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Role of the zone of aeration in the formation of groundwater chemical composition

Interpretation of the data collected during this research project indicate that the basic processes leading to the formation of the chemical composition of groundwaters occur mostly in the soil zone. Soil mineralogical composition, organic material content, and the type of plant cover principally decide the type and amount of dissolved components found in shallow groundwater.

Understanding of the evolution of the chemistry of rain water, into soil water, and groundwater requires description of the chemical character of the precipitation including the character of pollution released into the atmosphere as well as knowledge of the mineralogical composition of the soil and bedrock. Acid precipitation enriched in sulphates and nitrates infiltrating the soil are subject to two mechanisms delaying migration of pollutants to groundwater: retention by mineral complexes in soils and biological accumulation (D. Małecka *et al.*, 1993).

A study area was chosen which was beyond the influence of industry and agriculture and where the influence of atmospheric pollutants on water chemistry was minimal. By filling these requirements, the processes going on in the soil and zone of aeration should be occurring in a natural state, unmodified by the immediate interference of man. Depending on the character of the interaction of water and soil we can distinguish a series of water types occurring in the soil: crystalline and inherent waters, retained waters — hygroscopic and osmotic, and free waters — capillary and gravity (E. Myślińska, 1990). Because the problem under study was evaluation of the changes in the chemical composition of infiltration water, research concerned only waters displaced by gravity.

The study site was established on the eastern boundary of the Northern Podlasie Lowland on the Białystok High. The bedrock geology of this region was strongly influenced by sedimentation and erosion processes from the Central Polish Glaciation. Characteristic for

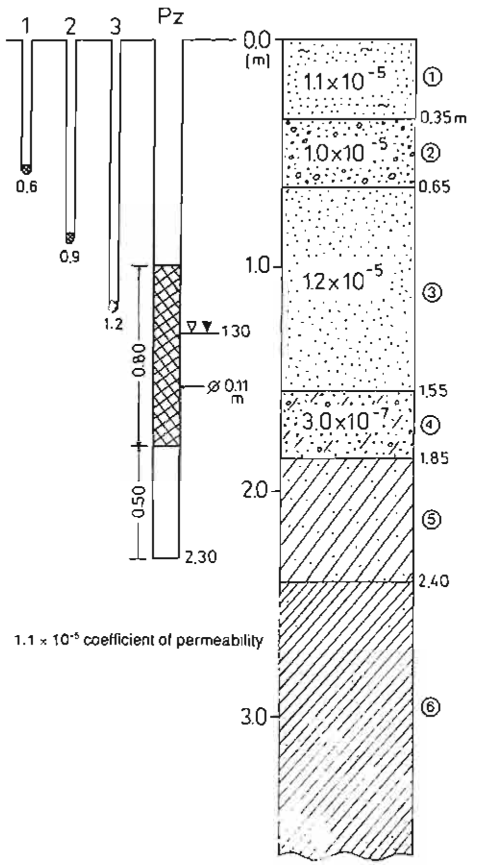

Fig. 1. Arrangement of ceramic cup lysimeters (1–3) and piezometer (Pz) in the lithological profile
Numbers in circles: 1 — sandy topsoil, 2 — silty sand, 3 — clayey sand, 4 — silty sand, 5 — sandy till, 6 — sandy cohesive till

Zespół próbników podciśnieniowych (1–3) i piezometr (Pz) na tle profilu litologicznego
Cyfry w kółkach: 1 — gleba piaszczysta, 2 — piasek gliniasty, 3 — piasek pylasty, 4 — piasek gliniasty, 5 — glina piaszczysta, 6 — glina piaszczysta zwięzła

the entire series of sediments are sequences of sands, gravels, as well as silts and loesses interbedded with tills. Study included the near surface part of the profile (Fig. 1). A practically impermeable sandy till, occurring at a depth of 1.85 m, forms the base of the zone of saturation of the unconfined aquifer. Fluctuations in the level of the water table between 1993 and 1994 were not large and oscillated around 1.3 m below the ground surface.

Detailed mineralogical study of the soil was carried out on samples taken from three depth intervals — 00.0–0.35, 0.35–0.65, and 0.65–1.85 m. The main components making up the soil in the zones of aeration and saturation were quartz and organic-clayey substances, including kaolinite, montmorillonite, and illite. Secondary components were orthoclase and albite. Accessory components were apatite, chlorite, muscovite, biotite, hematite, calcite, dolomite, and the following sporadically occurring minerals: pyrope, almandine, tourmaline, richterite, tremolite, zircon, staurolite, epidote, clinozoisite, rutile, cyanite, andalusite, sillimanite, and titanite. The average volume percentages of the secondary (15–16%) and the accessory (1%) minerals were independent of the depth of the sample, while the main components varied with depth. The percentage of quartz grew with depth: from 47% in the first zone, 65% in the second, to 74% in the third one. A reverse, declining tendency was shown by clay minerals, which constituted 37% of the composition in the first zone, 21% in the second zone, and 9% in the third zone (M. Manecki *et al.*, in press).

The study area was equipped with chemically neutral rain water collectors and ceramic cup lysimeters to collect gravitational water in the zone of aeration installed at 0.6, 0.9, and 1.2 m below the ground level, and a piezometer collecting water from the zone of saturation (Fig. 1). Hydrochemical sampling was carried out in monthly observation cycles in 1993–1994. The basic physical-chemical characteristics of the water — temperature,

(Fig. 1). Hydrochemical sampling was carried out in monthly observation cycles in 1993–1994. The basic physical-chemical characteristics of the water — temperature, conductivity, pH, and redox potential — were measured in the field at the time of sampling. A complete chemical analysis covering major and trace components and a series of chemical indicators was carried out in the laboratory, using the following analytical techniques: Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (ISP), Liquid Chromatography (HPLC), and classical analyses (weighing methods, spectrophotometry, ion-selective electrode (ISE), titration, and fluorometry). High sensitivity of the analytical methods and quality control by analyzing samples using several different methods (ICP, AAS, classical analysis) allowed complete evaluation of the chemical composition of the studied waters.

Chemical processes occurring in a natural water solution infiltrating through the zone of aeration, include among others: dissolution, precipitation, disassociation, hydrolysis, formation of ionic pairs and ionic complexes, redox reactions, etc. (A. Macioszczyk, 1987). Element stability diagrams introduced by J. D. Hem allow qualitative evaluation of elements dissolved in water, but only on individual elements without taking into account the hydrochemical complexity of the entire assemblage (M. Fic, E. Osmęda-Ernst, 1989). Hydrogeochemical models were created to remedy this defficiency by solving a set of equations incorporating the thermodynamic equilibrium constants of individual reactions and mass balance of analyzed components. All chemical reactions occurring in groundwaters show a tendency to reach a state of compositional equilibrium with mineral phases in the host rocks driven by changes in thermodynamic potential. The groundwater-soil system is almost never in a state of complete chemical equilibrium due to water movement. However, to simplify the calculations aiming at numerical description of divergence of a given water from equilibrium with a specific mineral phase in soil, a theoretical assumption was made that soil-solution equilibrium has been reached. The calculated values of ionic strength of solutions — from 0.00058 (average for rain water) to 0.00935 M (average for phreatic groundwater) — allowed application of the Debye-Hueckel formula for all calculations (P. A. Domenico, F. W. Schwartz, 1990). Using geochemical analysis packages PCWAT-4 and PHREEQE, the ionic activity and SI (saturation index) of minerals making up the soil reacting with water samples was determined. SI is defined as:

$$\mathrm{SI} = \log \frac{\text{product of the activities of the reacting ions}}{\text{equilibrium constant for formation of the mineral at the given temperature}}$$

A negative saturation index suggests a potential for dissolution of a given mineral in the analyzed solution, while a positive SI suggests a potential for precipitation of the specified mineral from the solution (C. A. J. Appelo, D. Postma, 1993).

The calculated saturation indices of thirteen minerals (quartz, kaolinite, montmorillonite, illite, orthoclase, albite, apatite, chlorite, muscovite, biotite, hematite, calcite, dolomite) which had direct contact with the solution showed different values dependent on the depth of sampling (Fig. 2). The most chemically aggressive solution was rain water: SI's are negative in the case of 11 minerals, while only biotite and hematite had positive values. Atmospheric dust is rich in these two minerals, which may have caused their saturation in rain water. The saturation indices of all the examined minerals show a tendency to increase

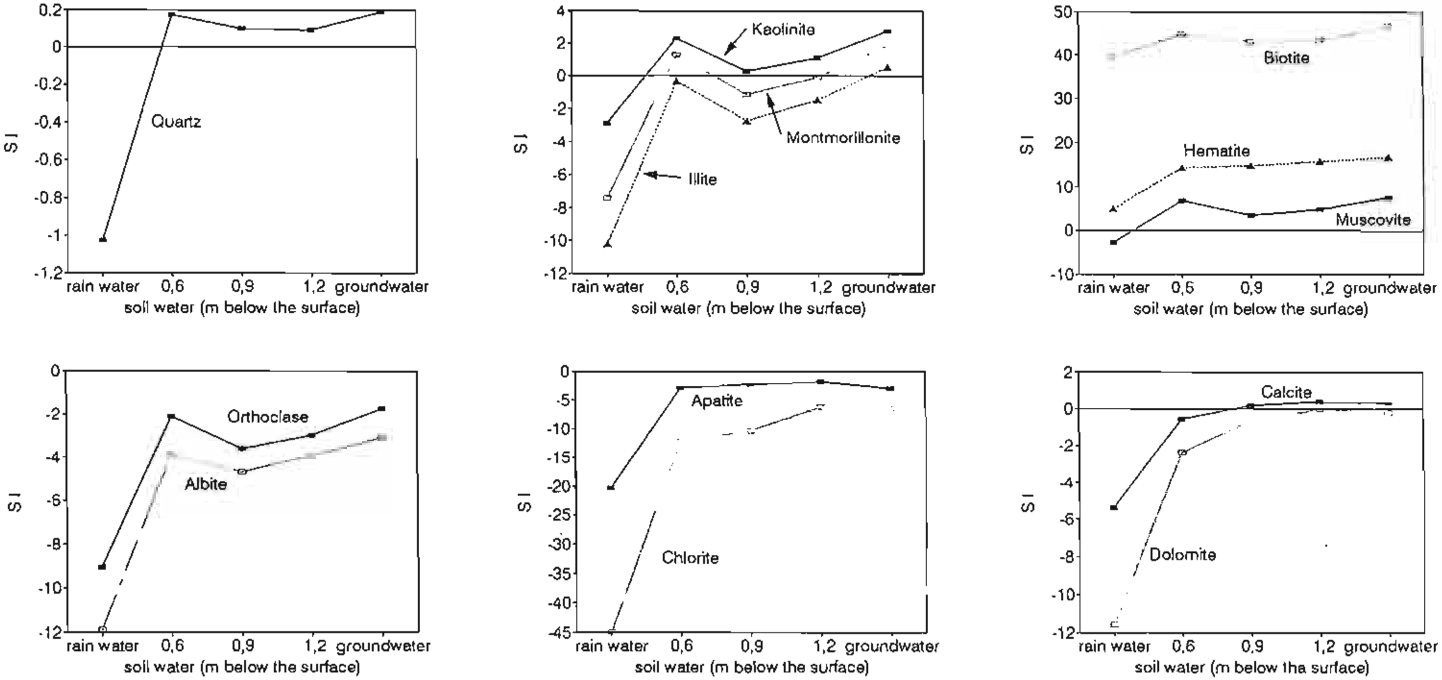

Fig. 2. Saturation index SI; average values from 1993–1994 ($n = 94$)
Wskaźnik nasycenia SI; wartości średnie z lat 1993–1994 ($n = 94$)

mineral, after some fluctuations between 60 and 90 cm, a relatively insignificant tendency to rise. On the basis of hydrochemical calculations, it can be concluded that the soil zone has the deciding influence on mineralization of shallow groundwaters. In this particular study area, this zone is made up of more than 50% clay minerals: kaolinite, montmorillonite, and illite. Reactions occurring at the interface of the solution and the cohesive soil are associated with the clay fraction and depend on many factors, such as chemical characteristics of the solution, mineral composition of the clay fraction, amount of organic material in the soil, availability of grain surface reaction area, fabric and texture of the soil, volume of ion exchange, temperature, etc. (B. Grabowska-Olszewska, 1990). As a very general conclusion, it seems that dissolution of clay minerals is basic for the formation of the chemical composition of shallow groundwaters. Independent confirmation comes from analysis of changes in the concentration of particular hydrochemical elements depending on the depth of sampling (Fig. 3). Study revealed that factors like dry residue, hardness, alkalinity, pH, concentration of chloride, sulphate, calcium, magnesium, and sodium rose along with depth. 10% of the substances in groundwater of the zone of saturation came from atmospheric dust in rain water, 47% from minerals dissolved in the 0.0 to 0.6 m zone, 25% in the 0.6–0.9 m zone, 7% in the 0.9–1.2 m zone, and 11% in the 1.2–1.5 m zone. It should be emphasized that not all the analyzed components showed the same dependencies. The concentration of nitrogen compounds, phosphorus, and potassium ion decreased with depth. In Poland it is practically impossible to find an area with precipitation unaffected by human activity. Elevated concentrations of nitrogen in rain water are the result of atmospheric pollution, most probably with a distant source. Increase in the concentrations of phosphorus and potassium is the result of nearby dry, agricultural pollution. These biophilic elements (N, P, K), indispensable to all living organisms, are caught and stored by plants, which causes a distinct drop in their concentration in the soil zone. The drop in potassium concentration is also influenced by ion exchanges with the clay fraction of the soil.

Table 1

Functional dependence of the concentration of analyzed element, *y*, on sampling depth in cm, *x*

Hydrochemical component	Dependence equation	Coefficients		Correlation coefficient
		a	*b*	
Dry residue [mg/dm^3]	$y = ax^b$	3.39	0.47	0.99
Hardness [mval/dm^3]	$y = ax^b$	–1.71	0.69	0.99
Alkalinity [mval/dm^3]	$y = ax^b$	–2.81	0.88	0.99
Reactivity [pH]	$y = ax^b$	1.64	0.08	0.99
Carbonate [mg/dm^3]	$y = ax^b$	1.25	0.87	0.99
Sulphate [mg/dm^3]	$y = ax^b$	1.93	0.36	0.92
Calcium [mg/dm^3]	$y = ax^b$	1.12	0.70	0.99
Magnesium [mg/dm^3]	$y = ax^b$	–1.08	0.63	0.94
Sodium [mg/dm^3]	$y = ax^b$	0.54	0.48	0.98
Nitrate [mg/dm^3]	$y = ax^b$	1.59	–0.69	–0.96
Nitrite [mg/dm^3]	$y = ax^b$	–2.75	–0.48	–0.92
Ammonium [mg/dm^3]	$y = ax^b$	0.68	–0.64	–0.98
Phosphates [mg/dm^3]	$y = ax^b$	–0.47	–0.61	–0.98

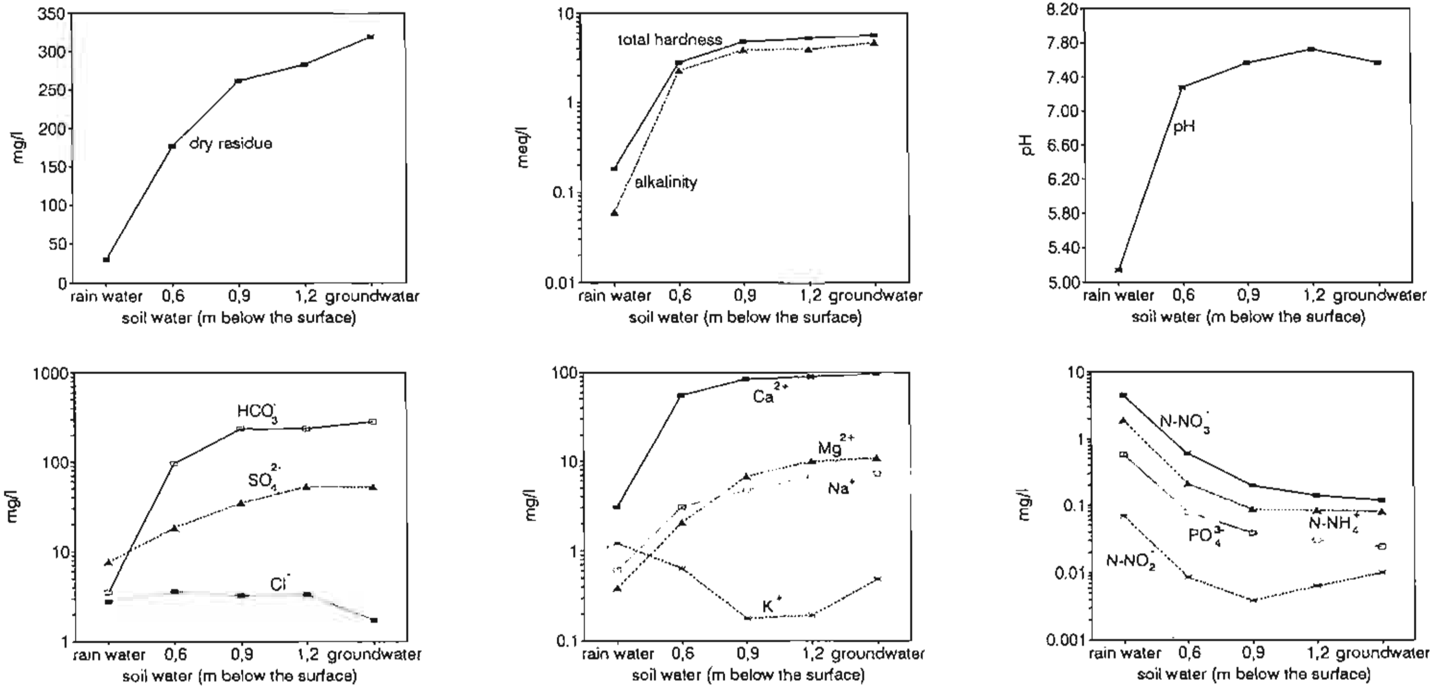

Fig. 3. Changes in concentration of the chosen indices and dominant ions in the groundwater; average values from 1993–1994 (*n* = 94)
Zmiany stężenia wybranych wskaźników i dominujących jonów w wodach gruntowych; wartości średnie z lat 1993–1994 (*n* = 94)

Potassium ions are adsorbed by clay minerals that, in turn, release ions of calcium, magnesium, and sodium (Fig. 3).

The best fit regression curves were used as a mathematical description of the examined dependencies. A clear dependence was accepted if the correlation coefficient of the studied differences exceeded |0.9|. Dependence functions were with the highest correlation coefficient were accepted. Student's test and the significance level for the calculated regression coefficients were used to verify the quality of the approximated numerical values and fitted regression curves. On the basis of 94 analyses of water sampled from five depths: 0.0 (rain water), 0.6, 0.9, and 1.2 m (infiltration water), 1.5 m (groundwater), the functional dependence was calculated (concentration of analyzed element versus sample depth; Tab. 1). The depth levels were constant and were determined by the method of rain water collection and depth of installed ceramic cup lysimeters. The value of 1.5 m for groundwater of the saturation zone is the depth of the middle part of the piezometer filter. In statistical calculations sampling depth was taken as the independent variable, while element concentration served as the dependent variable.

Of fifteen basic hydrochemical elements, thirteen clearly showed correlations with depth (Tab. 1). Only in the case of chloride and potassium concentrations did the statistical analysis not show any such dependence. It should be stressed that in all the remaining cases the change in concentration with depth was best described by power-product dependence. The regression curve supports the previously noted regularity that the dominant changes in concentration occur in the shallowest depth interval.

Interpretation of all the results unequivocally indicates that the basic processes for the formation of the chemical composition of groundwater occur mainly in the soil zone. Its mineralogical composition, organic matter content, and type of vegetation principally determine the type and quantity of dissolved components occurring in shallow groundwater.

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ROLA STREFY AERACJI W FORMOWANIU SKŁADU CHEMICZNEGO WÓD PODZIEMNYCH

Streszczenie

Rozpoznanie poszczególnych ogniw zależności między chemizmem wód opadowych, przesiąkowych i podziemnych wymaga określenia charakteru emitowanych do atmosfery zanieczyszczeń, a także znajomości składu mineralnego gleb i ich podłoża.

Stację badawczą założono na wschodnich krańcach Niziny Północnopodlaskiej w obrębie Wysoczyzny Białostockiej. Decydujący wpływ na budowę geologiczną badanego terenu wywarły procesy sedymentacyjne i erozyjne zlodowacenia środkowopolskiego. Badaniami objęto przypowierzchniowy odcinek profilu do głębokości 1,85 m, zbudowany z piasków gliniastych i pylastych. Glina piaszczysta, praktycznie nieprzepuszczalna, stanowi spąg strefy saturacji pierwszego, swobodnego poziomu wodonośnego.

Szczegółowe badania mineralogiczne gruntów wykonano dla średniej próbki z trzech przedziałów głębokości: 0–0,35, 0,35–0,65 i 0,65–1,85 m. Składnikami głównymi budującymi szkielet gruntowy strefy aeracji i saturacji są kwarc, minerały ilaste (kaolinit, montmorillonit i illit) oraz substancja organiczna. Składniki poboczne to: skalenie — ortoklaz i albit, a składniki akcesoryczne — apatyt, chloryt, muskowit, biotyt, hematyt, kalcyt i dolomit. Objętościowa zawartość procentowa składników pobocznych (15–16%) oraz akcesorycznych (ok. 1%) jest niezależna od głębokości opróbowania. Różnice zawartości w poszczególnych przedziałach głębokości stwierdzono w ocenie składników głównych. Procentowa zawartość kwarcu rośnie z głębokością i wynosi: w pierwszej strefie 47%, w drugiej — 65% i w trzeciej — 74%. Odwrotną, malejącą tendencję wykazują minerały ilaste, których zawartość w strefie pierwszej wynosi 37%, w drugiej — 21% i w trzeciej — 9%.

Dla określenia składu chemicznego wód poligon badawczy wyposażono w chemicznie obojętne pojemniki do zbierania wód opadowych, próbniki podciśnieniowe zainstalowane na głębokości 0,6, 0,9 i 1,2 m poniżej poziomu terenu, ujmujące wody przesiąkowe, oraz piezometr ujmujący wody strefy saturacji. Badania hydrochemiczne prowadzono w miesięcznych cyklach obserwacyjnych w latach 1993–1994.

Modele geochemiczne wód były tworzone przez rozwiązywanie układów równań uwzględniających stałe równowagi poszczególnych reakcji oraz bilans analizowanych składników. Obliczone wartości siły jonowej roztworów od 0,00058 (średnia dla wód opadowych) do 0,00935 M (średnia dla wód strefy saturacji) pozwoliły na zastosowanie dla całości obliczeń podstawowej formuły Debye-Hueckla.

Wskaźniki nasycenia względem 13 minerałów (kwarc, kaolinit, montmorillonit, illit, ortoklaz, albit, apatyt, chloryt, muskowit, biotyt, hematyt, kalcyt, dolomit), mających bezpośredni kontakt z roztworem wodnym, wykazują zróżnicowane wartości zależne od głębokości pobrania próbki. Najbardziej agresywne są wody opadowe, w przypadku 11 minerałów wartości SI (*saturation index*) są ujemne, jedynie 2 minerały: biotyt i hematyt mają wartości dodatnie. Można to tłumaczyć składem mineralnym pyłów atmosferycznych zasobnych w te minerały, co mogło spowodować wysycenie nimi wód już w atmosferze. Podstawową tendencją dla wszystkich rozpatrywanych minerałów jest wzrost wskaźnika nasycenia analizowanego roztworu wraz z głębokością. Należy podkreślić, że przebiega on najintensywniej w strefie glebowej. Na pierwszych 60 cm następuje skokowe podwyższenie wskaźnika SI, następnie w zależności od rozpatrywanego minerału z pewnym wahnięciem w przedziale 60–90 cm obserwuje się stosunkowo nieznaczną tendencję rosnącą. Na podstawie obliczeń hydroche-

micznych należy wnioskować, że decydujący wpływ na mineralizację płytkich wód podziemnych ma strefa glebowa profilu gruntowego. Przyjmując za 100% mineralizację wód podziemnych strefy saturacji, ok. 10% stanowią substancje rozpuszczone na skutek kontaktu z pyłami atmosferycznymi wód opadowych, 47% — substancje rozpuszczone w strefie najpłytszej do 0,6 m poniżej poziomu terenu, 25% — substancje rozpuszczone na głębokości 0,6–0,9 m oraz 7 i 11% — na głębokości odpowiednio 1,2 i 1,5 m.

Interpretacja uzyskanych wyników badań wskazuje, że podstawowe procesy dla formowania się składu chemicznego pierwszego poziomu wód podziemnych zachodzą głównie w warstwie glebowej. Jej skład mineralny, zawartość substancji organicznej i rodzaj roślinności decydują w sposób zasadniczy o rodzaju i ilości rozpuszczonych składników znajdujących się w płytkich wodach podziemnych.