Kwartalnik Geologiczny, t. 35, nr 4, 1991 r., str. 477–490

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The forecast of the anthropogenic transformations of the chemical composition of groundwaters in the urban areas

The estimation of the anthropogenic transformations of the chemical composition of groundwater and the forecast of changes were given on the basis of the results of investigations made in the urban areas of towns: Zakopane, Nowy Targ and Białystok. Independently from the economic functions of the urban agglomerations and the degree of anthropopression, the anthropogenic changes in the water quality are best documented by the concentrations of chlorides, sulphates and nitrogen compounds. The dry residue, interpreted in the sphere of separated local subpopulations is not a senstive index, but its usefulness increases in the case of regional estimations. The prognosis of the anthropogenie changes of concentrations showed, that potentially small changes may appear in the composition of deep groundwater. On the contrary, the shallow groundwater in both areas will succumb farther violent degradation. According to the forecast, the upper limit of the sulphate background for these waters in the area of Białystok will attain in the year 2000 the normative value, and in the case of nitrate nitrogen the limit will overstep more than twice the sanitary norm.

The town areas with fundamentally different scale of anthropopression were chosen as test areas. These areas belong to two different natural regions, that is the mountainous and lowland region. The first consists of the drainage basin of the Biały Dunajec River with two townships of the region called Podhale — Zakopane and Nowy Targ. The economic interdependence of these two towns and the close buildup of the whole the Biały Dunajec Valley allow to treat this region as one test area. In the lowland region the drainage basin of the the Biała River (left-sided tributary of the Supraśl River was chosen, in the sphere of which the agglomeration of the town Białystok is found. While the drainage basin of the Biały Dunajec River represents essentially several lithologic-structural units, the drainage basin of the Białka River is more uniform in its geological structure. The formations present here are genetically connected with Middle-Polish Glaciation.

The different type of the geological structure and the character of groundwater recharge, circulation and drainage did not allow to accept identical investigational scheme for both test areas. In the drainage basin of the Biały Dunajec River only shallow groundwater, beeing the main supply for the population, was investigated. In the drainage basin of the Biała River, where the intermorainal aquifers are beeing mostly exploited, the investigation covered shallow groundwater and deep groundwater alike.

The interpretation of geological structure and hydrogeological conditions in both test areas showed, that the most susceptible to the anthropogenic transformations of the chemical composition are shallow groundwaters (J. Małecki, 1989). The anthropogenic factor takes part differently in the shaping of the chemical composition of the deep groundwater. The aquifers underlying the flysch in the mountainous regions are practically tightly isolated from the surface influence (D. Małecka, W. Murzynowski, 1989). However, in the region of Białystok the intermorainal aquifers contact immediately with the shallow groundwater through the zones of deep erosional scours. The anthropogenic changes in the chemical composition of deep groundwater are here caused by the existence of the exploitational depressions, which, especially in the area of tectonic windows, accelerate the penetration of the pollutions from the surface (J. Małecki, 1989).

The evaluation of the hydrogeochemical and anthropogenic transformations of the chemical composition of deep groundwater was done on the basis of the analyses of samples of water taken in the years 1971–1986. All interpretations made and the premises given in the papers of P. A. Domenico, F. W. Schwartz (1990), J.D. Hem (1985), S.R. Krajnov, W.M. Shviec (1980), A. Macioszczyk (1987), H. Schneider (1988), S.L. Shvarcev (1982) and H.J. Voigt (1989) caused, that the influence of the agglomerations of towns on the chemical composition of water was evaluated mainly at a basis of the occurrence of the chloride, sulphate and nitrate ions.

The chloride ion in the deep groundwater forms complex compounds, does not take part in the processes of oxidation and reduction, practically does not participate in the reactions of adsorption and ionic exchange and so becomes one of the most active water migrating ions (A.J. Perelman, 1971). The pollution caused by the industrial sewage or the sewage from the human settlements, because of its salt content, is registered quickly as the increase of the concentration of chloride ion.

In order to interpret the anthropogenic increases of the concentration of sulphate ions in the groundwaters, it is necessary to evaluate in the first line the level of the atmospheric emission of sulphur compounds, which cause the acidification of the rainfall and the increase of its sulphate contents. The acid rains cause the areal pollution of shallow groundwater recharged by infiltration. The sulphate pollution of point character is caused mainly by the influx of the industrial or communal sewage.

The communal pollutions are most fully registered in the form of the concentrations of nitrogen compounds. In the oxidating conditions in shallow groundwater the most often represented mineral forms of nitrogen are the nitrate

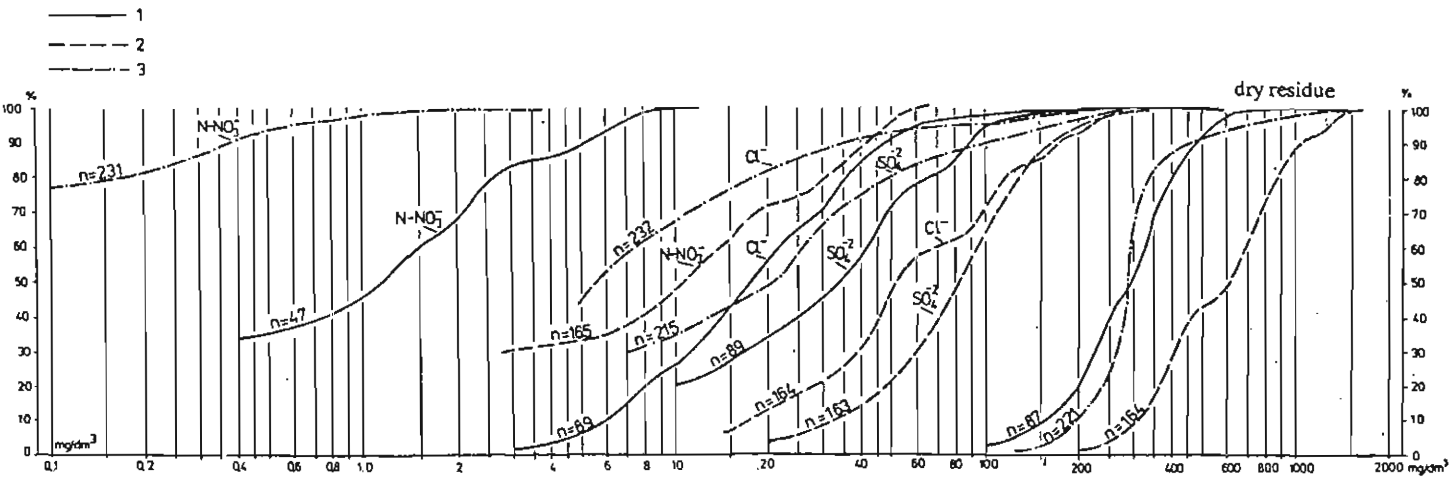

Fig. 1. Cumulative curves for the dry residue and the concentrations of Cl^-, SO_4^{2-} and $N\text{–}NO_3^-$ in the shallow groundwater of the Biały Dunajec Valley, and the shallow groundwater and deep groundwater from the drainage basin of the Biała River and environs from the years 1971–1986

Shallow groundwaters: 1 — of the Biały Dunajec Valley, 2 — of the drainage basin of the Biała River and environs; 3 — deep groundwater of the drainage basin of the Biała River and environs

Krzywe kumulacyjne suchej pozostałości stężeń Cl^-, SO_4^{2-} i $N\text{–}NO_3^-$ wód gruntowych doliny Białego Dunajca oraz wód gruntowych i wgłębnych zlewni Białej i okolic z wielolecia 1971–1986

Wody gruntowe: 1 — doliny Białego Dunajca, 2 — zlewni Białej i okolic; 3 — wody wgłębne zlewni Białej i okolic ions. In the environment of this type the nitrate ions are characterized by the best migration in water.

The chemical composition of the investigated waters is shown in the most legible graphical form of the cumulative diagram. These diagrams, because of the use of the logarithmic scale, allowed to compare the hydrochemical materials, even possessing great differences of concentrations up to several orders of magnitude.

The region of Podhale and Tatry Mts are characterized by the greatest rainfall in Poland, what, taking into account the strongly differentiated morphology of the terrain causes quicker drainage and water exchange. This fact and lack of industrial pollution, oppressive for the environment, causes that the main role in the forming of chemical composition of waters play the natural factors. In this light, the anthropogenic disturbance of the chemical composition of shallow groundwater in the Biały Dunajec Valley, found in the most urbanized part of Zakopane and Nowy Targ Basin, indicate the scale of their menace (J. Małecki, 1987). Białystok Upland is characterized by far lower, more uniform during the year, values of rainfall with the preponderance of the infiltration over the overland flow. The mild landforms and the existence of many levels of the aquifers influence the more slow drainage and water exchange. The high industrialization of Białystok agglomeration, lack of the sewage treatment plants and the defective sewerage system cause, that the main factor forming the chemical composition of waters (mainly shallow groundwaters) is the anthropopression. Comparing the present distribution of the concentrations of macroelements, mostly susceptible to the anthropogenic influences in both test areas

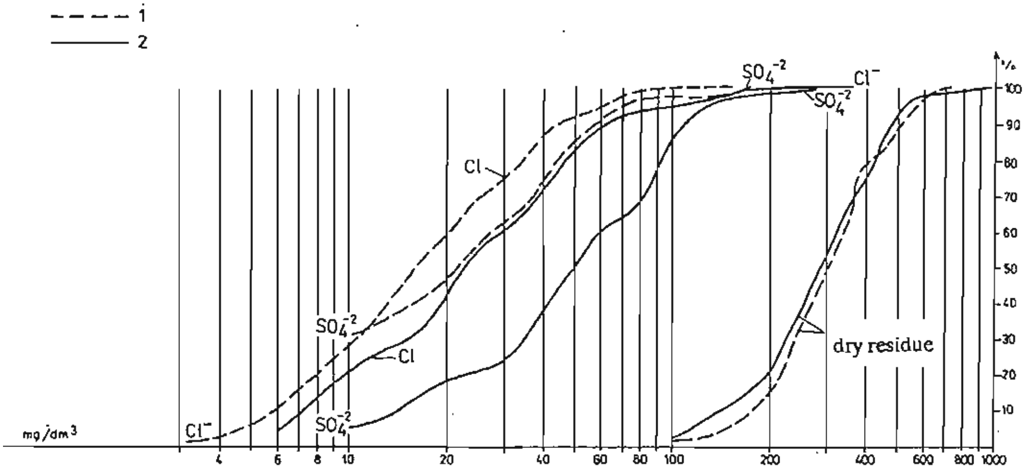

Fig. 2. Cumulative curves for the concentrations of Cl^-, SO_4^{2-} and the dry residue in the shallow groundwater of the Biały Dunajec Valley from the years 1971–1973 and 1985–1986

Values from the years: 1 — 1971–1973 (n = 44), 2 — 1985–1986 (n = 45)

Krzywe kumulacyjne stężeń Cl^-, SO_4^{2-} i suchej pozostałości w wodach gruntowych doliny Białego Dunajca z okresów 1971–1973 i 1985–1986

Wartości z lat: 1 — 1971–1973 (n = 44), 2 — 1985–1986 (n = 45)

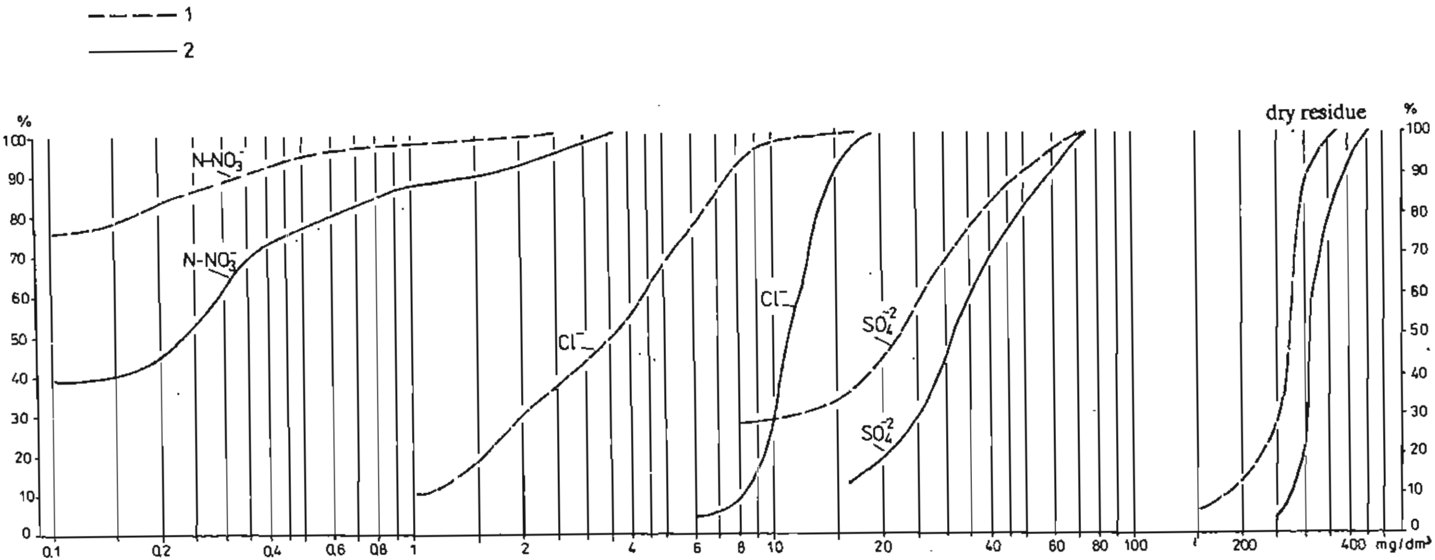

Fig. 3. Cumulative curves for the dry residue, and the concentrations of Cl^-, SO_4^{2-} and $N–NO_3^-$ in the shallow groundwater of the area of water intakes for Białystok (Wasilków — Jurowce) from the years 1971–1976 and 1982–1983

1 — archival analyses from the years 1971–1976 (n=28); 2 — author's own analyses from the years 1982–1986 (n=23)

Krzywe kumulacyjne suchej pozostałości i stężeń Cl^-, SO_4^{2-} i $N–NO_3^-$ wód gruntowych strefy ujęć dla Białegostoku (Wasilków — Jurowce) z okresów 1971–1976 i 1982–1986

1 — analizy archiwalne z lat 1971–1976 (n=28); 2 — analizy własne z lat 1982–1986 (n=23)

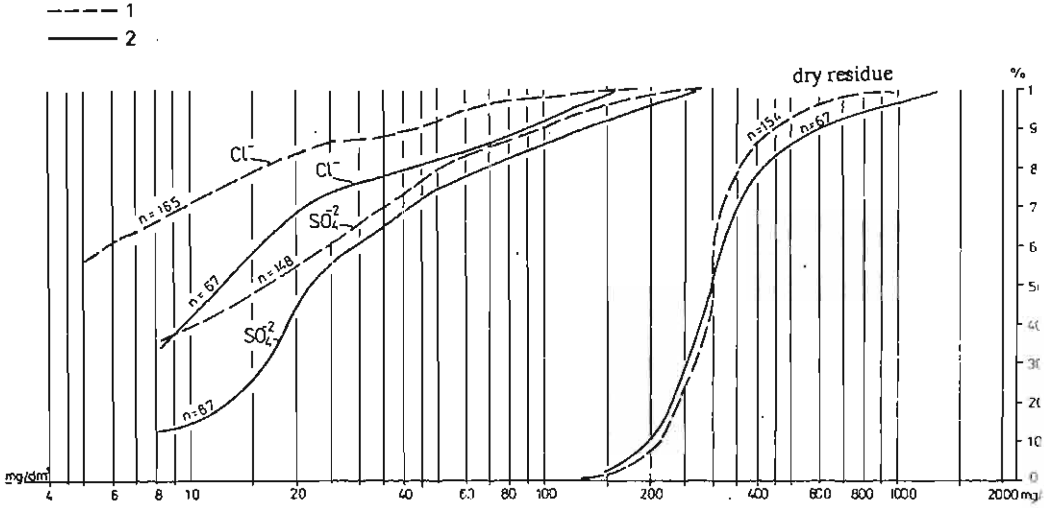

Fig. 4. Cumulative curves for the dry residue and the concentrations of Cl^- and SO_4^{2-} in the deep groundwater of the drainage basin of the Biała River and environs from the years 1971–1982 and 1982–1986

1 — archival analyses from the years 1971–1982; 2 — author's own analyses from the years 1982–1986

Krzywe kumulacyjne suchej pozostałości i stężeń Cl^- i SO_4^{2-} w wodach wgłębnych zlewni Białej i okolic z okresów 1971–1982 i 1982–1986

1 — analizy archiwalne z lat 1971–1982; 2 — analizy własne z lat 1982–1986

(Fig. 1), it is possible to observe following regularities: the concentrations of Cl^-, SO_4^{2-}, $N-NO_3^-$ and the dry residue in the shallow groundwater of the Biały Dunajec Valley achieve the intermediate values oscillating between that of shallow groundwater and of deep groundwater of the drainage basin of the Biała River. Further, the shallow groundwaters of both test areas, in spite of the essential differences in the concentrations of the elements analysed, have similar character in the statistical distribution (asymmetric with the positive obliqueness and J-shaped without the peak). Only the dry residue, beeing the sum of all elements dissolved, shows greater analogies between the shape of the cumulative curves, representing the shallow groundwater of the Biały Dunajec Valley and the deep groundwater of the drainage basin of the Biała River, showing the distributions approaching the symmetrical.

In spite of much higher degree of mineralization of the shallow groundwater of Białystok agglomeration, the coefficients of variation of this parameter in both test areas achieve the similar value: $W = 0.53$ and $W = 0.54$. It shows the great stability of mineralization in the area of the populations interpreted.

The complete chemical analysis of groundwaters of the areas tested showed, that the trace elements are the sensitive indices of pollution. The trace elements allowed to document distinctly the degree of anthropogenic transformation and the genesis of the composition of waters (J. Małecki, 1991). However, because of the lack of the archive records for the trace elements, the method given above had to be accepted, and the basic anions were used for the prognosis.

In order to document the eventual changes in the concentrations of hydrochemical elements analysed, two subpopulations of archival analyses and recent analyses were formed. Because of the need of achieving the highest possible frequencies, the collections of analyses compared have different time intervalls. In spite of this inconvenience, it is possible to state decidedly that the concentrations of the elements analysed in shallow groundwaters of both test areas (Fig. 2 and 3), just as in the deep groundwater of the test area of Białystok (Fig. 4) distinctly increased. The dry residue only, which is the resultant of the concentrations of all elements present in water, did not document so distinctly these changes. This stability of the value for dry residue in time may be explained by the great amount of influences, which leave no remainder of the opposing tendencies, and as the example by the changes in the proportions of ions with the preservation of the approximate concentrations of the sum of ions. In the shallow groundwater of the Biały Dunajec Valley, with the increase of the concentrations of sulphate and chloride ions in the second period of the investigations, smaller concentrations of the ion HCO_3^- were noted (J. Małecki, 1987).

The high concentration of the macroelements, especially in shallow groundwater, in connection with their great velocity of growth, found in the period of fifteen years (1971–1986) in both test areas create the danger of very inconvenient changes in the composition of water in the near future. Using the collections of data for the concentrations of chloride, sulphate and nitrate ions in two test periods, the evaluation of the forecast increase of the contents of the interpreted ions was made. In order to avoid the mistakes caused by the great dispersion of the collections analysed, only the values included in the limits of presently established hydrogeochemical background were taken into the computations. It was accepted, that the scale of the inconvenient changes in the composition of the groundwaters caused by the economical factors will be approaching the present scale. Because of the lack of material allowing to determine the character of the changes in the chemical composition and to approximate it through the concrete form of the non-linear function, it was supposed that the dynamics of the increase was uniform in time, accepting the linear character of changes. The author used two methods of interpretation: the average from the background range was forecast by the arithmetic computetions, and the upper limit of the background was established using the graphical method. At the basis of the average concentration in the background range y_1 corresponding to the period x_1 (the year 1971) and analogically the average concentration y_2 corresponding to the period x_2 (1986), the forecast concentration y_3 for x_3 (2000) was computed:

$$y_3 = (x_3 - x_1)\,\mathrm{tg}\alpha + y_1,$$

where

$$\mathrm{tg}\alpha = \frac{y_2 - y_1}{x_2 - x_1}$$

The achieved results of the computations, given in Table 1, because of the earlier accepted suppositions, ought to be treated as the estimated values.

Table 1

Forecast concentrations of the average from the background range and the upper boundary of hydrogeochemical background (mg/dm^3)

Period of investigation	The Biały Dunajec Valley						Drainage basin of the Biała River and environs											
	shallow groundwater						shallow groundwater						deep groundwater					
	Cl^-		SO_4^{2-}		$N\text{–}NO_3^-$		Cl^-		SO_4^{2-}		$N\text{–}NO^{3-}$		Cl^-		SO_4^{2-}		$N\text{–}NO_3^-$	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
x_1 (1971)	2–40	17.6	0–40	18.4	0–0.5	0.4	–	14.6	–	47	–	5.2	1–20	5.2	0–60	24.2	0–0.5	0.15
x_2 (1986)	2–60	24.6	0–70	33.2	0–3.0	0.96	2–132	46	0–140	64	0–20	7.0	1–20	10.5	0–60	25.4	0–1.0	0.3
x_3 (2000)	80	31.2	105	47.1	5.5	1.48	240	75.3	200	79.8	26	8.7	–	15.4	–	26.5	–	0.44

x_3 — forecast value; I — background, II — average

It results from the data, that the greatest increase of the indices analysed will happen in the shallow groundwater. The calculations above show also, how important role plays the isolation of water from the surface by the impermeable formations. In spite of the disadvantageous changes in the composition of the deep groundwater of Białystok agglomeration, the velocity of these transformations is so slow, that before achieving the concentrations overreaching the sanitary norms, the methods counteracting the degradation of waters will certainly be found.

The high increase of the forecast average of the elements of shallow groundwaters analysed in both test areas allowed for the graphical interpretation of the upper boundary of the hydrogeochemical background for the year 2000. Supposing the same characteristics of the dispersion of the population of the element interpreted, achieved from the recent collections of data, the forecast upper boundary of the hydrogeochemical background was marked out moving the cumulative curve by the computed value of the increase of the average (Fig. 5). The suppositions made allowed to accept the same shape and inclination for the cumulative curve forecast. In ought to be pointed out, that in spite of the different scale of the anthropogenic transformations of shallow groundwaters in both test areas, the dynamics of the increase of the concentrations of Cl^-, SO_4^{2-} and NO_3^- ions is at similar level. These waters succumb to the violent degradation proportionally to the degree of urbanization of the area. In the region of Białystok the forecast upper boundary of the sulphate background for the year 2000 will achieve the normative value, but in case of the nitrate nitrogen this boundary will overstep the sanitary norm more than twice.

The majority of the authors, while characterizing the chemical composition of the groundwaters, accept the average value of the concentration of the element investigated for the whole collection of data as a basic hydrogeochemical characteristics. This approach, especially in the case of strongly contaminated groundwaters, is not reasonable. The local punctual pollution, giving the extremal values of the indices analysed, cause the distinct distortion of the characteristics founded on the average values (A. Macioszczyk et al., 1989). Nevertheless, in order to represent the results in connection with the generally used methods, the autor interpreted the average concentrations forecast according to the average values from the whole collection of analyses. Using the earlier accepted foundations, the value of the average, and the year in which this value will exceed the sanitary norm, were computed (Table 2). It can be seen from the computations that, while keeping the present tendencies, the concentrations of the macroelements which are most susceptible to the anthropogenic influences in the shallow groundwater of the Biały Dunajec Valley will in next 12 years attain the concentrations typical for Białystok agglomeration. In this last region the shallow groundwater are so strongly transformed, that the average of the concentration of the nitrate ions exceeds the value of the sanitary norm. In the author's forecast, after the year 2022 the shallow groundwaters of the Biały Dunajec Valley will have to be fully excluded from the communal use because of attaining of the higher than normative concentrations of nitrate ions.

The author is conscious, that the method of forecasting of the anthropogenic transformations of the chemical composition of waters, used by him, allows to treat

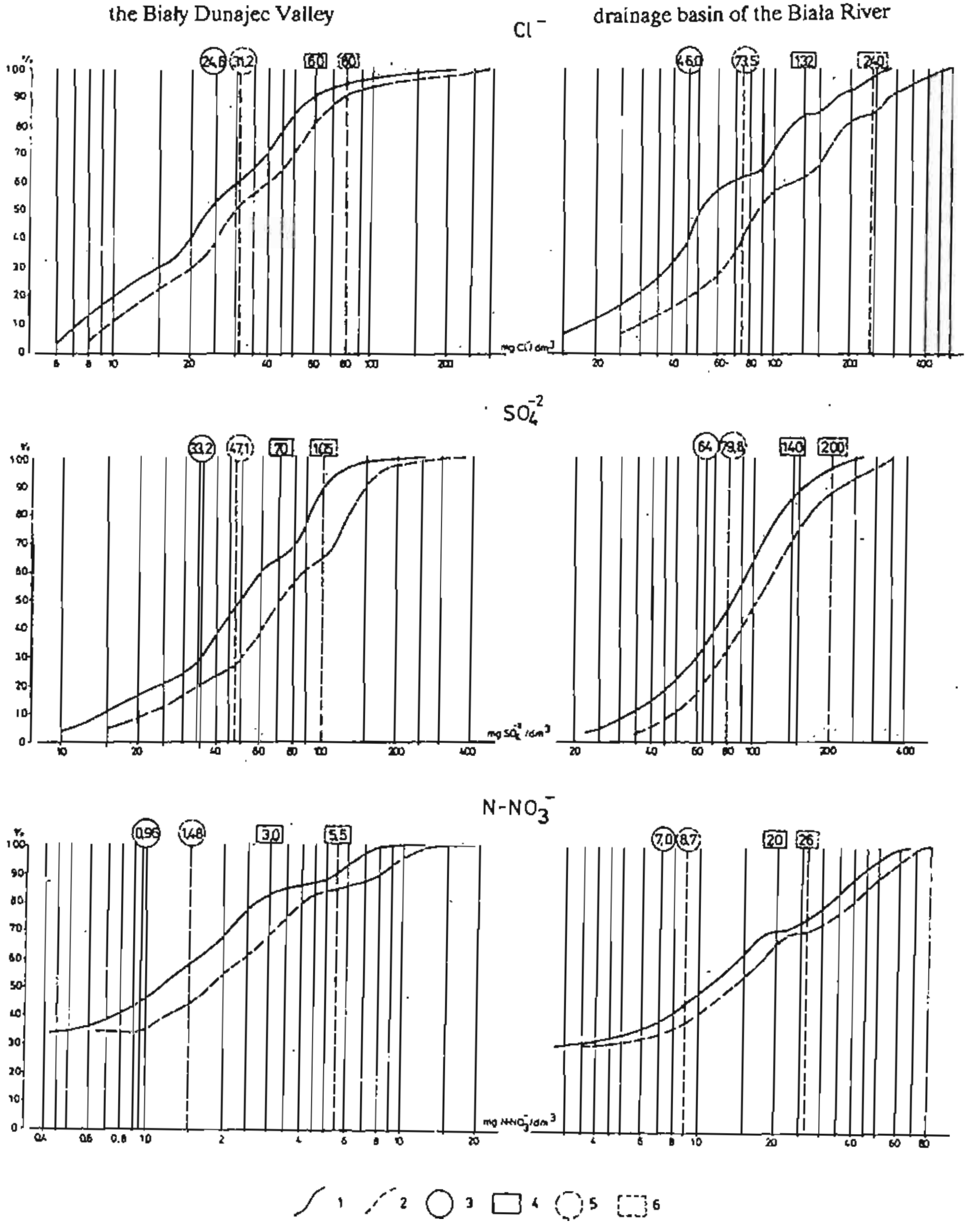
the Biały Dunajec Valley
drainage basin of the Biała River
Cl⁻
24,6
31,2
60
80
46,0
73,5
132
240
mg Cl⁻/dm³
SO₄⁻²
33,2
47,1
70
105
64
79,8
140
200
mg SO₄⁻²/dm³
N-NO₃⁻
0,96
1,48
3,0
5,5
7,0
8,7
20
26
mg N-NO₃⁻/dm³
1
2
3
4
5
6

Table 2

Forecast average values of the concentrations of Cl^-, SO_4^{2-} and $N\text{-}NO_3^-$ in the groundwaters (mg/dm^3)

Period of investigation	The Biały Dunajec Valley			Drainage basin of the Biała River and environs					
	shallow groundwater			shallow groundwater			deep groundwater		
	Cl^-	SO_4^{2-}	$N\text{-}NO_3^-$	Cl^-	SO_4^{2-}	$N\text{-}NO_3^-$	Cl^-	SO_4^{2-}	$N\text{-}NO_3^-$
x_1 (1971) y_1	22.5	28.7	0.41	23.7	60.4	–	14.4	28.4	0.24
x_2 (1986) y_2	45.1	56.5	3.21	66.3	82.2	14	26.7	46.6	0.83
x (2000) y	66.2	82.4	5.8	106.1	102.5	–	38.2	63.6	1.38
x $y_{norm.}$	2155 300	2063 200	2022 10	2068 300	2067 200	– 10	2319 300	2112 200	2219 10

the achieved results as estimated values only because of the accepted suppositions, and because of not taking into consideration of several factors influencing potentially the changes of the chemical composition of waters. The moving of the cumulative curve by the forecast average value calculated allows to interpret the estimated values of the upper boundary of the hydrochemical background, but it does not allow to observe the changes in the whole intervall of values of the forecast hydrochemical element. It must be pointed out, that the eventual mistakes of the interpretation are derived also from the mistakes in the hydrochemical materials, for instance the different quality and methodics of the determinations, too low frequency of the subpopulations compared, the nonuniform way of sampling of the area investigated and so on. In spite of these restrictions, it can be stated that the method used allowed to show in a legible way the negative tendencies of the changes in the chemical

Fig. 5. Forecast of the shapes of the cumulative curves for the concentrations of Cl^-, SO_4^{2-} and $N\text{-}NO_3^-$ in the shallow groundwater for the year 2000

1 — stężenia z 1986 r.; 2 — przewidywane stężenia w 2000 r.; 3 — średnie stężenie z zakresu tła obliczone na podstawie danych z 1986 r.; 4 — górna granica współczesnego tła hydrogeochemicznego; 5 — średnie stężenie prognozowane metodą arytmetyczną; 6 — górna granica prognozowanego tła hydrogeochemicznego

Prognozowane przebiegi krzywych kumulacyjnych stężeń Cl^-, SO_4^{2-} i $N\text{-}NO_3^-$ w wodach gruntowych dla 2000 r.

1 — concentrations for the year 1986; 2 — forecast concentrations for the year 2000; 3 — average concentrations from the range of background, computed according the data for the year 1986; 4 — upper boundary of the recent hydrogeochemical background; 5 — average concentrations forecast using the arithmetic method; 6 — upper boundary of the forecast hydrogeochemical background

composition of groundwaters and to forecast the estimated values of concentrations of the hydrochemical elements in the areas investigated.

Studium Ochrony Środowiska i
Zasobów Naturalnych
Uniwersytetu Warszawskiego
Warszawa, al. Żwirki i Wigury 93
Received: 28.08.1991

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PROGNOZA ANTROPOGENICZNYCH PRZEKSZTAŁCEŃ SKŁADU CHEMICZNEGO WÓD PODZIEMNYCH W OBSZARACH MIEJSKICH

Streszczenie

Ocenę antropogenicznych przekształceń chemizmu wód podziemnych oraz prognozę zmian przedstawiono na podstawie wyników badań przeprowadzonych w obszarach miejskich Zakopanego, Nowego Targu i Białegostoku. Bez względu na spełniane funkcje gospodarcze aglomeracji miejskich oraz stopień antropopresji najlepiej antropogeniczne zmiany jakości wód dokumentują stężenia chlorków, siarczanów i związków azotu. Sucha pozostałość interpretowana w obrębie wydzielonych lokalnych subpopulacji jest wskaźnikiem mało czułym, natomiast przydatność jej wzrasta w przypadku ocen regionalnych. Przeprowadzona prognoza antropogenicznych zmian stężeń wskazała na potencjalnie niewielkie zmiany mogące wystąpić w składzie wód wgłębnych. Wody gruntowe natomiast w obu poligonach ulegną dalszej gwałtownej degradacji. Prognozowana górna granica tła siarczanowego dla tych wód w rejonie Białegostoku w 2000 r. osiągnie wartość normatywną, a w przypadku azotu azotanowego granica ta przekroczy ponad dwukrotnie normę sanitarną.