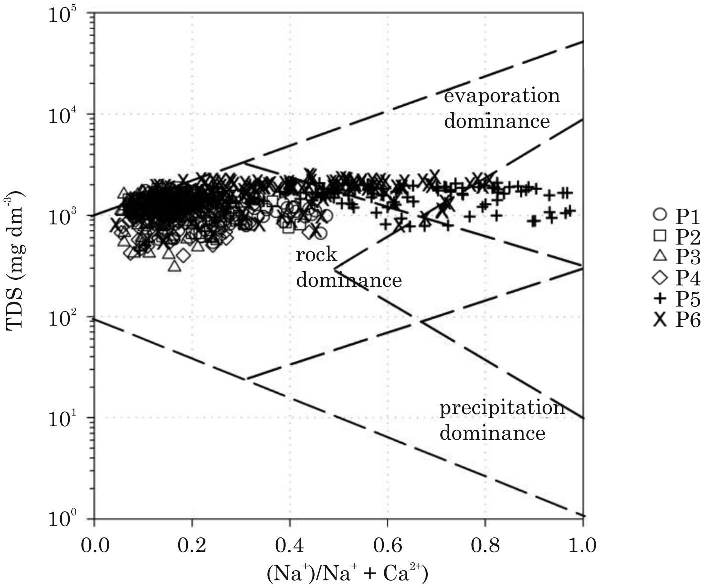

Fig. 4. Gibbs plot showing geochemical processes in groundwater of the studied area

Carbonate weathering and dissolution

Calcium and magnesium dominated among the cations present in groundwater, whereas bicarbonate was the prevalent anion. The weathering of calcite or dolomite contained in sedimentary rocks, such as glacial till and glacifluvial clay, is the primary source of carbonates in water. It reveals that this product of weathering might have been dissolved and leached to the groundwater system during rainfall infiltration and percolation. In the plot of Ca^{2+}+Mg^{2+} versus alkalinity+SO_4^{2-} (Figure 5*a*), the majority of points corresponding to the groundwater samples occur above and along the equiline, showing that the weathering of carbonates and sulphate minerals as well as silicate weathering were the main processes leading to the HCO_3^-+SO_4^{2-} increase in groundwater (DATTA, TYAGI 1996, FISHER, MULLICAN 1997). Carbonate weathering by carbonic acid and water saturated with CO_2 is an intensive process. This water can easily dissolve carbonate minerals and simultaneously enrich the groundwater in calcium, magnesium and bicarbonate ions. A few samples located on the Ca^{2+}+Mg^{2+} side indicate that these ions originate from other processes such as the reverse ion exchange reaction. Furthermore, if the Ca^{2+} and Mg^{2+} were obtained only from the weathering of carbonates and silicate, their presence should be balanced solely by alkalinity. The ratio of Ca^{2+} to HCO_3^- in groundwater where Ca^{2+} and HCO_3^- derive exclusively from calcite weathering equals 1:2, whereas in groundwater in which they come from dolomite weathering, it is 1:4 (GARRELS, MACKENZIE 1967, SUBRAMANI et al. 2010). In the Ca^{2+} vs alkalinity scatter diagram (Figure 5*b*), some points follow the 1:2 and 1:4 lines, which means that the weathering of calcite and

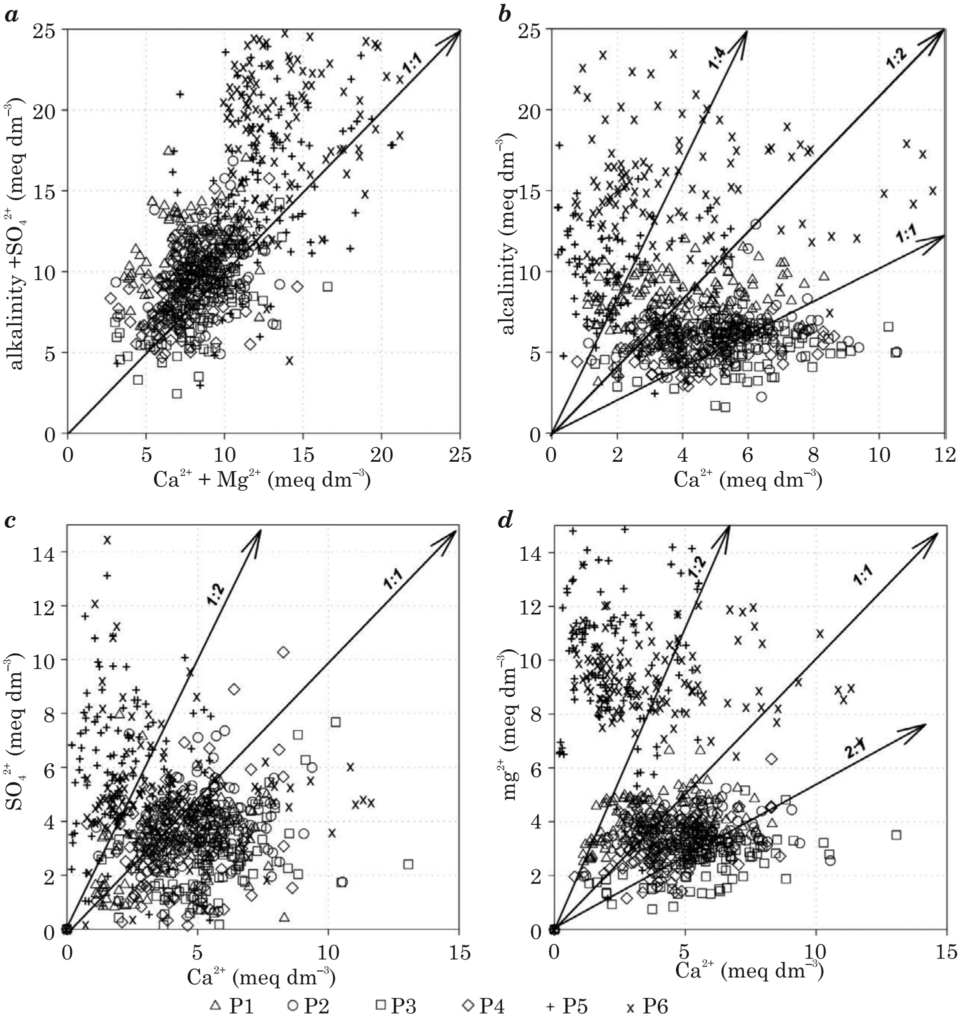

Fig. 5. Relationship between Ca, Mg, SO_4 and alkalinity in the groundwater

dolomite occur in the groundwater analysed. The groundwater samples from P5 and P6 piezometers follow only the 1:4 line, while the water samples from P1-P4 piezometers adhere to the 1:2 line. This indicates that dolomite weathering occur in the pediment of the soil catena and calcite and dolomite weathering take place in the remaining parts of the slope. The ratio Ca^{2+} to SO_4^{2-} in water in which calcium and sulphate are derived from gypsum and anhydrite weathering is 1:1 (Das, Kaur 2001). Most samples from P1-P4 piezometers show excess of Ca^{2+} over SO_4^{2-}, and only a few water samples follow the 1:1 equiline (Figure 5*c*). This clearly shows that the weathering of calcite in the presence of sulphuric acid dominates over the weathering of dolomite (Garrels, Mackenzie 1967). Excess of SO_4^{2-} over Ca^{2+} in groundwater from the footslope (P5 and P6) indicates that calcium is removed from water, most likely by calcite precipitation or the weathering of magnesium sulphate minerals. If mainly the weathering of dolomite occurs, then the molar ratio of calcium to magnesium is one, whereas if the ratio is higher than one then the weathering of calcite takes place (MAYO, LOUCKS 1995). Moreover, KATZ et al. (1998) have explained that if the molar ratio of calcium to magnesium is higher than two, the source of calcium and magnesium is also the weathering of silicates. The majority of the water samples from P1-P4 soils presented in the plot of Ca^{2+}+ versus Mg^{2+} (Figure 5*d*) fall between 1:1 and 2:1 lines, indicating that the weathering of calcite is the main process, followed by the weathering of dolomite and silicates minerals. The Ca^{2+}/Mg^{2+} molar ratio in the groundwater from the footslope (P5-P6) was completely different. Most of these groundwater samples show magnesium excess over calcium, which means that the weathering of Mg-rich silicate minerals occurs as an additional process (HEM 1991).

Silicate weathering

Weathering of silicates is one of the major geochemical processes that create the chemical composition of groundwater (GARRELS, MACKENZIE 1967). Quantitative assessment of products of the degradation of silicates is very difficult because the weathering of silicates generates many solid phases (DAS, KAUR 2001). The process of silicate weathering is usually identified by the ratio between $Na^+ + K^+$ and total cations (TZ+). Most samples presented in the plot of Na^+ + K versus TZ+ occur above the 1:2 line, indicating less intensive silicate (alkali feldspar) weathering (Figure 6*a*). In the Na^+ + K versus TZ+ scatter diagram, only a few groundwater samples are close to the 1:2 equiline, pointing out that the process of silicate degradation can occur (SARIN et al. 1989). In the plot of $Ca^{2+}+Mg^{2+}$ versus total cations (TZ+) – Figure 6*b*, the majority of the groundwater samples from P1-P4 soils occur along the equiline 1:1, implicating that calcium and magnesium in groundwater have originated from the weathering of Ca^{2+} and Mg^{2+} rich rocks and minerals. A few samples from P5 and P6 piezometers are close to the 1:0.6 line ($Ca^{2+}+Mg^{2+}$ =0.6TZ+), indicating that silicate degradation occurs in addition to carbonate dissolution (SUBRAMANI et al. 2010).

Ion exchange

Effect of ion exchange on the groundwater chemistry was evaluated by the two Chloro-Alkaline Indices (CAI1 and CAI2) suggested by SCHOELLER (1967):

$$CAI1=Cl^- - (Na^+ + K^+)/Cl^-,$$

$$CAI2=Cl^- - (Na^+ + K^+)/(SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-).$$

All values are expressed in meq dm^{-3}. In geochemical system when there is exchange between Ca^{2+} or Mg^{2+} in the water with Na^+ or K^+ in the aquifer material, both of the above indices are negative, while if there is exchange of

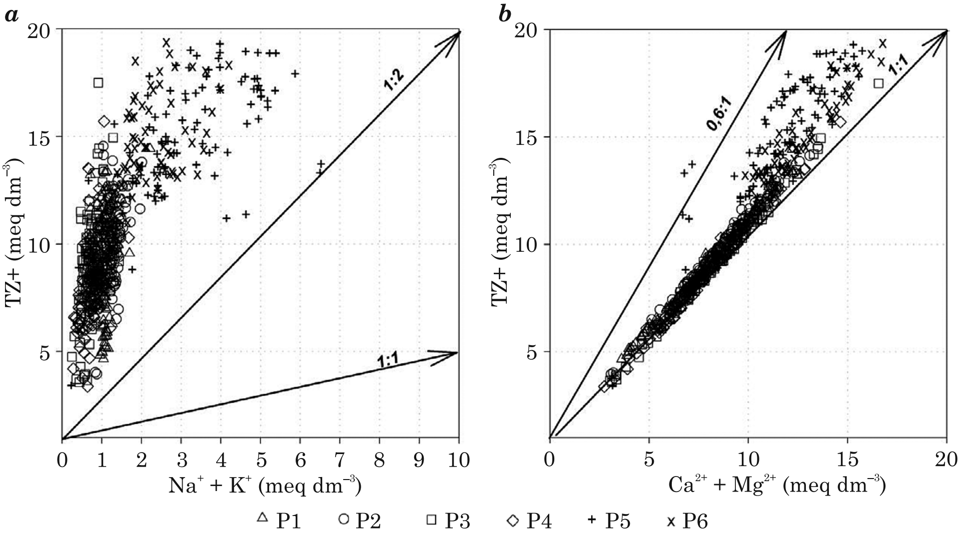

Fig. 6. Relationship between total cation, Na +K and Ca+Mg in the study region

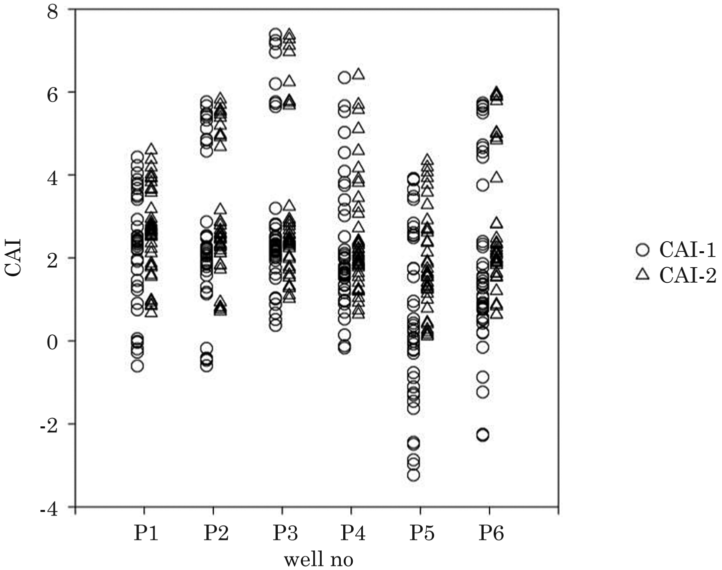

Fig. 7. Chloro-alkaline indices (CAI) indicating ion exchange process

Na^+ or K^+ from the water with Mg^{2+} or Ca^{2+} from the rocks, then both these indices will be positive (SCHOELLER 1967). CAI-1 and CAI-2 values for the groundwater samples are mostly positive, while only a few samples show negative values of CAI-1 (Figure 7). This points out the dominance of ion-exchange of Na^+ and K^+ in the water with Ca^{2+} and Mg^{2+} in the rocks. Furthermore, if the ion exchange process dominates over the reverse ion exchange, the groundwater samples in the plot of Ca^{2+}+Mg^{2+} versus HCO_3^- + SO_4^{2-} have a tendency to shift to the right due to the excess of HCO_3^- + SO_4^{2-}. Otherwise, water samples are positioned on the left due to a large excess of Ca^{2+} + Mg^{2+} over HCO_3^- + SO_4^{2-}. In the plot of Ca^{2+} + Mg^{2+} versus alkalinity + SO_4^{2-} (Figure 5*a*), the majority of the groundwater samples occur above and along the line 1:1, pointing out that the ion exchange dominates over the reverse-ion exchange.

Evaporation

Evaporation is a natural process that increases the concentration of ions in groundwater. An increase in the salinity at a constant value of Na/Cl is an indicator that evaporation is the dominant environmental process (JANKOWSKI and ACWORTH 1997). The data presented in the plot of Na^+/Cl^- ratio versus EC (Figure 8) indicate that evaporation is not the basic process in the analysed groundwater. Different values of the Na/Cl ratio with increasing EC indicate that exchange reactions and silicate weathering dominate over evaporation. However, the weathering of sodium silicates (Na/Cl>1) occurs mainly in the groundwater from the footslope (P5 and P6). In most samples, a low Na/Cl ratio with increasing EC indicates that the removal of Na from the groundwater system may be attributed to the reverse ion exchange processes of Na for Ca and Mg in clay (RAJMOHAN, ELANGO 2004, ZHU et al. 2008).

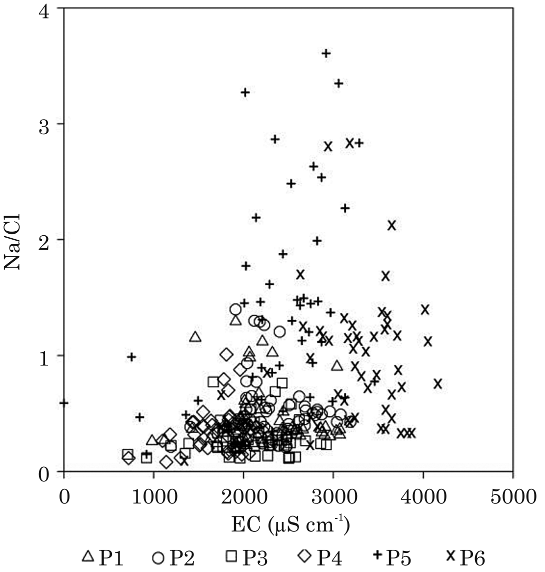

Fig. 8. Relationship between EC and Na/Cl in the groundwater

Cluster analysis (CA)

The objective of CA was to classify the groundwater studied on the basis of ionic composition. Many authors have used successfully this technique to classify water samples (FARNHAM et al. 2000, MENG, MAYNARD 2001). A classification scheme using th Euclidean distance for similarity, together with the Ward's method for linkage, produces the most distinctive groups.

Cluster analysis suggests two groups of piezometers (Figure 9). Group 1 is composed of piezometers P1, P2, P3 and P4 located higher in the relief. Groundwater from the piezometers of this group has a mean EC of 2 mS cm^{-1} and Ca,Mg–HCO_3,SO_4, Ca,Mg-mixed or Ca,Mg–HCO_3 type of water, with calcium being the dominant cation and bicarbonate the dominant anion. In the groundwater from this group, dissolution of calcite is the dominant geochemical process, followed by dissolution of dolomite and silicate minerals. Moreover, Group 1 can be divided into two subgroups, a division which seems to be related to the position of the piezometers on the slope. Subgroup 1 is composed of the piezometers located at the summit of the slope (P1 and P2), while subgroup 2 consists of the piezometers placed at the shoulder (P3) and pediment (P4). Group 2 is represented by the piezometers located within the footslope of the catena. The electrical conductivity of the groundwater from this group is 2.72 mS cm^{-1}. *Magnesium predominated* over other cations in most of *water* samples from Group 2 piezometers, and therefore mainly Mg–HCO_3,SO_4 and Mg–HCO_3 hydrochemical facies are concluded to have taken place at these sites. Most of Group 2 samples show excess magnesium over calcium, which could be a result of water interacting with Mg-rich silicate minerals as an additional process to the dissolution of dolomite.

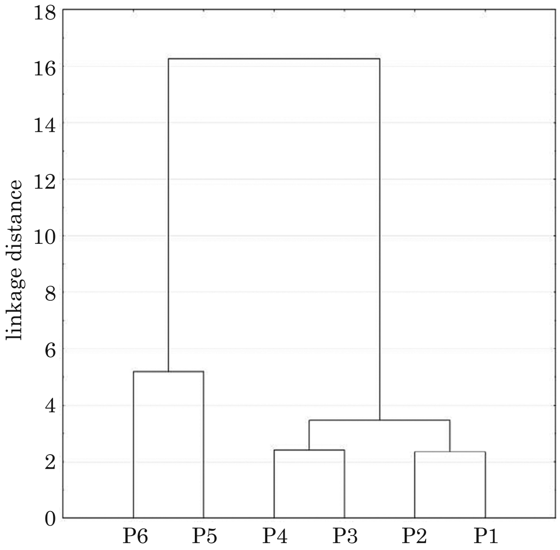

Fig. 9. Dendrogram of the hydrochemical piezometers

CONCLUSIONS

This hydrogeochemical investigation was carried out in the soil catena of an undulating ground moraine of the Poznan Lakeland in oder to identify the major geochemical processes influencing groundwater chemistry. The quantity of dissolved components in groundwater was connected with the location of piezometers in the relief studied and the properties of soil parent materials. The groundwater of soil located higher in the soil catena was characterised by smaller concentrations of the analysed components when compared with the composition of water from the lowest sites on the slope. In the groundwater from P1-P4 piezometers, the abundance of cations decreases in the order $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$, whereas in the groundwater from P5 and P6 piezometers, it decreases as $Mg^{2+}>Ca^{2+}>Na^{+}>K^{+}$ in P5 and P6. The abundance of anions decreases in the order $HCO_3^{-}>SO_4^{-2}>Cl^{-}$ in all piezometers. The Gibbs diagram suggests that rock-water interaction dominates, although the data obtained for a few water samples from P5-P6 indicate that evaporation can influence the chemical composition of groundwater in the lower part of the catena. This indicates that surface contamination sources, for example fertilisation, seem to affect the groundwater quality in the area with a shallow groundwater table. The dominant hydrochemical facies are Ca,Mg–HCO_3,SO_4, Ca,Mg-mixed or Ca,Mg–HCO_3 types in the groundwater from higher part of the slope and Mg–HCO_3,SO_4 and Mg–HCO_3 types in the groundwater from lower part of the catena.

The water chemistry of the studied soil catena is controlled by the weathering of carbonate minerals as well as silicate weathering. Calcite and dolomite weathering can occur in the groundwater samples from P1-P4 piezometers, while only dolomite weathering can take place in the groundwater of the catena's pediment (P5-P6). The Ca^{2+}/Mg^{2+} molar ratio in the groundwater samples from the footslope (P5-P6) shows an excess of magnesium over calcium, which could be a result of water interacting with Mg-rich silicate minerals, as an additional process to the dissolution of dolomite. Cluster analysis grouped groundwater piezometers of similar characteristics into two groups, indicating the influence of the location of each piezometer in the soil catena on the groundwater chemistry.

REFERENCES

Apadaca L.E., Bails J.B., Smith C.M. 2007. *Water quality in shallow alluvium aquifers, Upper Colorado River basin Colorado*. J. Am. Water Resour. Assoc., 38(1): 133-148. DOI: 10.1111/j.1752-1688.2002.tb01541.x

Das B.K., Kaur P. 2001. *Major ion chemistry of Renuka Lake and weathering processes, Sirmaur district, Himachal Pradesh, India*. Environ. Geol., 40(7): 908-917. DOI: 10.1007/s002540100268

Datta P.S., Tyagi S.K. 1996. *Major ion chemistry of groundwater in Delhi area: Chemical weathering processes and groundwater flow regime*. Geol. Soc. India, 47(2): 179-188.

Elango L., Kannan R., Kumar M.S. 2003. *Major ion chemistry and identification of hydrogeochemical processes of ground water in a part of Kancheepuram district, Tamil Nadu, India.* Ind. J. Geo-Marine Sci., 10(4): 157-166. DOI: 10.1306/eg100403011

Farnham I.M., Stetzenbach K.J., Singh A.K., Johannesson K.H. 2000. *Deciphering groundwater flow systems in Oasis Valley, Nevada, using trace element chemistry, multivariate statistics, and geographical information system.* Math. Geol., 32(8): 943-968. DOI: 10.1023/A:1007522519268

Frazee J.M. 1982. *Geochemical pattern analysis: method of describing the Southeastern Limestone regional aquifer system.* Stud. Hydrogeol. Southeastern U. S., Spec., 1: 46-58.

Garrels R.M., Mackenzie F.T. 1967. *Origin of the chemical compositions of some springs and lakes.* Equilibrium concepts in natural water systems, 67: 222-242.

Gibbs R.J. 1970. *Mechanisms controlling world water chemistry.* Science, 170(3962): 1088-1090. DOI: 10.1126/science.170.3962.1088

Hem J.D. 1991. *Study and interpretation of the chemical characteristics of natural water.* U. S. Geol. Surv. Water-Supply Paper 2254, Scientific Publishers.

Jankowski J., Acworth R.I. 1997. *Impact of Debris-Flow Deposits on Hydrogeochemical Processes and the Developement of dryland salinity in the Yass River Catchment, New South Wales, Australia.* Hydrogeol. J., 5(4): 71-88. DOI: 10.1007/s100400050119

Katz B.G., Catches J.S., Bullen T.D., Michel R.L. 1998. *Changes in the isotopic and chemical composition of ground water resulting from a recharge pulse from a sinking stream.* J. Hydrol., 211(1): 178-207. DOI: 10.1016/S0022-1694(98)00236-4

Kozłowski M., Komisarek J. 2013. *Temporal variability of selected dissolved components content in groundwater of the catena system of Poznan Lakeland.* Annu. Set Environ. Prot., 15: 1965-1981. (in Polish)

Kozłowski M., Komisarek J., Wiatrowska K. 2012. *Chemical speciation of selected dissolved components of groundwater in the catena of the Poznań Lakeland.* Annu. Set Environ. Prot., 14: 607-622. (in Polish)

Kumar M., Ramanathan A.L., Ra M.S., Kumar B. 2006. *Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India.* Environ. Geol., 50(7): 1025-1039. DOI: 10.1007/s00254-006-0275-4

Laluraj C.M., Gopinath G. 2006. *Assessment on seasonal variation of groundwater quality of phreatic aquifers–a river basin system.* Environ. Monit. Assess., 117(1-3): 45-57. DOI: 10.1007/s10661-006-7675-5

Mayo A.L., Loucks M.D. 1995. *Solute and isotopic geochemistry and ground water flow in the central Wasatch Range, Utah.* J. Hydrol., 172(1): 31-59. DOI: 10.1016/0022-1694(95)02748-E

Meng S.X., Maynard J.B. 2001. *Use of statistical analysis to formulate conceptual models of geochemical behavior: Water chemical data from the Botucatu aquifer in Sao Paulo state, Brazil.* J. Hydrol., 250(1): 78-97. DOI: 10.1016/S0022-1694(01)00423-1

Piper A.M. 1944. *A graphic procedure in the geochemical interpretation of water-analyses.* Eos Trans. Am. Geophys. Union, 25(6): 914-923. DOI: 10.1029/TR025i006p00914

Rajmohan N., Elango L. 2004. *Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India.* Environ. Geol., 46(1): 47-61. DOI: 10.1007/s00254-004-1012-5

Raju N.J., Shukla U.K., Ram P. 2011. *Hydrogeochemistry for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India.* Environ. Monit. Assess., 173(1-4): 279-300. DOI: 10.1007/s10661-010-1387-6

Rao N.S. 2006. *Seasonal variation of groundwater quality in a part of Guntur District, Andhra Pradesh, India.* Environ. Geol., 49(3): 413-429. DOI: 10.1007/s00254-005-0089-9

Rao N.S., Rao P.S., Reddy G.V., Nagamani M., Vidyasagar G., Satyanarayana N.L.V.V. 2012. *Chemical characteristics of groundwater and assessment of groundwater quality in Varaha*

River Basin, Visakhapatnam District, Andhra Pradesh, India. Environ. Monit. Assess., 184(8): 5189-5214. DOI: 10.1007/s10661-011-2333-y

Reddy A.G.S., Kumar K.N. 2010. *Identification of the hydrogeochemical processes in groundwater using major ion chemistry: a case study of Penna–Chitravathi river basins in Southern India.* Environ. Monit. Assess., 170(1-4): 365-382. DOI: 10.1007/s10661-009-1239-4

Reddy D.V., Nagabhushanam P., Sukhija B.S., Reddy A., Smedley P.L. 2010. *Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India.* Chem. Geol., 269(3): 278-289. DOI: 10.1016/j.chemgeo.2009.10.003

Sarin M.M., Krishnaswami S., Dilli K., Somayajulu B.L., Moore W.S. 1989. *Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal.* Geochim. Cosmochim. Ac., 53(5): 997-1009. DOI: 10.1016/0016-7037(89)90205-6

Schoeller H. 1967. *Qualitative evaluation of groundwater resources.* In: *Methods and techniques of groundwater investigation and development.* Water Res. Ser., UNESCO, Paris (33), 44-52.

Senthilkumar M., Elango L. 2013. *Geochemical processes controlling the groundwater quality in lower Palar river basin, southern India.* J. Earth Syst. Sci., 122(2): 419-432. DOI: 10.1007/s12040-013-0284-0

Sikdar P.K., Sarkar S.S., Palchoudhury S. 2001. *Geochemical evolution of groundwater in the Quaternary aquifer of Calcutta and Howrah, India.* J. Asian Earth Sci., 19(5): 579-594. DOI: 10.1016/S1367-9120(00)00056-0

Szafrański Cz., 1993. *Water management of areas with rich relief and need of their amelioration.* Rocz. AR Pozn. Rozpr. Nauk. 244.

StatSoft, I. 2011. STATISTICA (data analysis software system), version 10: www.statsoft.com.

Subramani T., Rajmohan N., Elango L. 2010. *Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India.* Environ. Monit. Assess, 162(1-4): 123-137. DOI: 10.1007/s10661-009-0781-4

Upchurch S.B. 1992. *Quality of water in Florida's aquifer systems.* Florida's Ground Water Quality Monitoring Program: Tallahassee, FL, Florida Geological Survey, 12-51.

Zhu G.F., Su Y.H., Feng Q. 2008. *The hydrochemical characteristics and evolution of groundwater and surface water in the Heihe River Basin, northwest China.* Hydrogeol. J., 16(1): 167-182. DOI: 10.1007/s10040-007-0216-7