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The role of evapotranspiration in the formation of the chemical composition of shallow groundwater (the Polish Tatras)

JERZY J. MAŁECKI AND MARZENA SZOSTAKIEWICZ

Warsaw University, Faculty of Geology, Żwirki i Wigury Str., 93; PL-02-089 Warszawa, Poland.
E-mails: Jerzy.Malecki@uw.edu.pl and Marzena.Szostakiewicz@uw.edu.pl

ABSTRACT:

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An attempt to estimate the role of evapotranspiration in the formation of the chemical composition of shallow groundwater, based on data from the Hala Gąsienicowa (the Polish Tatras) is presented. The effective infiltration was estimated based on a two-year period of evapotranspiration and precipitation data. The calculated value compared to the effective rainfall allows estimation of the rainwater concentration. This, in turn, leads to an attempt at quantitative evaluation of the role of physical and chemical factors in the formation of the chemical composition of shallow groundwater. In the study area, composed of a carbonate-free weathering mantle of crystalline rocks, meteoric factors play a dominant role in shaping the chemical composition of shallow groundwater. Vadose and saturation zone waters inherit, to a large extent, the hydrochemical features of rainwaters.

Key words: Evapotranspiration, Rainwater, Soilwater, Concentration of water solution.

INTRODUCTION

Evapotranspiration leads to an increase in the concentration of the dissolved chemical constituents in rainwater, and thus to an increase in the saturation indexes of the dissolved species. This article describes an attempt to estimate the role of evapotranspiration in the formation of the chemical composition of shallow groundwater. The investigations required a thorough study of the geology, climate, and hydrogeological conditions of the area, including the chemical composition of rain and groundwater and changes in the physical and chemical parameters of the water through infiltration and groundwater flow processes. The study, carried out during the hydrological year 1993–1994, focused on changes in the water chemistry occurring in the vadose zone and the uppermost part of the saturation zone. To minimize the effect of anthropogenic factors, such as the influence of agriculture and industrial activity, as well as the effects of pollution sources, the experimental area was located in Hala Gąsienicowa (the Polish Tatras Mts., upper part of the Sucha Woda drainage basin) within the Tatra National Park (Text-fig 1). The near-surface zone is composed of very acidic, carbonate-free residual

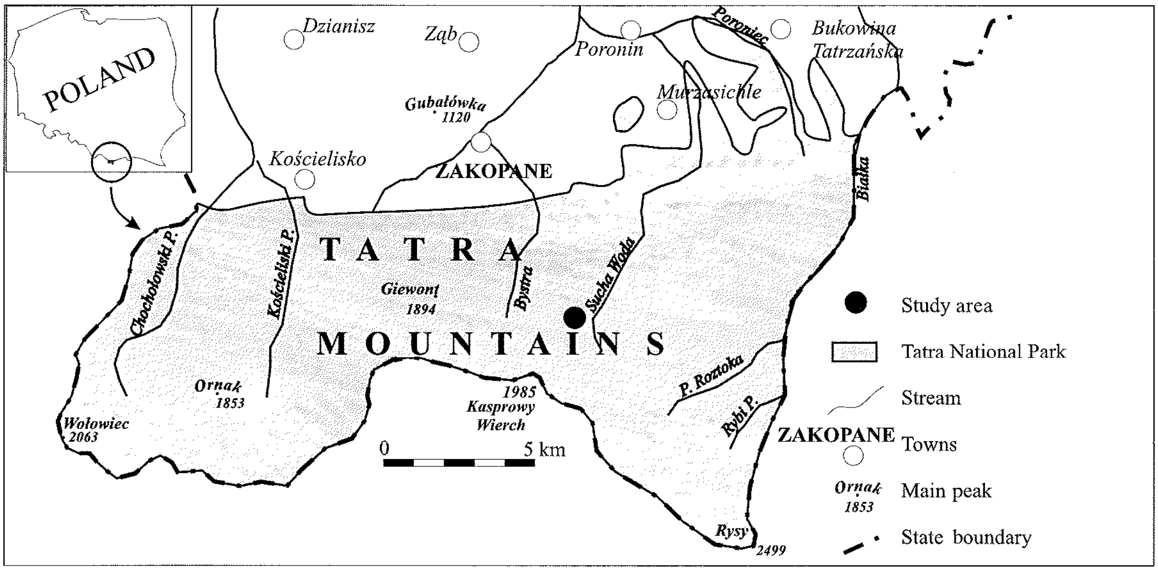

Fig. 1. Location of the study area

soils, with thicknesses ranging from several to several tens of centimetres. The soils are poorly developed from the weathering of hard parent rocks represented by the granitoids of the High Tatra Mts. (Bac-Moszaszwili & *al.* 1979; Małecki 1998).

CLIMATIC CONDITIONS

Of many climatic factors, precipitation, air temperature and evapotranspiration exert the greatest influence on the chemical composition of groundwater (Fetter 1994).

The climate of the study area exhibits the mountainous characteristics that are typical of the whole Tatra Massif. The amount of precipitation increases with elevation. The rainfall gradient in the upper part of the massif between Hala Gąsienicowa and Kasprowy Wierch Mt. is 30 mm/100 m (Małecka 1981). The experimental area is characterized by high total annual precipitation. The average annual precipitation for the period 1951–1995 was 1637 mm. The lowest values (1282 mm and 1435 mm) were recorded in 1993 and 1994 respectively (Text-fig. 2).

In general, the lowest precipitation is observed during the winter (January, February, March) and the highest in summer (June–August), with the maximum in June. Another typical feature of the mountainous climate is the high frequency of precipitation. In Hala Gąsienicowa there were 216 days with precipitation events in 1993, and 218 days in the following year. The period of snow cover is long in the area (over 230 days per year recorded at the Kasprowy Wierch weather station). The cover is usually thick, periodically in

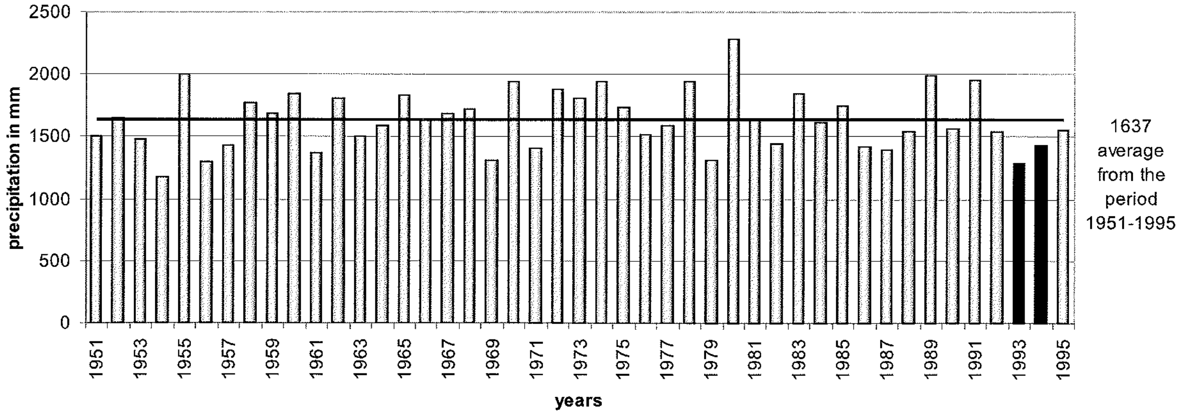

Fig. 2. Total annual precipitation

Period	Precipitation index [mm/year]	Actual precipitation* [mm/year]	Average annual air temperature [°C]	Turc' method [mm]	Konstantinov' method [mm]
1993	1282	1497	2.8	365.1	214.1
1994	1435	1676	3.4	380.9	245.0
1993–1994	1359	1587	3.1	377.8	229.5

*corrections after Chomicz (1976)

Tab. 1. Evapotranspiration calculated by the Turc and Konstantinov methods, and selected climatic data (Hala Gąsienicowa weather station)

excess of 3 metres. Long periods of snow cover are due to low average annual temperatures of approximately 3°C. In 1993, the average annual air temperature (2.8°C) was slightly lower than that recorded in 1994 (3.4°C).

Noteworthy are also high annual temperature amplitudes (exceeding 30°C in 1993 and 1994). Two distinct periods are observed over the year in the distribution of average temperatures: the warm period (May–October), with dominant temperatures above zero and the cool period (November–April), when temperatures below zero dominate.

Evapotranspiration

The evapotranspiration as understood herein, is the total of all types of evapotranspiration over the whole experimental area. It includes evaporation from rainwater remaining on vegetation and other surfaces, evaporation from the soil, plant transpiration and snow and ice sublimation. The effects of these climatic factors are difficult to estimate due to both technical difficulties in measuring procedures and in the empirical or physical calculation methods. The Turc formula (SOCZYŃSKA 1993), adapted to Polish conditions by MIKULIK (1961, formula 1) and, due to significant variations in the seasonal amount of evapotranspiration (CETNAROWICZ 1971), the Konstantinov method, were used to calculate evapotranspiration values. Daily amounts of evapotranspiration have been determined from the Konstantinov nomogram, as modified by DĘBSKI (1963), based on the air temperature and vapour pressure values.

$$E = \frac{P}{\sqrt{0.5 + \frac{P^2}{L^2}}} \qquad \text{(formula 1)}$$

where:

E – annual evapotranspiration (mm/year)

P – actual annual precipitation (mm)

L – evaporation potential ($L=300+25t+0.05t^3$)

t – average annual air temperature (°C)

The Turc formula enables the determination of the annual evapotranspiration based on the average annual air temperature and the amount of precipitation (Tab. 1).

The Konstantinov method is based on turbulent diffusion and requires the knowledge of vertical air humidity gradients and wind speeds over the active

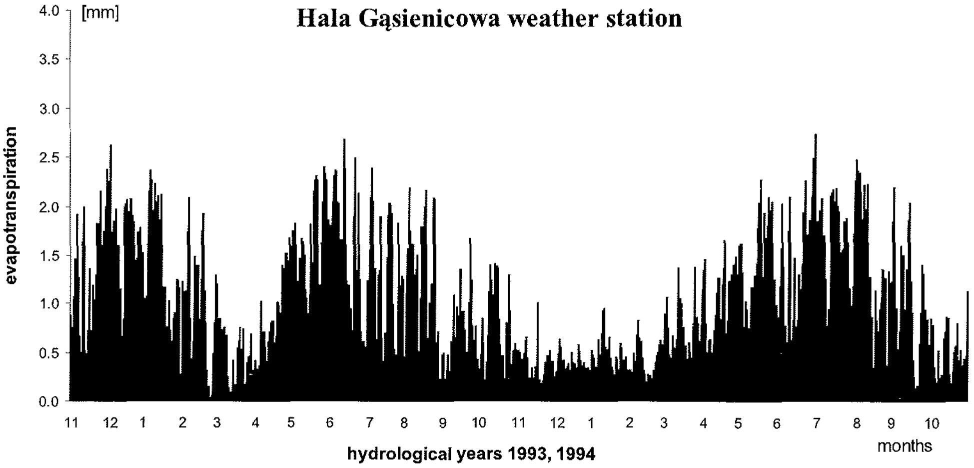

Fig. 3. Mean daily evapotranspiration from the Hala Gąsienicowa weather station

Mn	0.025	Na	4.75	SiO_2	1.0
Fe	0.05	K	1.06	Al	0.06
Cu	0.052	NH_3	2.03	F	0.29
Zn	1.106	Ca	13.1	NO_2	0.45
Sr	0.034	Mg	0.85	NO_3	8.49
Ba	0.025	Cl	10.2	pH	6.63
Ni	0.044	SO_4	23.0	alkalinity	0.3 mval/dm^3
dry residue	116	HCO_3	18.0	EC*	0.0106 mS/cm

* EC – electrical conductivity of water sample

Tab. 2. Concentration of chemical constituents in rain water [mg/dm^3]

surface, as well as of air temperature and actual vapour pressure. This method enables an estimation of evapotranspiration variability over a hydrological year that is necessary to estimate seasonal variations in the degree of sample concentration. Based on values of mean daily temperature and mean daily actual vapour pressure from the hydrological years 1993 and 1994, the mean daily value of evapotranspiration has been calculated (Text-fig. 3) using the method of the Konstantinov nomogram, modified by DĘBSKI (1963).

Summing up the values for each year, the amounts of annual evapotranspiration were obtained for individual hydrological years and for the whole period studied (Tab. 1). The authors realize that numerical modelling methods can yield more reliable results, but they require more data before this can be undertaken.

Hydro-chemical element	Water evaporating factor and corresponding concentrations of chemical constituents							
	1.32		1.68		2.51		5.05	
	mg/dm^3	*	mg/dm^3	*	mg/dm^3	*	mg/dm^3	*
Mn	0.038	1.52	0.049	1.960	0.070	2.800	0.141	5.600
Fe	0.050	1.00	0.059	1.180	0.073	1.460	0.136	2.720
Cu	0.066	1.27	0.081	1.560	0.115	2.210	0.222	4.270
Zn	1.521	1.38	1.930	1.740	2.809	2.540	5.242	4.740
Sr	0.049	1.44	0.060	1.760	0.090	2.650	0.182	5.350
Ba	0.037	1.48	0.450	1.800	0.070	2.800	0.141	5.640
Ni	0.059	1.34	0.077	1.750	0.115	2.610	0.227	5.160
Al	0.080	1.33	0.120	2.000	0.150	2.500	0.300	5.000
Na	6.000	1.26	7.680	1.620	11.60	2.440	23.78	5.000
K	1.480	1.40	1.900	1.790	2.760	2.600	5.300	5.000
Ca	18.30	1.40	23.40	1.780	34.60	2.640	69.70	5.320
Mg	1.080	1.27	1.360	1.600	2.030	2.390	4.090	4.810
Cl	13.60	1.33	17.10	1.670	-	-	-	-
$S0_4$	29.70	1.29	39.00	1.700	-	-	-	-
NO_3	11.40	1.34	14.50	1.710	-	-	-	-
F	0.330	1.14	0.420	1.450	-	-	-	-
EC** [mS/cm]	159.0	1.50	180.0	1.700	258.0	2.430	488.0	4.600
Average		1.33		1.69		2.47		4.86

* degree of increasing of concentration of individual components in relation to original values (rain water)
** EC – electrical conductivity of water sample

Tab. 3. Contents of hydrochemical elements at various levels of sample concentration

JAWORSKI & KRUPA (1987) showed that the values of the mean monthly evapotranspiration determined from a mathematical model (JAWORSKI's method, 1990), as currently used by the Institute of Meteorology and Water Management, did not differ significantly from those calculated using the Konstantinov method.

THE EFFECT OF EVAPORATION ON THE CHEMICAL COMPOSITION OF AN AQUEOUS SOLUTION (LABORATORY INVESTIGATIONS)

Physical and chemical properties of groundwater result from a number of interplaying processes, of which evaporation is a physical factor that causes concentration of the chemical constituents dissolved in infiltrating rainwater. Quantitative evaluation of the influence of this process in the formation of the chemical composition of groundwater, based exclusively on field investigation, is very difficult or even impossible. For this reason, a laboratory experiment relying on a repeated analysis of the same water sample with different solution concentration was carried out. The solution concentrating was performed in a special teflon vessel, using the CEM-USA MDS-81D microwave device. The process was controlled by adjusting the output power of the device, so that the temperature of the solution could fluctuate around 80°C. This investigation was carried out on a rainwater sample representing a single rainfall event dated May 1996 (Tab. 2).

Determinations were made at four solution concentration levels, after evaporation of about 20, 40, 60 and 80% of the sample volume. To obtain precise results, the concentration coefficients were mass recalculated, and are as follows: 1.32 at the first level, 1.68 at the second, 2.51 at the third and 5.05 at the fourth. Only samples that did not undergo phase changes of the existing chemical constituents were considered (Tab. 3).

No significant difference in the increase of the concentrations of anions and cations (1.33 on average) were observed at about 20% of the sample evaporation, when comparing the degree of solution concentration (mass recalculated) to the increase in concentrations of the elements analysed. The same result was observed by further evaporation of about 40% of the original sample volume. Differences appeared only after evaporation of about 60% of the original sample volume. Further determination of the main anions was unnecessary due to precipitation of salts from the solution at the solution concentration level 2.51, giving erroneous results.

The concentrations of cations were measured in the next phase of the experiment. These showed a similar trend in concentrations even if the sample was evaporated to 80%. Only the Fe concentrations changed in a different way. Fe freely precipitated as iron hydroxide as a result of oxidation of Fe^{2+} to Fe^{3+}. This chemical reaction caused a significant decrease in concentrations in relation to the degree of sample concentration (MAŁECKI 1998).

By comparison of the degree of sample concentration and changes in the electrical conductivity (reflecting the mineralization of the sample) it was found that these variables show a high degree of correlation. It enabled the conclusion to be drawn that chemical processes disturbing the simple relationship between sample concentration and increase in concentration of elements played a relatively insignificant role (MAŁECKI 1998).

THE ROLE OF EVAPOTRANSPIRATION IN SHAPING THE CHEMICAL COMPOSITION OF SHALLOW GROUNDWATER IN HALA GĄSIENICOWA

Assuming that the laboratory experiment of the rainwater sample concentration faithfully reflects natural physical processes, an attempt was made to estimate the role of evapotranspiration in the concentration of chemical components in vadose zone water. Taking into account the actual average annual precipitation (1587 mm) and evapotranspiration (229.5 mm) for the whole study period, an approximate rate of recharging infiltration was calculated (1357 mm/year). By comparing this value with the latter value of actual precipitation (1587:1357 = 1.17), the natural concentration of rainwater was estimated at **1.17**. Using the calculated natural concentration coefficient of rainwater and the previously defined assumptions, it was possible to make a quantitative assessment of the contribution of individual factors affecting the mineralization of shallow groundwater:

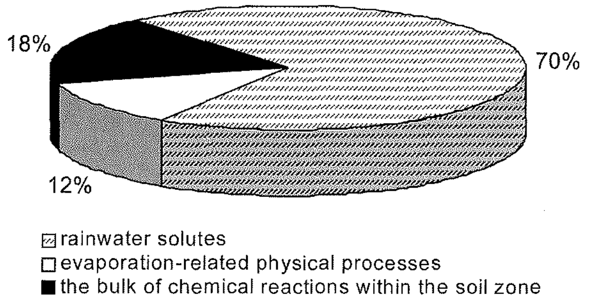

Fig. 4. Contribution of individual factors (in %) affecting chemical composition of shallow groundwater in Hala Gąsienicowa, using the climatic data

- rainwater components (**15.2 mg/dm^3**),
- evapotranspiration-related physical processes: [15.2 mg/dm^3 × 1.17] – 15.2 mg/dm^3 = **2.58 mg/dm^3**,
- chemical reactions within the soil zone: 20.8 mg/dm^3 – [15.2 mg/dm^3 + 2.58 mg/dm^3 = **3.02 mg/dm^3**.

The correctness of the assumed concentration of substances was assessed on changes in concentration of chlorides in a vertical soil profile. Concentrations of chlorides – chemically conservative components – are controlled mainly by physical processes and, theoretically, should not be proportional to the degree of water concentration. A disturbance of the relationship may be caused, among others, by interaction between infiltration water and the soil structure. However, hydrogeochemical conditions in the Hala Gąsienicowa experimental area indicate the lack of such interactions between chlorides and the soil structure.

Nkedi-Kizza (1982) and Griffioen (1992) are of the opinion that, at pH of the soil solution above 6.0, the chloride ion is not subjected to adsorption, being neutral towards the main soil minerals.

The assessment was made on a selected sample of rainwater (collected from the rainfall event dated October 10, 1993) and subsoil water. The chemical composition of the two types of water corresponded, in view of the duration of percolation from the ground surface (approximately 13 hours).

The tests were carried out (October 10, 1993) during a period with daily evapotranspiration, calculated by the Konstantinov method, equal to the average daily value for 1993–1994. Seepage water samples were collected using a vacuum pumping method. Ceramic membrane samplers were used (Text-fig. 5). To eliminate water flow along the sampler wall, the device was protected by a bentonite seal.

The concentration of chlorides in the rainwater was 1.09 mg/l, and 1.24 mg/l in the soil water, hence the degree of solution concentration, estimated on the change in the concentrations of chlorides, was 1.14. This value is very similar to that obtained using climatic factors.

The correctness of the estimated concentrations of rainwater solutes and of the role of evapotranspiration in shaping the chemical composition of the water was confirmed by a hydrogeochemical model developed using the PHREEQC v. 2.11 software (Appelo & Postma 1993; Parkhurst & Appelo 1999). Calculations were made using the PHREEQ database. In the first stage of the analysis, a reverse model was developed. It enabled the identification

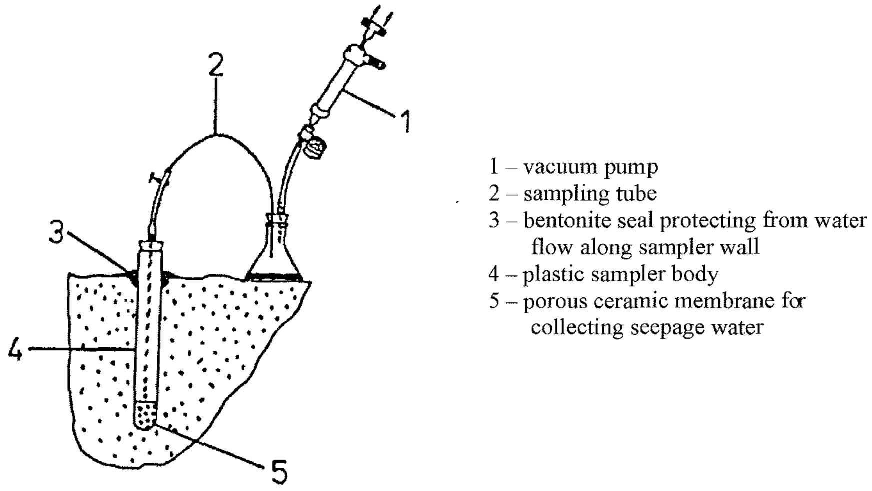

Fig. 5. Pressure-vacuum soil water sampler for collecting water samples from the zone of aeration

Precipitation		→		**Groundwater**				**Error***
				Physical and chemical parameters of the model		*Physical and chemical parameters measured*		
	mol/l		**mol/l**		**mol/l**		**mol/l**	**%**
Na	3.48E-05	Potassium feldspar	2.15 E-05	Na	3.97E-05	Na	4.35E-05	4.61
K	5.63E-05	Al $(OH)_3$	1.94 E-05	K	7.73E-05	K	9.21E-05	8.71
Ca	5.24E-05	SiO_2	9.04 E-05	Ca	6.08E-05	Ca	4.99E-05	-9.87
Mg	1.23E-05	Gypsum	9.60 E-07	Mg	9.32E-06	Mg	1.28E-05	15.54
Fe	5.37E-06			Fe	1.72E-06	Fe	1.79E-06	2.14
Mn	0.00 E+00			Mn	2.21E-06	Mn	1.64E-06	-14.75
Al	0.00 E+00			Al	2.96E-06	Al	4.08E-06	15.84
SiO_2	3.33E-06			SO_4	4.25E-05	SO_4	5.17E-05	9.79
Cl	3.08E-05	Illite	1.67 E-05	Cl	3.51E-05	Cl	3.50E-05	-0.1
SO_4	3.63E-05	Hematite	1.93 E-06	SiO_2	1.14E-04	SiO_2	1.15E-04	0.31
HCO_3	4.92E-05	Pyrolusite	1.93 E-06	HCO_3	5.22E-05	HCO_3	4.92E-05	-3.01
		$CO_2(g)$	3.36 E-06					
pH	5.93			pH	6.13	pH	6.05	
pe	4.96			pe	5.43	pe	5.67	

* calculated from the formula:
[(analytical data – data from the model)/(analytical data + data from the model)] * 100%

Tab. 4. A schematic summary of the geochemical model for the Hala Gasienicowa experimental area

of the determined mineral phases which were subjected to dissolution and to precipitation. The output data from the reverse model and the results of field and laboratory measurements of physical and chemical properties of rain- and groundwaters, including data about the mineral composition of the bedrocks in the experimental area, allowed the development of a forward model (Tab. 4).

Besides evapotranspiration, the model also involves reactions of dissolution and precipitation of minerals, as well as temperature changes along the route rainfall – groundwater. Verification of the forward model was performed through the comparison of the output data from the reverse model with analytical data obtained from field and laboratory investigations, achieving conformity in excess of 84% (Tab. 4). According to the modelling, the role of individual processes in the formation of the chemical composition of groundwater is as follows:

- rainwater components **(13.48 mg/dm^3)**,
- evapotranspiration - related physical processes **(1.89 mg/dm^3)**,
- chemical reactions within the soil zone **(6.23 mg/dm^3)**.

The contributions of individual processes shaping the chemical composition of groundwater in the experimental area, as identified by the modelling, are similar to those calculated from climatic data. The authors are of the opinion that it proves the correctness of the results obtained (Tab. 5).

The analysis performed shows that the physical and chemical properties of groundwater from Hala Gąsienicowa depend mostly on the chemical composition of the rainwater infiltrating into the

Method	Rainwater components	Evapotranspiration-related physical processes	Chemical reactions within the soil zone
Climatic data-based analysis (Fig. 4)	70	12	18
Geochemical model (Tab. 4)	62	9	29

Tab. 5. Results of investigations of the contribution of individual factors (in %) affecting chemical composition of shallow groundwater in Hala Gąsienicowa, using the two investigative methods

aquifer; soil processes and evapotranspiration are less significant (Tab. 5).

The large contribution of the meteoric factor results from both the geological structure of the area and the very short time of percolation of infiltration water through the soil. The presented calculations indicate that it is necessary to take into account climatic factors when estimating the role of individual factors affecting the chemical composition of groundwater. Moreover, it should be stressed that the proportions obtained are characteristic of specific climatic and geochemical conditions.

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