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# Hydrogeochemical background in the region of liquidated open cast sulphur mines on the basis of geostatistical modelling and probability curves

#### Key words

Hydrogeology, hydrogeochemical background, geostatistics

#### Abstract

Geostatistical modelling procedures initially developed for the documenting of ore is finding wider application in hydrogeological studies. As a result of the possibility of interpreting sampling data as for regional variations, some authors suggest the application of geostatistical estimation when defining the spatial characteristics of the hydrogeochemical background.

This paper presents on the basis of geostatistical analysis and probability curves the actual hydrogeochemical background for groundwater of the Quaternary formation in the surrounds of ex-open cast sulphur mines in the Tarnobrzeg region. The area under study has an area of about 900 km<sup>2</sup>. The indicator chloride and sulphate ions were selected as being a threat to the quality of groundwater and surface waters in the area under inspection.

An estimation of the spatial variability of the indicator ions was achieved geostatisticaly (kriging procedure) using the Geo-EAS computer program. The kriging method estimation of the spatial distribution was preceded by choosing a semivariogram model. For both cases the best approximation of the calculated empirical semivariogram (averaged) was obtained by using a Gaussian model. The best choice of theoretical model enabled the course of relative semivariograms.

The characteristic arrangement of the content of indicatory ions with the help of the isoline map was preceded by the kriging block method estimation (as a result of the irregular arrangement of sampling points) of the content of chloride and sulphate ions in the counting blocks (2000 m by 2000 m) covering the area being examined. For each case a relative error estimation map of the content of indicator was prepared.

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# Introduction

The geostatistical modelling procedure initially developed for documentation of ores is also finding wide application in hydrogeological studies (Soares, ed., 1993; Pawlowsky-Glahn, ed., 1997). Calvete and Ramirez (1996) published their handbook in which they presented the theory and practical usage of geostatistical procedures in hydrogeology.

The possibility of basing this method of data interpretation on a relatively small population of data makes it very effective, especially when considering the high cost of laboratory analysis, sampling and the maintenance of monitoring networks. Macioszczyk and Witczak (1999) suggest applying geostatistical analysis during spatial characterization of the hydrogeochemical background. Such trials were undertaken by Bednarczyk (1999) and Zurek (1995) in the course of their work.

The aim of this study was to estimate the actual hydrogeochemical background in the groundwater of the Quaternary formation in the surrounds of liquidated open cast sulphur mines in the Tarnobrzeg region. The study area has a surface area of about 900 km<sup>2</sup>. The present study was realised at the Academy of Mining and Metallurgy under KBN contract no. 1517/T12/99/16

# 1. Methodical assumptions of geostatistical modelling

Geostatistical modelling allows the structural variability of the analysed parameter to be described and estimates the technical errors of the analysis. The basis for the geostatistical description of variability is the function formulating the relation between the average variation of the parameter value and the distance between its measurement points. This function named the variogram (semivariogram) allows the variability model of the hydrogeochemical field to be described and to estimate (in concordance with the model) the spatial distribution of the analysed parameter. For the discrete and regular measurement grid, the shape of the semivariogram is defined by the Matheron formula (1962—1963):

$$\gamma(h) = \frac{1}{2n_{h}} \sum_{i=1}^{n_{h}} (z_{\bar{h}H} - z_{i})^{2}$$

where:

 $z_i$ ,  $z_{\overline{h+i}}$  — parameter values at points distanced by the vector h,  $n_h$  — number of measurement point pairs distanced by the vector h.

For an irregular spaced measurement network, which is often the case during groundwater sampling, the calculation procedure is more complicated and has an approximate character. Measurement points are grouped within respective distance classes  $\Delta h$  and angular sectors  $\Delta \theta$  in relation to each measurement point separately (fig. 1). Following this the averaged difference squared for all pairs formed by the value of the parameter, defined at the base point  $X_o$  and at each point which is found in the region of grouped data, was calculated. The semivariogram is prepared by ascribing the average distance between point  $X_o$  and the points from the data



 Fig. 1. Empirical semivariogram calculation diagram for an irregular sampling network (Nieć, Kokesz 1988; Mucha 1994)
 1 — base point with assigned value parameter, 2 — sampling points with assigned value parameter, 3 — data counting sector

Rys. 1. Schemat obliczenia semiwariogramu empirycznego dla nieregularnej sieci opróbowań (wg Nieć, Kokesz 1988; Mucha 1994)

1— punkt bazowy z przypisaną mu wartością parametru, 2 — punkty opróbowań z przypisanymi im wartościami parametru, 3 — sektor zliczania danych

counting sector to the averaged difference squared. The entire procedure is repeated for the subsequent distance division and further, for subsequent measurement points, which then adopt the role of base points (Mucha 1994).

The semivariogram determined on the basis of measurement results from the network sampling points is called the empirical semivariogram. Its shape (most often in the form of a point graph) expresses the variability structure of the studied parameter.

Further geostatistical treatment is necessary to approximate the empirical semivariogram with the analytical function, which in subsequent steps will be treated as the geostatistical variability model. Generally there are three different types of theoretical models (Mucha 1994):

- model without asymptote (linear, de Wijs, exponential) - characterised with having a theoretically unlimited semivariogram increase,

- model with asymptote (Matheron: spherical - fig. 2 and linear, Formery, Gauss) with a limited semivariogram increase,

- random model - defines the random difference of the parameter value (lack of autocorrelation between observations).

To approximate the empirical semivariogram with the theoretical model the automatic fit method (by least square method) or the graphic fit method (by trial and error) is applied. Most geostatisticians tend to apply the second method where the best fit is analysed visually.

To ascertain or exclude the existence of variability anisotropy of the studied parameter, the directional semivariograms for different orientations of the countable partitions are compared. If the difference in the shape of the directional semivariograms is small then the variability



structure of the parameter is in practice assumed to be isotropic. For further calculations the averaged semivariogram is then used.

Defining the estimate error of the parameter value is defined by considering its variability structure expressed by using the model approximating the empirical semivariogram. Measuring the estimate error for the average value of the parameter is the standard deviation difference between the actual averaged parameter value and its estimation. In most cases the error analysis is conducted during the value parameter estimation for a point or for the averaged parameter value estimation in a computational grid block. Matheron (1962–1963) showed that the variance of the error parameter value estimation  $\sigma_{\epsilon}^2$  can be expressed with the help of the averaged values of the semivariogram in the form:

$$\sigma_{\epsilon}^{2} = 2\sum_{i=1}^{n} w_{i} \cdot \overline{\gamma}(S_{i}, A) - \sum_{i=1}^{n} \sum_{j=1}^{n} w_{i} \cdot w_{j} \cdot \overline{\gamma}(S_{i}, S_{j}) - \overline{\gamma}(A, A)$$

where:

- $\bar{\gamma}(S_{i},A)$  average value of the semivariogram for all possible intervals connecting the sampling points with the estimated area,
- $\bar{\gamma}(S_i, S_j)$  average value of the semivariogram for all possible intervals connecting sampling points,
- $\overline{\gamma}(A,A)$  average value of the semivariogram for all intervals with both ends contained within the estimated area,

w<sub>i</sub>, w<sub>j</sub> — weight coefficients ascribed to the i-th (j-th) observation; their acceptance depends on the interpolation procedure,

n — number of sampling points.

A quantifiable definition of the error estimation degree is carried out by applying one of three primary methods (Mucha 1994):

- analytical method,

- method using tables and help functions graphs,

- approximation method based on computer calculations.

The choice of method depends on the distribution of sampling points and counting blocks as well as their shape. In regional studies, with an irregular sampling points network, the method of computer calculation is preferred.

The geostatistical method for estimating the average value of the studied parameter at a point or in a counting block is the kriging procedure, supported by measurement data and the recognised structure of their variability expressed as a semivariogram. In comparison to other interpolation procedures, the kriging procedure is characterised by greater precision due to the minimization of the parameter error estimation. For each of the interpolation grid points or computational blocks the following is calculated:

- average parameter value:

$$\mathbf{z}_{k}^{\bullet} = \sum_{i=1}^{n} \mathbf{w}_{ik} \cdot \mathbf{z}_{i}$$

where:

- w<sub>ik</sub> kriging weight coefficient depends on the size of the block for which the average parameter value is estimated, the distance between the sampling points as well as the mutual auto-correlation between observations defined by the variogram model,
- $z_i$  parameter value at the i-th sampling point;

— implicit standard error estimation of the average parameter value  $\sigma_k$  with its variance defined by the equation:

$$\sigma_k^2 = \sum_{i=1}^n w_{ik} \cdot \overline{\gamma}(S_i, A) + \lambda - \overline{\gamma}(A, A)$$

where:

 $\overline{\gamma}(S_i, A) - as above,$  $\overline{\gamma}(A, A) - as above,$ n - as above, $w_{ik} - as above,$  $\lambda - Lagrange multiplier;$  — relative standard error estimation of the average parameter value  $\sigma_{kw}$ :

$$\sigma_{kw} = \frac{\sigma_k}{z_k^*}$$

In practice the relative semivariogram is assigned by dividing the value of the empirical semivariogram by the square averaged parameter value for the sampling points taken into consideration during selection. Then the attained error of the averaged parameter value estimation, based on the kriging procedure, at a point or for a block is immediately the relative standard error (Englund, Sparks 1991).

The end effects of the calculations are isoline maps of both the average parameter value and estimation error, in that of particular significance is the error interpolation map, which states the reliability of the parameter distribution map.

### 2. Distribution of indicator ion concentrations in a Quaternary aquifer formation

The characterisation of the hydrogeochemical background for the study region was conducted using the results of water chemistry analyses for the Quaternary aquifer formation gleaned from documentation materials, which included regional and local monitoring studies. Chlorides and sulphates were chosen as indicator ions representing the pollution threat to the ground and surface water quality.

The spatial variability of the indicator ions from the point identification chemical composition of the Quaternary aquifer formation waters was achieved using geostatistical methods (kriging procedure) and Geo-EAS software (Englund, Sparks 1991).

The kriging method estimation of the spatial distribution was preceded by the selection of a semivariogram model. In both cases the best approximation of the calculated empirical (averaged) semivariogram was obtained using the gaussian model (fig. 3). The best fit of theoretical model allowed the run of the relative semivariograms. The high values for parameter  $C_o$  indicate the existence of local variations for the studied indicators.

The characteristic distributions of indicator ion concentrations using isoline maps were preceded by kriging block method estimation (as a result of the nested distribution of sampling points) of the concentrations of  $Cl^-$  and  $SO_4^{2-}$  ions in the computational blocks (dimensions 2000 m by 2000 m accorrding to discretization of hydrodynamical regional model) covering the study area. In each case a relative error estimation map of the indicator concentrations was prepared. Fig. 4—7 presents the results of geostatistical calculations.

In estimating the reliability of the spatial distribution of the studied indicators, the differences resulting from conducting the analysis in successive years and in different laboratories must be remembered. Nevertheless this forms the only basis for setting the actual hydrogeochemical background.

In the case of both chlorides and sulphates the highest concentrations, exceeding  $130 \text{ mg/dm}^3$  (chlorides — fig. 4) and  $380 \text{ mg/dm}^3$  (sulphates — fig. 5), occur in the central part of the study area in the region of ex — open cast sulphur mines. The high sulphate concentrations in the



Fig. 3. Empirical semivariograms and their approximating theoretical models for the chloride (a) and sulphate (b) ion content in waters of the Quaternary formation

Rys. 3. Semiwariogramy empiryczne oraz przybliżające je modele teoretyczne dla zawartości jonów chlorkowych (a) i siarczanowych (b) w wodach piętra czwartorzędowego





Rys. 4. Mapa rozkładu stężeń jonów chlorkowych w wodach piętra czwartorzędowego na podstawie modelowania geostatystycznego (oszacowanie metodą krigingu blokowego — bloki o wymiarach 2000 m na 2000 m, dla modelu Gaussa o parametrach: C<sub>o</sub> = 0,55, C = 0,45, a = 20000 m — rys. 3a)
1 — izolinie stężeń jonu chlorkowego w mg/dm<sup>3</sup>, 2 — cieki i zbiorniki powierzchniowe, 3 — miasta i miejscowości, 4 — granice obszarów górniczych, 5 — granice wyrobisk górniczych, 6 — zewnętrzne i wcwnętrzne granice modelu hydrogeologicznego, 7 — punkty pomiarowe



Fig. 5. Distribution map of sulphate ion concentrations in waters of the Quaternary formation on the basis of geostatistical modelling (estimation by kriging block method — blocks of dimensions 2000 m by 2000 m, for the Gaussian model with parameters:  $C_0 = 0.60$ , C = 0.38, a = 17000 m — fig. 3b)

1 — isolines of sulphate ion concentrations in mg/dm<sup>3</sup>, 2 — surface reservoirs and water courses, 3 — towns and places, 4 — boundaries of mining areas, 5 — boundaries of mine workings, 6 — external and internal boundaries of hydrogeological model, 7 — sampling points

Rys. 5. Mapa rozkładu stężeń jonów siarczanowych w wodach piętra czwartorzędowego na podstawie modelowania geostatystycznego (oszacowanie metodą krigingu blokowego — bloki o wymiarach 2000 m na 2000 m, dla modelu Gaussa o parametrach: C<sub>0</sub> = 0,60, C = 0,38, a = 17000 m — rys. 3b)

1 — izolinie stężeń jonu siarczanowego w mg/dm<sup>3</sup>, 2 — cieki i zbiorniki powierzchniowe, 3 — miasta i miejscowości, 4 — granice obszarów górniczych, 5 — granice wyrobisk górniczych, 6 — zewnętrzne i wewnętrzne granice modelu hydrogeologicznego, 7 — punkty pomiarowe



Fig. 6. Relative error estimation map of chloride ion concentrations in waters of the Quaternary formation on the basis of geostatistical modeling (estimation by kriging block method — blocks of dimensions 2000 m by 2000 m, for the Gaussian model with parameters: C<sub>o</sub> = 0.55, C = 0.45, a = 20000 m — fig. 3a)
 1 — isolines of relative errors estimation of chloride ion concentrations in %, 2 — surface reservoirs and water courses, 3 — towns and places, 4 — boundaries of mining areas, 5 — boundaries of mine workings, 6 — external and internal boundaries of hydrogeological model, 7 — sampling points

Rys. 6. Mapa błędów względnych oszacowania stężeń jonów chlorkowych w wodach piętra czwartorzędowego na podstawie modelowania geostatystycznego (oszacowanie metodą krigingu blokowego — bloki o wymiarach 2000 m na 2000 m, dla modelu Gaussa o parametrach: C<sub>0</sub> = 0,55, C = 0,45, a = 20000 m — rys. 3a) 1 — izolinie błędów względnych oszacowania stężeń jonu chlorkowego w procentach, 2 — cieki i zbiorniki powierzchniowe, 3 — miasta i miejscowości,

4 — granice obszarów górniczych, 5 — granice wyrobisk górniczych, 6 — zewnętrzne i wewnętrzne granice modelu hydrogeologicznego, 7 — punkty pomiarowe



2

Fig. 7. Relative error estimation map of sulphate ion concentrations in waters of the Quaternary formation on the basis of geostatistical modeling (estimation by kriging block method — blocks of dimensions 2000 m by 2000 m, for the Gaussian model with parameters: C<sub>o</sub> = 0.60, C = 0.38, a = 17000 m — fig. 3b)
 1 — isolines of relative error estimation of sulphate ion concentrations in %, 2 — surface reservoirs and water courses, 3 — towns and places, 4 — boundaries of mining areas, 5 — boundaries of mine workings, 6 — external and internal boundaries of hydrogeological model, 7 — sampling points

Rys. 7. Mapa błędów względnych oszacowania stężeń jonów siarczanowych w wodach piętra czwartorzędowego na podstawie modelowania geostatystycznego (oszacowanie metodą krigingu blokowego — bloki o wymiarach 2000 m na 2000 m, dla modelu Gaussa o parametrach: C<sub>o</sub> = 0,60, C = 0,38, a = 17000 m — rys. 3b)
1 — izolinie błędów względnych oszacowania stężeń jonu siarczanowego w procentach, 2 — cieki i zbiorniki powierzchniowe, 3 — miasta i miejscowości,
4 — granice obszarów gómiczych, 5 — granice wyrobisk górniczych, 6 — zewnętrzne i wewnętrzne granice modelu hydrogeologicznego, 7 — punkty pomiarowe

Piaseczno area can be related to the direct contact between the Tertiary and Quaternary aquifer formation waters. The reason for the increased sulphate concentrations in the region of the Machów mine is difficult to explain. This is probably linked to anthropogenic contamination. Perek (1995) discusses the possibility of pressured Tertiary ore water contacting via conduits formed by interconnecting sand lenses in Cracow clays. The high sulphate concentrations observed in the region of the Jeziórko mine fields is related to the well exploitation of sulphur (e.g. ore water eruptions occur, leaking conduits flanking the walls of the exploitation wells exist). The increased chloride concentration is a result of the exploitation method. Saline waters from injection and solution of selected deeper sulphur bearing layers contaminate Quaternary waters upon their ascent (Malinowski, Perek 1994). In the remaining area covered by the model the average concentration of indicator ions are clearly lower and are in the region of  $20-80 \text{ mg/dm}^3$  (Cl<sup>-</sup> ion) and  $40-200 \text{ mg/dm}^3$  (SO<sup>2-</sup>/<sub>4</sub> ion).

Relative error distribution maps also have an approximating character (fig. 6 and 7). The size of the relative error parameter value estimation  $\sigma_{kw}$  of up to 40% covers close to 80% of the surface area of the study area. The relationship between the error size and the amount of points upon which the estimation is based, is clearly visible. In areas of greatest sampling point density distribution the error estimation size does not exceed 30%.

## 3. Hydrogeochemical background on the basis of probability curves

Geostatistical research allowed an isoline distribution map of the indicator ion concentrations (chlorides and sulphates) for the entire modelled study area to be produced and this demarcated the spatial distribution of the regional hydrogeochemical background (Macioszczyk 1990).

Based on regional criteria (mainly managing the densification of the sampling points) the study area was divided into regions (fig. 8) and for each of these a detailed hydrogeochemical background range was defined. Due to the small number of studied regions samples (7–26) the analysed hydrogeochemical background should be used for orientation purposes.

The interpretation of the hydrogeochemical background of the selected regions was achieved on the basis of probability curves (fig. 9). The logarithmic-normal (or approximate) distribution of the studied characteristics results in the indicator ion concentration values, projected onto Laplaces' logarithmic probability net to approach a straight line. For the limits of the hydrogeochemical background (table 1) the concentration values of the chloride and sulphate ions were assumed to correspond to 1 standard deviation ( $\overline{z} \pm Sd$ ) from the estimated average parameter value  $\overline{z}$  (50% probability), which is the probability occurrence 16% (lower background limit) and 84% (upper background limit).

The slope of the straight line on the probability plot is a graphical measure of the indicator ion concentration variability in respective selected regions. The logarithmic-normal distribution character requires the introduction of a linear scale in order to estimate the variability. By using the logarithmic ion concentration coefficient  $Y = \log (z)$ , where z is the concentration of the indicator ion in mg/dm<sup>3</sup>, for the quantity-quality estimation differentiation of the hydrogeo-chemical environment, the classification accepted by Krasny (1993) for the hydrogeological environment variability estimation, can be adopted (table 2).



Fig. 8. Sampling point distribution map of the Quaternary aquifer formation in seperate regions

1 — sampling points in the Machów region, 2 — sampling points in the Jeziórko region, 3 — sampling points in the Osiek region, 4 — sampling points in the southern part of the area, 5 — surface reservoirs and water courses, 6 — towns and places, 7 — boundaries of mining areas, 8 — boundaries of mine workings, 9 — external and internal boundaries of hydrogeological model

Rys. 8. Mapa rozmieszczenia punktów opróbowujących czwartorzędowe piętro wodonośne w wydzielonych rejonach 1 — punkty opróbowujące rejon Machowa, 2 — punkty opróbowujące rejon Jeziórka, 3 — punkty opróbowujące rejon Osieka, 4 — punkty opróbowujące południową część obszaru, 5 — cieki i zbiorniki powierzchniowe, 6 — miasta i miejscowości, 7 — granice obszarów górniczych, 8 — granice wyrobisk górniczych, 9 — zewnętrzne i wewnętrzne granice modelu hydrogeologicznego



Fig. 9. Variability of indicator ion concentrations on the probability curve in groundwater of the Quaternary aquifer formation for the selected regions

1 - the Machów region, 2 - the Jeziórko region, 3 - the Osiek region, 4 - the southern part of the study area

Rys. 9. Zmienność stężeń jonów wskaźnikowych na wykresie prawdopodobieństwa w wodach podziemnych piętra czwartorzędowego dla wybranych rejonów

1 — rejon Machowa, 2 — rejon Jeziórka, 3 — rejon Osieka, 4 — południowa część badanego obszaru

## TABLE 1

Indicator ion hydrogeochemical background in groundwater of selected regions on the basis of probability curves

TABELA 1

Tło hydrogeochemiczne jonów	wskaźnikowych w wodaci	h podziemnych v	wybranych rejonów	na podstawie wykresów
	prawdopo	odobieństwa		

Hydrogeochemical background		Regions			
		Machów region	Jeziórko region	Osiek region	Southern part of study area
Chloride ion concentration [mg/dm <sup>3</sup> ]					
Lower limit	īz − Sd	21	25	16	12
Average value	ī	65	60	21	26
Upper limit	₹+Sd	200	140	27	59
Sulphate ion concentration [mg/dm <sup>3</sup> ]					
Lower limit	$\overline{z} - Sd$	80	40	80	41
Average value	ī	230	105	96	73
Upper limit	$\overline{z} + Sd$	650	280	115	130

#### TABLE 2

Hydrogeochemical environmental differentiation depending on the standard deviation of the coefficient Y

TABELA 2

Zróżnicowanie środowiska hydrogeochemicznego w zależności od odchylenia standardowego wskaźnika Y

Standard deviation of the coefficient Y	Variability class		Type of hydrogeochemical environment
<0.2	a	very small	very weakly differentiated
0.20.4	b	small	weakly differentiated
0.4—0.6	c	average	average differentiated
0.60.8	d	large	strongly differentiated
>0.8	e	very large	very strongly differentiated

As a measure of the variability of the hydrogeochemical field the size of the standard deviation (Sd) measured on the ions concentration coefficient scale (Y) was applied. The greatest variability, corresponding to an averagely differentiated environment, is characterised by the occurrence of chloride and sulphate ions in waters of the Quaternary formation in the Jeziórko (sulphates — Sd = 0.42) and Machów region (chlorides Sd = 0.49 and sulphates — Sd = 0.46). The lowest values of the standard deviation coefficient Y (very weakly differentiated environment) for both ions occurred in the Quaternary formation of the Osiek region.

#### Conclusions

The preparation of chloride and sulphate ion concentration distribution maps as a result of geostatistical modelling indicates that the highest values are present in the central part of the studied region in the area of ex open cast sulphur mines. Their origin is of a natural character (direct contact between Quaternary and Tertiary aquifer formation waters in the surrounds of Piaseczno) as well as a possible anthropogenic character (increased sulphate concentration in the region of the Machów excavations).

Relative error maps of indicator ion concentration estimation (for close to 80% of the surface area the degree of relative error for indicator ion concentration estimation does not exceed 40%) show the acceptance of the calculated spatial distributions as actual hydrogeochemical background of sulphates and chlorides in groundwater of the Quaternary formation for the area under study.

For selected regions, on the basis of probability curves, the detailed hydrogeochemical background range along with differentiation estimation for indicator ions was defined. The greatest variation in the hydrogeochemical field was in Machów region and the least variation was in the surrounds of Osiek. These findings are supported by geostatistical research results.

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#### TŁO HYDROGEOCHEMICZNE W REJONIE LIKWIDOWANYCH KOPALŃ ODKRYWKOWYCH SIARKI NA PODSTAWIE MODELOWANIA GEOSTATYSTYCZNEGO I WYKRESÓW PRAWDOPODOBIEŃSTWA

#### Słowa kluczowe

Hydrogeologia, tło hydrogeochemiczne, geostatystyka

#### Streszczenie

Modelowanie geostatystyczne, wypracowane pierwotnie na potrzeby dokumentowania złóż, znajduje coraz szersze zastosowanie również w badaniach hydrogeologicznych. Z uwagi na możliwość interpretacji danych pochodzących z opróbowania jako zmiennych zregionalizowanych, niektórzy autorzy sugerują stosowanie oceny geostatystycznej przy określaniu przestrzennej charakterystyki tła hydrogeochemicznego.

W niniejszym artykule przedstawiono, w oparciu o analizę geostatystyczną i wykresy prawdopodobieństwa, aktualne tło hydrogeochemiczne w wodach podziemnych piętra czwartorzędowego, w otoczeniu byłych odkrywkowych kopalń siarki w rejonie Tarnobrzega. Poddany ocenie obszar badań objął powierzchnię około 900 km<sup>2</sup>. Jako jony wskaźnikowe wybrane zostały chlorki i siarczany, stanowiące zagrożenie jakości wód podziemnych i powierzchniowych na rozpatrywanym obszarze.

Oceny przestrzennej zmienności jonów wskaźnikowych dokonano metodami geostatystycznymi (procedury krigingu) z wykorzystaniem programu komputerowego Geo-EAS. Oszacowanie metodą krigingu rozkładu przestrzennego poprzedzono wyborem modelu semiwariogramu. W obydwu przypadkach najlepszą aproksymację obliczonego semiwariogramu empirycznego (uśrednionego) otrzymano za pomocą modelu Gaussa. Najlepszy dobór modelu teoretycznego umożliwiał przebieg semiwariogramów relatywnych.

Charakterystyka rozmieszczenia zawartości jonów wskaźnikowych za pomocą map izoliniowych poprzedzona została oszacowaniem metodą krigingu blokowego (z uwagi na "gniazdowy" rozkład punktów opróbowań) zawartości jonów Cl<sup>-</sup> i SO<sub>4</sub><sup>2-</sup> w blokach obliczeniowych (o wymiarach 2000 m na 2000 m) pokrywających rozpatrywany obszar. Dla każdego przypadku sporządzono również mapę błędów względnych oceny zawartości wskaźnika.