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Vadose zone – challenges in hydrochemistry

JERZY MAŁECKI [1] & MAREK MATYJASIK[2]

[1] *Department of Geology, Warsaw University, AL. Żwirki i Wigury 93, PL-02-089 Warsaw, Poland*
[2] *Department of Geosciences, Weber State University, 2507 University Circle Ogden, UT 84408-2507, USA*

ABSTRACT:

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Hydrochemical studies conducted in Bialystok, north-eastern Poland are used to illustrate the complexity of water chemistry in the vadose zone in clayey and silty sands. Field samples were collected from rain water, ceramic-cup lysimeters located at depths 0.6 m, 0.9 m, and 1.2 m and in a piezometer in the phreatic zone at a depth of 1.5 m. Analysis of chemical constituents in the water and mineral constituents in the sediments allowed saturation indices to be estimated for dominant minerals. Laboratory evaporation experiments showed significant affects of this physical processes on water chemistry in the vadose zone. Detailed mineralogic analysis allowed the cation exchange capacity of sediments to be estimated. More detailed study on Cu and Zn transport in the vadose zone indicates increasing diversification of Cu and Zn species with depth, and a degree of sorption saturation ranging from 9% to 90%.

A relatively dramatic change in the average TDS from 30.2 mg/L in rain water to 318 mg/L in the phreatic zone, and in the hydrochemical type from SO_4-Cl-Ca-NH_4 in rain water to HCO_3-SO_4-Ca-Mg confirms a hypothesis that in relatively uniform unconsolidated sediments, subsurface water chemistry is determined more by processes and reactions occurring in the vadose zone than in the phreatic zone. Significant complexity of these processes and reactions limit the applicability of available hydrochemical models based on chemical equilibrium at the present time, and emphasize the importance of new experimental techniques which would allow the in-situ interaction along water/mineral surfaces to be observed at preferably molecular level.

Results of this research characterize processes in the vadose zone in north-eastern Poland and can be compared to similar studies known from other regions and climatic zones.

Key words: Rainwater, Groundwater, Evaporation, Solution, Sorption.

INTRODUCTION

One of the more important and interesting, but often overlooked, hydrochemical facts is that in areas with relatively well developed soils and a relatively thick vadose zone, the chemistry of underlying shallow groundwater is often determined more by processes which take place in the vadose zone and less by processes in the phreatic zone (ARTHUR & FAHEY 1993, HANSEN & POSTMA 1995, LANGMUIR 1997, SEARS 1976, WHITE & *al.* 1998). The chemical composition of the water infiltrating in the vadose zone evolves with depth and is influenced by the properties of the precipitation and the mineralogical composition of the sediments. The composition of subsurface water is a very complex function of several factors including, but limited to, the composition of infiltrating water, the petrologic and mineralogic composition of subsurface rocks, and dynamics of groundwater flow controlling rock/water interaction. Only in very unique environments rock/water interaction is controlled almost entirely by thermodynamics. This occurs when flow velocity is very slow, the water/rock ratio is low and residence time is very long.

Recent advances in hydrogeochemistry, which applied experiments at the molecular level, for example using atomic force microscopy, allowed several chemical reactions on mineral surfaces to be observed for the first time. Hydrochemistry has been moving to new areas of research which were not accessible before. These new research techniques also indicate that the already very complex system of chemical reactions is in fact even more complicated.

Regardless of how complex the system is in the phreatic zone, the multiphase system in the vadose zone, combined with periodic wetting and drying provides an environment for significantly more complicated physical processes and chemical reactions. In addition to the major processes affecting water chemistry such as chemical weathering, carbonate chemistry, adsorption-desorption reactions, buffering of aqueous species, and ionic exchange processes, water chemistry is also affected by the order of encounter (ARTHUR & FAHEY 1993, HANSEN & POSTMA 1995, KEHEW 2001, PALMER & CHERRY 1984). For various flow paths (especially in sedimentary rocks and sediments) the final chemical composition depends not only on rock types but also on the sequence of mass-transfer in each rock layer. The order of encounter on a smaller, but not less important, scale occurs also in the vadose zone. In this zone, however, wetting/drying cycles significantly complicate reaction kinetics (TINDALL & KUNKELL 1999).

Many concepts have been applied in geochemical and transport computer models. These models assume either chemical equilibrium of aqueous systems or apply simplified sorption/retardation concepts. Even though conclusions derived from geochemical computer models are frequently used in environmental litigation, the fact is that extremely complex systems become even more unpredictable in the vadose zone. Here the effects of drying/wetting cycles on chemical processes are not well understood. Great fluctuations of soil moisture affect ion activity and literally all chemical reactions and physical processes throughout the entire thickness of the vadose zone (ALLISON & *al.* 1994, GREEN & FREYBERG 1995).

Water samples, which chemical composition are discussed in this paper, were collected in ceramic cup lysimeters at depths 0.6 m, 0.9 m, and 1.2 m, and in the phreatic zone at a depth of 1.5 m in Bialystok, north-east Poland. The complex vadose zone chemistry is reflected in the effects of evaporation on water chemistry, in dissolution/precipitation reactions, cation exchange, and adsorption processes (ARTHUR & FAHEY 1993; HANSEN & POSTMA 1995; KELLER & *al.* 1991; REARDON & *al.* 1983; WEBER & *al.* 1991, 1992; ZABOWSKI & *al.* 1992). Ionic ratios and saturation indices reflect further chemical evolution of water infiltrating into the vadose zone.

RAIN WATER

A complete chemical analysis of water samples was conducted using atomic absorption spectrometry (AAS), atomic emission spectrometry (ISP), liquid chromatography (HPLC), ion selective electrode (ISE), and flourometry. The average rain water in Bialystok is characterized by 30.19 mg/L of total dissolved solids (TDS), 15.4 T/km^2/yr of total dry atmospheric fallout, and 607 mm/yr average annual rain precipitation. The average values of electrical conductivity and pH determined for all rain events greater than 3 mm are 69 μS/cm and 5.1 respectively. In Bialystok sulfates, nitrates, bicarbonates, ammonia, calcium, chloride and potassium are dominant ions in monitored rain precipitation (Table 1).

Typically rainwater in Europe and North America at distances less than 100 km inland has 11.8 mg/L dissolved ions (GALLOWEY & *al.* 1982) and is weakly acidic (pH 4-6). Ionic composition of rainwater is strongly affected by a distance from the sea (HANSEN & POSTMA 1995). Some ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl, are derived mostly from particles in the air, while other ions such as SO_4^{2-}, NH_4^+ and NO_3^- originate mostly from atmospheric gases. With increasing distance from marine basins, concentrations of terrestrially dominated species, including Ca^{2+}, K^+, NO_3^-, SO_4^{2-}, NH_4^+ increase and concentrations of marine aerosols, including Cl^-, Na^+, and Mg^{2+}, decrease (STALLARD & EDMOND 1980). The average residence time in the atmosphere for sea salt is about 3 days (JUNGE 1972), which determines the areal extent of air fluxes enriched in sea-salt particles. The average ionic ratio of Cl/Na in rain water in Bialystok is 2.7 (Table 2), and is higher than in seawater (1.2), indicating that some chlorides might have anthropogenic origin. Ratios of Cl/K and Cl/Ca in rain water in the study area are reduced to 5% and 2%, respectively, of their equivalents in the sea water, indicating the dominating influence of continental sources.

EVAPORATION

The precipitation in the Bialystok field station is characterized by a total dissolved solids content of 30.2 mg/L. As the chemical composition of the infiltrating water evolves with depth, values of total dissolved solids change from 30.2 mg/L in rain water, to 176.7 mg/L, 261.6 mg/L, and 283.6 mg/L at depths 0.6 m, 0.9 m, and 1.2 m respectively. A sample collected from the phreatic zone at a depth of 1.5 m was characterized by 318 mg/L of total dissolved solids. An average chemical

ANIONS (mg/L)							
	HCO_3^-	Cl^-	F^-	NO_2^-	NO_3^-	SO_4^{-2}	PO_4^{-3}
Rain	3.6	2.8	0.02	0.07	4.4	7.5	0.60
Depth 0.6 m	120.59	3.6	0.19	0.01	0.59	18.29	0.08
Depth 0.9 m	237	3.25	0.17	0.00	0.2	34.68	0.04
Depth 1.2 m	256.11	3.31	0.14	0.01	0.14	52.08	0.03
Saturation zone	281.55	1.71	0.13	0.01	0.12	51.99	0.02

CATIONS (mg/L)						
	Na^+	K^+	NH_4^+	Ca^{+2}	Mg^{+2}	SiO_2
Rain	0.60	1.2	1.9	3.3	0.40	0.3
Depth 0.6 m	3.03	0.63	0.21	43.16	2.03	6.10
Depth 0.9 m	4.72	0.18	0.09	79.83	6.69	4.42
Depth 1.2 m	6.65	0.19	0.089	85.07	9.88	4.85
Saturation zone	7.21	0.48	0.08	90.97	10.86	6.60

MICROELEMENTS (mg/L)							
	Zn	Fe	Mn	Cu	Sr	Ba	Al
Rain	0.015	0.09	0.040	0.0025	0.0095	0.015	0.1
Depth 0.6 m	0.042	0.038	0.008	0.048	0.116	0.023	0.05
Depth 0.9 m	0.039	0.031	0.004	0.047	0.090	0.009	0.01
Saturation zone	0.018	0.150	0.018	0.009	0.104	0.013	0.12

Table 1. Major ions and microelements in water samples in the study area (number of samples analyzed 67 in years 1993-1994)

composition of samples collected in the vadose zone at depths of 0.6 m, 0.9 m, and 1.2 m is presented in Table 1. Processes other than evaporation more intensely affect the composition of water in the vadose and phreatic zone.

Comparing the composition of the rain water, the infiltrating water affected by evaporation, and the composition of the water at depths of 0.6 m, 0.9 m, and 1.2 m in the vadose zone, a significant part of the chemical composition results from evaporation of water at and near the surface in the area of study. Using either Turc's or Konstantinov's method, the average annual evaporation from the study are estimated to be 432-439 mm/yr (Turc 1955, Debski 1963). Since the average annual rain fall in the study area was 607 mm/yr, the amount of water infiltrating into the sediment is reduced by evaporation to 29% of the amount of rain fall.

	Cl/Na	Cl/K	Cl/Mg	Cl/Ca
Bialystok	2.7	2.7	5.1	1.0
Sea Water	1.2	53.4	10.3	52.9

Table 2. Ionic ratios (Cl/Na, Cl/K, Cl/Mg, Cl/Ca) in average sea water and in rain water in the study area

Laboratory experiments were conducted in a teflon coated container placed in a microwave oven in order to understand better how evaporation in the study area changes water chemistry. After evaporating 20%, 40%, 60%, and 80% of the rain water, respectively, an analysis of the concentrations of 20 dominant constituents indicated that the ionic concentrations were increased on average by factors of 1.32, 1.68, 2.51, and 5.05 respectively.

Comparing these results with the estimated annual evaporation in the study area leads to the conclusion that infiltrating water has an average concentration of dissolved constituents that has been increased by 2.49 times (Table 3), and its TDS has increased from 30.3 mg/L in the rain water to 74.9 mg/L in the infiltrating water. Assuming that at depths greater than 0.6 m evaporation is negligible, it was estimated that 42.4%, 28.6%, 26.4%, and 23.5% of TDS in the infiltrating water originated from rain water at depths of 0.6 m, 0.9 m, 1.2 m in the vadose zone and 2.2 m in the saturated zone, respective-

	RAIN	EVAPORATION	OTHER PROCESSES AND REACTIONS IN THE VADOSE ZONE
Depth 0.6 m	17%	25.3%	57.7%
Depth 0.9 m	11.5%	17.1%	71.4%
Depth 1.2 m	10.6%	15.8%	73.6%
Saturation zone	9.5%	14%	76.5%

Table 3. Contribution of rain chemistry and evaporation to water chemistry in the vadose zone at depths 0.6 m, 0.9 m, 1.2 m, and 1.5 m respectively

ly. These results are important to estimate the initial composition of water, which will interact with mineral surfaces in the vadose zone. From the difference it may concluded that approximately 57.6%, 71.4%, 73.6%, and 76.5 % of the average concentrations of dissolved solids were subsequently contributed to the composition of water due to other processes, like ion exchange, redox, adsorption, dissolution and precipitation.

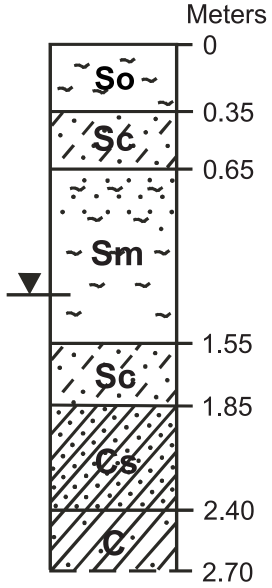

Fig. 1. Lithologic section of the study area: So – clayey sands with organic substances, Sc – clayey sands, Sm – slity sands, Cs – sandy clay, C – clay

INTERACTION BETWEEN SEDIMENTS AND WATER

Unconsolidated sediments in the study area are mostly composed of clayey and silty sands in the upper part of the profile, changing to glacial till with a greater amount of clay below 1.85 m. Quartz and illite are the dominant constituents of the sediment. A generalized lithologic profile (Text-fig. 1) and grain size distribution curves representative of the various depth intervals (Text-fig. 2) indicate significant presence of fines which suggests relatively slow flow velocity, thus allowing one to assume that equilibrium conditions can be achieved for most chemical reactions. Chemical analysis of the solid phase indicated that SiO_2 was most dominant throughout the entire thickness with a significantly smaller amount of Al_2O_3 and even smaller amounts of other compounds (Table 4). Differences in dominant constituents between samples from different depth intervals are not very significant, however many less dominant constituents (Fe_2O_3, TiO_2, CaO, Na_2O, K_2O, MnO) are slightly less common at greater depths in the vadose zone. Since the chemical composition of the infiltrating water in the vadose zone is altered by interaction along water/mineral surfaces, saturation indices were calculated for the thirteen most dominant minerals present in the solid phase. Changes in saturation indices between rain water, water in the vadose zone

SOLID PHASE COMPOSITION (VOLUMETRIC %)									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	MnO
Depth Interval 0-0.35 m	89.27	5.20	1.50	0.26	0.35	0.42	1.04	1.92	0.04
Depth Interval 0.35-0.65 m	90.50	4.80	1.10	0.26	0.33	0.53	0.93	1.6	0.04
Depth Interval 0.65-1.85 m	91.90	4.00	0.80	0.11	0.21	0.47	0.8	1.48	0.02

Table 4. Average chemical composition of solid phase in sediments representing average values for depth intervals 0-0.35 m, 0.35-0.65 m, and 0.65-1.85 m respectively, concentrations in sample volumetric % (Manecki & *al.* 1995)

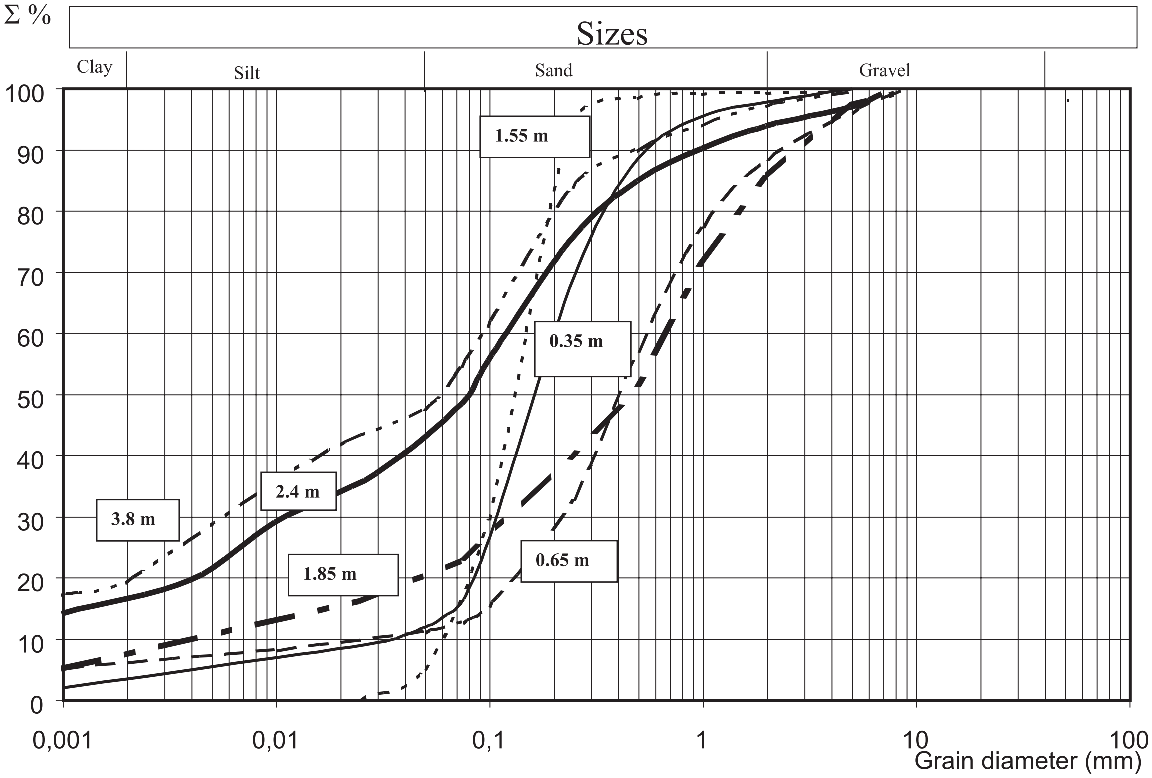

Fig. 2. Grain size distribution curves for samples representing various depths in the vadose zone

collected at a depth of 0.9 m and water in the phreatic zone are compared in Text-fig. 3, which shows that as water infiltrates from the surface to the water table it becomes increasingly more saturated with respect to all constituents and reaches saturation only with respect to muscovite in the vadose zone and with respect to kaollinite and amorphous iron hydroxides below the water table. All samples were oversaturated with respect to biotite (not indicated on the graph). Infiltrating water becomes more saturated with respect to all constituents

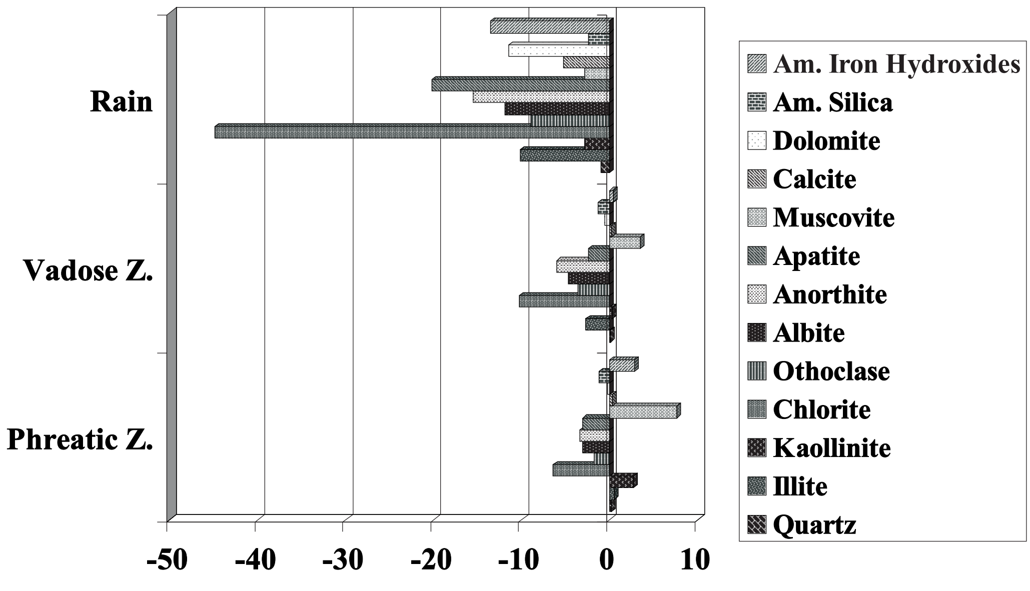

Fig. 3. Saturation indices in rain water, in vadose zone, and in phreatic zone with respect to thirteen dominant constituents of the solid phase

due to vigorous interaction between water and mineral surfaces but evaporation, an insignificant factor in the phreatic zone, strongly affects water chemistry in the vadose zone.

SORPTION

Based on the mineral composition, pH and ionic piezoelectric constants, it is assumed that cation exchange would be a dominant process in the sorption complex exchange reaction. General estimation of cation exchange capacity and saturation degree of sorption complexes can be conducted based on the content of clay-size grains and the amount of organic carbon in the sediment (APPELO & POSTMA 1993, KELLER & *al.* 1991). Cation exchange capacity (CEC) calculated based on these two factors decreases from 7.35 cmol(+)/kg at a depth of 0.35 m to 4.55 cmol(+)/kg at a depth of 0.65 m, mainly because of a decreasing amount of organic carbon in the sediment, and increases again to about 20 cmol(+)/kg at a depth of 2.7 m because of a much greater amount of clay-size particles (Text-fig. 4). Slightly different values of CEC were obtained using hydrolitic acidity and cation concentrations.

Among other elements, sorption of Zn and Cu were studied in detail because of the active complexation and speciation of both elements, and because heavy metals such as Zn and Cu are very sensitive indicators of the anthropogenic contamination. Both metals, however, show different mobility, with Zn species being typically more mobile than Cu species. Clay minerals, hydrated metal oxides and organic matter contribute to sorption of several microelements such as Zn and Cu (SPOSITO 1984). Compunds of these elements often form the colloidal phase. Under typical pH values the surface of the colloidal phase is negatively charged.

Many researchers indicated that adsorption of Zn and Cu by soils and sediments can be described by the Langmuir adsorption equation. A significant fraction of Zn and Cu can be irreversibly fixed by the sediment mineral surfaces (MCLAREN 1981). This type of hysteresis indicates that other processes than only ion exchange reactions contribute to the immobilization of Zn and Cu on mineral surfaces. The Cu and Zn contents and sediment sorption capacity were determined in the sediments at various depth intervals (Text-fig. 5). Since Langmuir isotherms best represented the results of sorption measurements, the maximum sorption obtained from Langmuir isotherms were used as the maximum sorption capacity with respect to Cu and Zn of the sediments studied (Text-fig. 5). Cu contents range from about 0.1 mmol/kg near the surface, then decrease slowly to about 0.06 mmol/kg at a depth of 1.5 m and increase again to almost 0.2 mmol/kg at a depth of 1.8 m. The amount of Cu remains constant up to a depth of 2.7 m. Similar but not identical changes characterize Zn contents in this profile. A relatively high amount 0.4 mmol/kg, near the surface decreases to less than 0.2 mmol/kg at a depth of 0.6-1.5 m, then increases to 0.45 mmol/kg and decreases again to slightly more than 0.2 mmol/kg. Values of sorbed Zn and Cu determined for various depth intervals were compared to the maximum sorption determined from laboratory measurements and the ratios of these two parameters were presented here as the degree of sorption capacity satu-

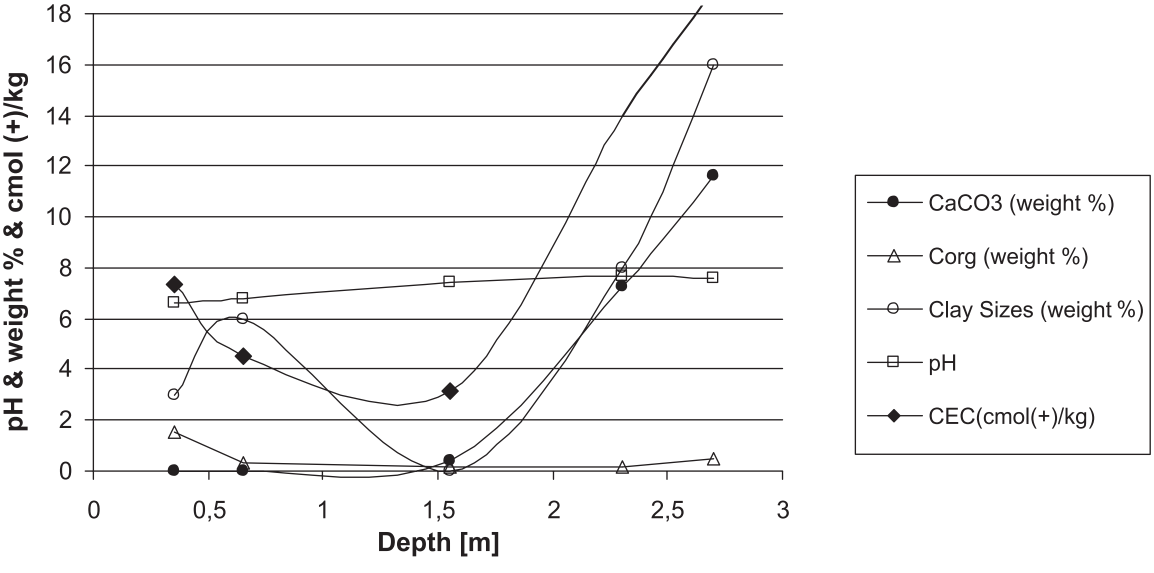

Fig. 4. Variability of pH, $CaCO_3$, organic carbon, clay sizes and cation exchange capacity in the vadose zone

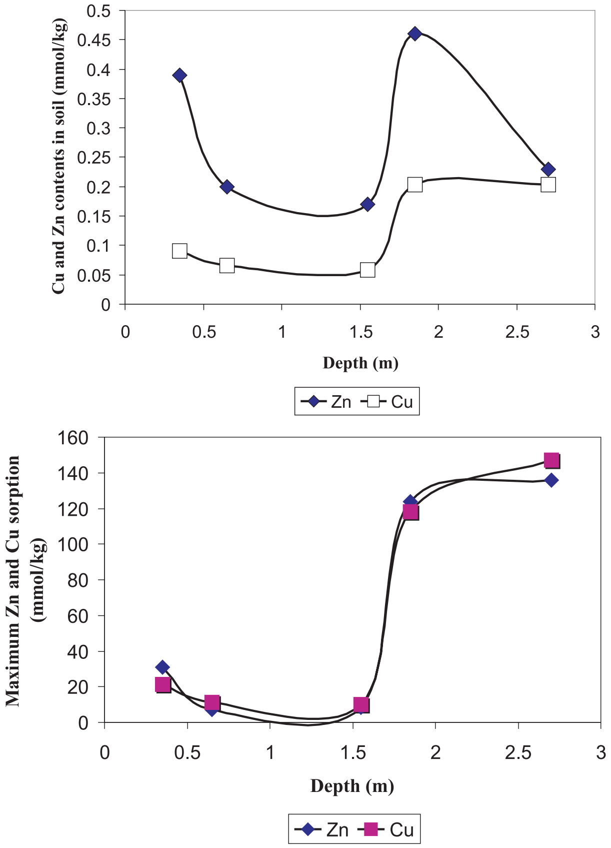

Fig. 5. Cu and Zn contents in sediments and sorption capacity with respect to Cu and Zn

ration which ranges from 2.7% to 0.17% at various depth intervals.

The average Zn concentration in rain water for the study area was 0.37 µmol/L and Cu concentration was 0.02 µmol/L. Cu and Zn concentrations in the infiltrating water were affected mostly by atmospheric precipitation. In water samples collected in the vadose zone, at depths greater than 1 m, Zn and Cu concentrations in the infiltrating water decreased significantly by about 60-80% (Text-fig. 6), although total Cu increased from the surface to a depth of 0. 8m.

Various species of Zn and Cu were analyzed in both rain water and the infiltrating water in the vadose zone. The ionic forms Zn^{2+} and Cu^{2+} are dominant in atmospheric precipitation and they influence water chemistry to various degrees throughout the entire vadose zone.

The Cu^{2+} ion dominates Cu species at the surface (100% of all Cu species)) and decreases to almost 0% at depth greater than 1.5 m. Cu^{2+} in the solution is however replaced by $Cu(OH)_2{}^0$ and $CuCO_3{}^0$, and in a smaller amount by $CuHCO_3{}^+$(Text-fig. 7). Similarly Zn^{2+} decreases from about 100% near the surface to less than 50% at a depth of 1.2 m and then slightly increases. Zn^{2+} is replaced predominantly by $ZnCO_3{}^0$ and $ZnHCO_3{}^+$, and in smaller quantities by $Zn(CO_3)_2{}^0$ and $ZnSO_4{}^0$(Text-fig. 7). The significant decrease in Zn and Cu concentrations in the vadose zone below a depth of about 1 m indicates that mineral surfaces have a relatively high sorption capacity (Text-fig. 6).

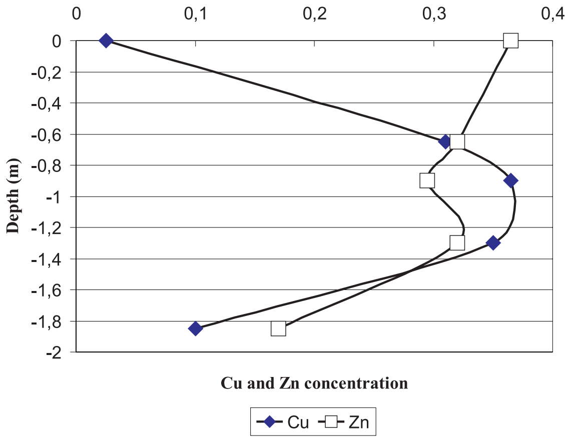

Fig. 6. Total Cu and Zn in infiltrating water in the vadose zone (in µmol/L)

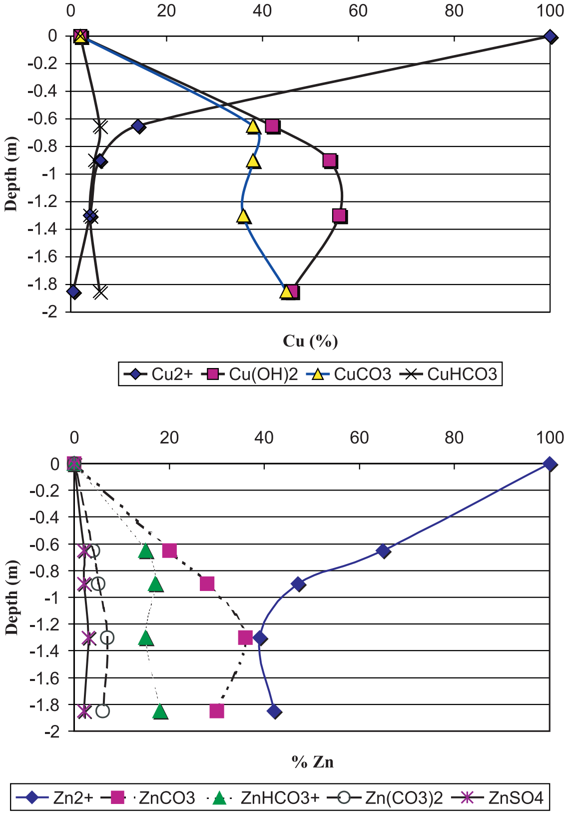

Fig. 7. Speciation of Cu and Zn species in the study area

WATER CHEMISTRY EVOLUTION

After analyzing water samples from precipitation, from lysimeters in the vadose zone, and in the piezometer installed in the phreatic zone, it is clear that this is a very dynamic system and one accompanied by complex chemical reactions and physical processes. A Piper diagram (Text-fig. 8) shows that the more diverse rain water chemistry tends to gradually approach certain type of equilibrium as a result of interaction along water/mineral surfaces. Areas represented by rain water in Text-fig. 8 (R symbol) are relatively large compared with the increasingly smaller areas representing shallow water in the vadose zone (0.6 m depth – symbol US), deep water in the vadose zone (1.2 m depth – symbol UD), and eventually water in the phreatic zone (depth 2.2 m – symbol S). Generally, hydrochemical water types change from SO_4-Cl-Ca-NH_4 in rain water to HCO_3-SO_4-Ca-Mg in the zone of saturation. This study confirms that water chemistry is often determined more significantly in the vadose zone rather than in the phreatic zone. The very diversified chemistry determined in the vadose zone (areas US and UD in Text-fig. 8) combined with the importance of evaporation on chemical composition of the infiltrating water (Tables 1 and 3), show that no one simple model can explain or predict all of the complex chemical reactions and physical processes occurring between the ground surface and the water table.

Two ionic ratios, Na/(Na+Ca) and Cl/(Cl+HCO_3), calculated for samples collected in the study area indicate maximum values of these ratios of 0.6 and 0.9 for rain water, respectively and less than 0.1 for both ratios in the groundwater (Text-fig. 9). These ratios clearly indicate the typical affect of interaction along water/mineral surfaces as water infiltrates through the vadose zone, which results in much lower ratios (APPELO & POSTMA 1993).

Even this very complex picture is rather simplified as it practically ignored wetting/drying cycles, which would certainly result in a greater departure from water chemistry predicted based on thermodynamic data and assumed equilibrium conditions. Recently introduced analytical techniques, such as atomic force microscopy,

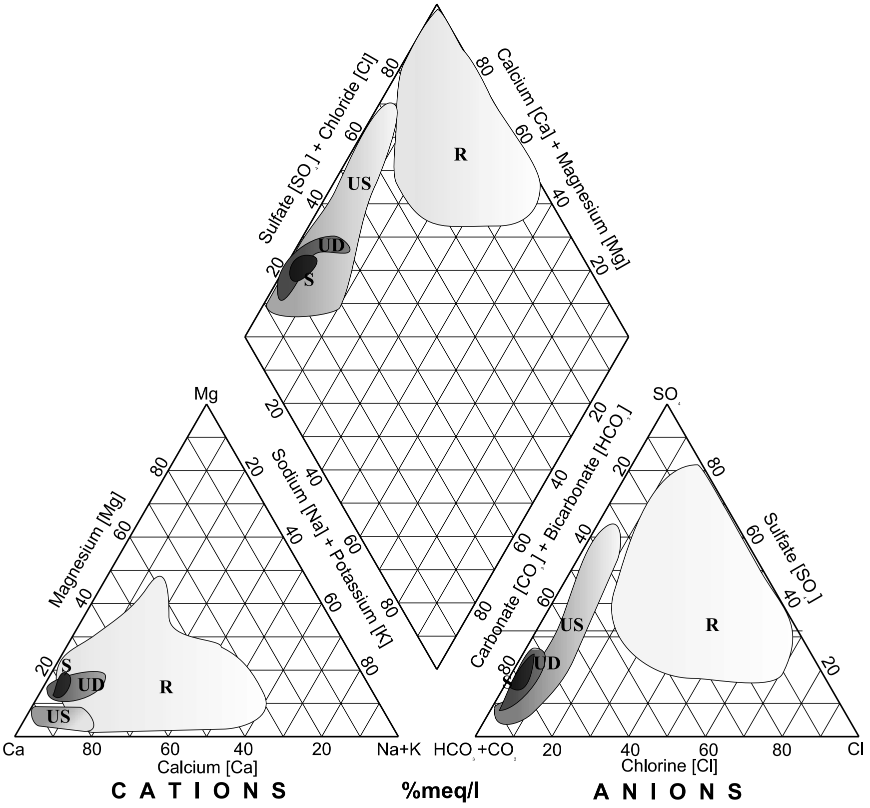

Fig. 8. Piper diagram illustrating rain water (R), shallow water in the vadose zone (US-depth 0.6 m), deep water in the vadose zone (UD-1.2 m), and water in the phreatic zone (S)

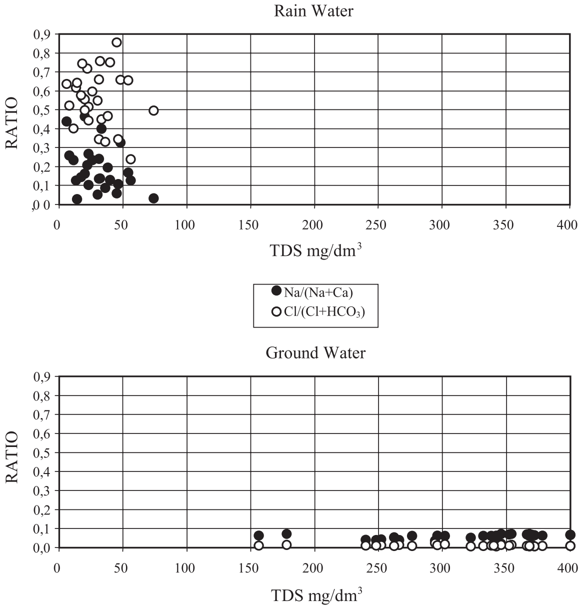

Fig. 9. Ionic ratios Na/Na+Ca and Cl/Cl+HCO$_3$ representing rain water and groundwater in the study area

allow chemical reactions and physical processes that occur on mineral surfaces to observed in-situ, including the effects of evaporation or wetting/drying cycles that are typical for the vadose zone. Some of these experiments confirm the applicability of equilibrium thermodynamic models, while others contradict their predictions (Manecki & *al.* 2001).

CONCLUSIONS

Results of this study estimate the effects of evaporation, dissolution/precipitation, cation exchange and sorption on the evolution of water chemistry in the vadose zone in clayey and silty sands in the study profile in Bialystok, North-Eastern Poland. Water infiltrating through the vadose zone is mostly undersaturated with respect to most of the dominant constituents in the sediments and approaches saturation with respect to biotite, muscovite, kaollinite and amorphous iron hydrodes in the phreatic zone at depths of 1.5 m and deeper. Evaporation seems to affect the chemical signature of the water more significantly than any other individual process, and accounts for about 23% to 42% of TDS in the infiltrating water at depths 1.5 m and 0.6 m, respectively. Cation exchange processes vary in the profile depending on the clay and organic carbon content. More detailed studies of Cu and Zn sorption indicate that sorption sites are variably saturated (0.17-2.7%) with respect to Cu and Zn, and that aqueous Cu and Zn speciation diversifies significantly with depth in the vadose zone. As the TDS content increases with depth, the ionic composition of the infiltrating water becomes increasingly more uniform, with smaller relative differences between ionic concentrations. Isotopic data were not available for this publication, but even they would only emphasize the complexity of chemical reactions and the heterogeneity of geologic media. Computer software which allows us to calculate chemical equilibria and speciations may provide reasonable boundary conditions to our interpretation but do not explain in detail the complexity of the hydrochemical processes. Results of this research provide information about processes in the vadose zone in northern Poland that can be compared with similar studies known from other regions and climatic zones (Arthur & Fahey 1993, Hansen & Postma 1995, White & *al.* 1998).

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