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GEOSTATISTICAL ANALYSIS OF SPACE VARIATION IN UNDERGROUND WATER VARIOUS QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA (SW PART OF POLAND)

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Abstract: This paper presents selected results of research connected with the development of a (3D) geostatistical hydrogeochemical model of the Kłodzko Drainage Basin, dedicated to the spatial variation in the different quality parameters of underground water in the water intake area (SW part of Poland). The research covers the period 2011–2012. Spatial analyses of the variation in various quality parameters, i.e., contents of: iron, manganese, ammonium ion, nitrate ion, phosphate ion, total organic carbon, pH redox potential and temperature, were carried out on the basis of the chemical determinations of the quality parameters of underground water samples taken from the wells in the water intake area. Spatial variation in the parameters was analyzed on the basis of data obtained (November 2011) from tests of water taken from 14 existing wells with a depth ranging from 9.5 to 38.0 m b.g.l. The latest data (January 2012) were obtained (gained) from 3 new piezometers, made in other locations in the relevant area. A depth of these piezometers amounts to 9–10 m.

Data derived from 14 wells (2011) and 14 wells + 3 piezometers (2012) were subjected to spatial analyses using geostatistical methods. The evaluation of basic statistics of the quality parameters, including their histograms of distributions, scatter diagrams and correlation coefficient values *r* were presented. The directional semivariogram function $\gamma(h)$ and the ordinary (block) kriging procedure were used to build the 3D geostatistical model. The geostatistical parameters of the theoretical models of directional semivariograms of the water quality parameters under study, calculated along the wells depth (taking into account the terrain elevation), were used in the ordinary (block) kriging estimation.

The obtained results of estimation, i.e., block diagrams allowed us to determine the levels of increased values of estimated averages Z^* of underground water quality parameters.

Key words: *underground water, hydrogeochemistry, quality parameters, space variation, geostatistics*

1. INTRODUCTION

The inhabitants of Kłodzko are supplied with water by a central water main drawing off water from underground intakes in Quaternary formations [2], [6]. Water is drawn off (siphoned or pumped) via dug and drilled wells located on both sides of the Kłodzko Nysa river. Generally, the depth of the wells ranges from 9.5 m to 38.0 m. The water abstraction depth (difference between the terrain elevation and the dynamic water table level) is ranged from 276–286 m a.s.l., with an average of 282.05 m a.s.l. Dynamic water table level is contained between 6.22–16.44 m b.g.l., with a mean value of 9.64 m b.g.l.

The Quaternary formations (Pleistocene deposits – the Cracow and Central Poland glaciation period, Quaternary – Holocen formations) are deposited directly on crystalline metamorphic rocks. Boreholes have shown that the oldest formations are Old Palaeozoic greenstones or their weathering waste, underlaying the Quaternary sand-gravel deposits. Greenstones were found in the deepest boreholes, maximally to 38 m below the terrain surface, but generally their roof is deposited at 20–36 m, coming closer (6–10 m) to the surface towards the edges of the formed through. The roof forms the uneven below-Quaternary surface of the Kłodzko Nysa valley. The profile of the geological structure in the Kłodzko water intake was presented in detail in the works [4], [6], [12].

The height of the Kłodzko area of underground water intake being analyzed varies in the range of 287.22–297.70 m a.s.l. with an average reaching 291.68 m a.s.l. The analyzed 22 wells are located in the terrain belonging to the Regional Board of Regional Water Management (RZGW) and Kłodzko Water Supply Systems [2], [6]. These wells were made in the years 1954–1998. The subject of spatial analyses were data coming from 14 wells which were selected from the above mentioned 22 wells, and also concerning the well collecting siphon. In the water intake area, in the region of Kłodzko the 3 piezometers (P1, P2, P3) were drilled a depth up to of 9–10 m, on the land owned by to the Agricultural Real Estate Agency ANR, RZGW and WKL (Polish names), in January 2012 [2], [6].

Kłodzko Valley is bounded on the N Valley Ścinawka and Bardzkie Mountains, on the S the Śnieżnik Mountains and Trench Upper Nysa, while on the W – the Table Mountains.

Geologically shows the structure channeled, the axis of which extends along the NW–SE. By Kłodzko Valley flows Glatzer Nysa, which together with its tributaries forms a dense hydrological network. There are 4 main catchments representing 4 mountain groups in this area. They are built of crystalline rocks, i.e., granite-gneiss, mica schists and crystalline limestones.

In the article geostatistical methods were used, previously applied in spatial modelling, estimating and forecasting of the phenomena emerging in 2D and 3D systems, including areas such as geology and mining, environment protection, energy and economy [5], and also hydrogeology [6]–[14].

The variation in different underground water quality parameters, such as iron Fe^{++}, manganese Mn^{++}, ammonium ion NH_4^+ content, nitrate anion NO_3^- content, phosphate anion PO_4^{-3} content, total organic carbon (TOC), pH redox potential and temperature °C, in the Kłodzko water intake area (the SW part of Poland) (Fig. 1) was subjected to spatial analyses, using geostatistical methods, i.e., directional semi-variogram function and an ordinary (block) kriging [1], [3], [5], [15], [16].

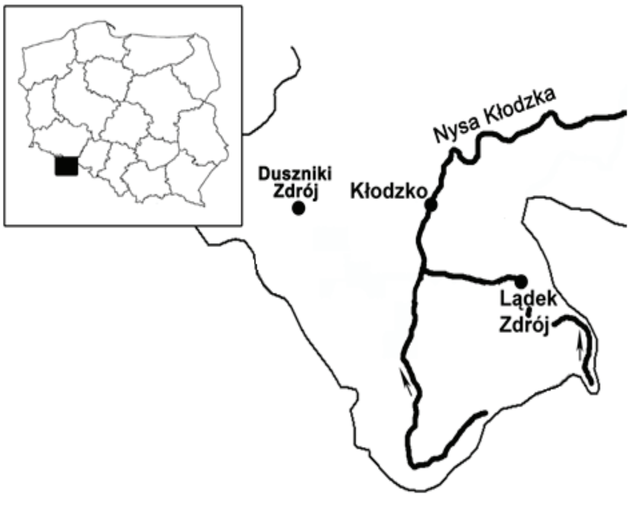

Fig. 1a. Location catchment in the Kłodzko Valley area (SW part of Poland) [2], [6], [14]

Fig. 1b. The catchment area of the river of Nysa Kłodzka (SW part of Poland); Characteristics of the balance sheet catchment area of the river Nysa Kłodzka, according to Jerzy Kondracki (J. Kondracki, *Geografia regionalna Polski*, wyd. 3 uzup., Wydaw. Naukowe PWN, Warszawa, 2002)

The selected results of modelling and estimating the Fe^{++} content and the Mn^{++} content in the underground water in 22 wells and in 3 piezometers and in the area considered for the years 1977–2012, as well as in the treated water and in the supply network water for the years 2007–2011 are reported in the author's previous papers published in scientific journals and conference proceedings [7]–[14].

Spatial and space-time analyses of quality parameters of underground water were carried out for several analytical variants, taking into account data from 22 wells, i.e., 14 wells, 3 piezometers and 14 wells + 3 piezometers located in the Kłodzko water intake area [6].

In the present study, the results of chemical analyses (covering 8 quality parameters) of underground water samples taken from 14 wells selected from the 22 wells in the Kłodzko water intake area and then from 3 new piezometers installed there and further 14 wells and 3 piezometers constituted the input for geostatistical investigations[1]. The chemical analyses were car-

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[1] These are selected results of research carried out as part of the National Centre for Research & Development grant No. N09-0036-10/2011, entitled "The technology of the biochemical remediation and storage of surface waters in underground hydrogeological structures for municipal water intakes in river valleys" funded by the Ministry of Science and Higher Education in War-

ried out on 15.11.2011 (14 wells) and 22–23.01.2012 (3 new piezometers) and presented in [6].

The geostatistical analyses[2] were carried out using databases containing the values of the quality parameters considered together with coordinates *X*, *Y* and *Z* (well depth – vertical direction of study).

The variation in the geostatistical water quality parameters was analysed downwards the depth of wells (along the *Z*-axis), using the directional semivariogram function $\gamma(h)$ and next the ordinary (block) kriging technique. The theoretical basis of the geostatistical methods can be found in the scientific works, e.g., [1], [3], [5], [15]–[17]. The analyses were preceded by the evaluation of the statistical parameters, i.e., basic statistics and the investigation of the correlation coefficients *r* between the underground water quality parameters.

Selected results of the spatial analyses performed were presented in the EGU 2016 European Geosciences Union – General Assembly, Austria Center Vienna (17–22 April 2016), at the Session HS3.2/NH1.26 "Spatio-temporal and/or geostatistical analysis of hydrological events, extremes, and related hazards" (Thursday, 21 Apr. 2016).

2. EVALUATION OF BASIC STATISTICS OF UNDERGROUND QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA

An increased concentration of Fe^{++} content in some wells occurred. All water samples contained elevated Mn^{++} content, many times exceeding the permissible concentrations in water intended for human consumption [2], [6], [12]. Water samples from the wells tested were characterized by higher content of Mn^{++} than Fe^{++} in some subareas (central part of the study area) and other subareas had to deal with the opposite situation, i.e., with higher concentrations of Fe^{++} than Mn^{++}, moreover also high values of pH potential in the same location area.

Exemplary base maps for some of the water quality parameters, namely Fe^{++} content, Mn^{++} content and pH redox potential, for the analysed configuration, the 14 wells + the 3 piezometers are shown respectively in Figs. 2a–2c.

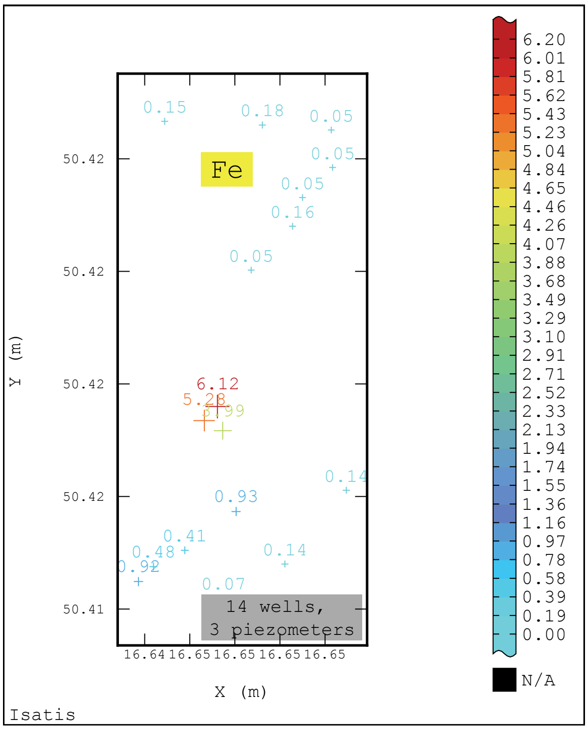

Fig. 2a. Base map of iron Fe^{++} [g Fe^{++}/m^3] content in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

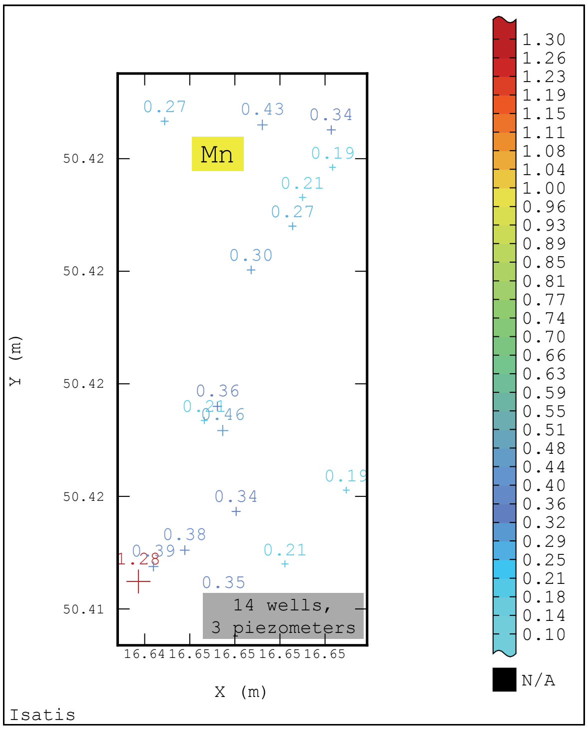

Fig. 2b. Base map of manganese Mn^{++} content [g Mn^{++}/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

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saw; project "Water" (2011–2016). Research task 3 entitled "Identification and hydrogeochemical models of the Kłodzko Drainage Area (2011–2012)" (2012) [6].

[2] Geostatistical spatial analyses were performed using the computing programmes included in the ISATIS software package – version 2015.3 (Isatis oftware User's Guide, ISATIS, Isatis version 2015, Ecole des Mines de Paris, Centre de Geostatistique, Fontainebleau, Geovariances, Avon Cedex, France, 2015).

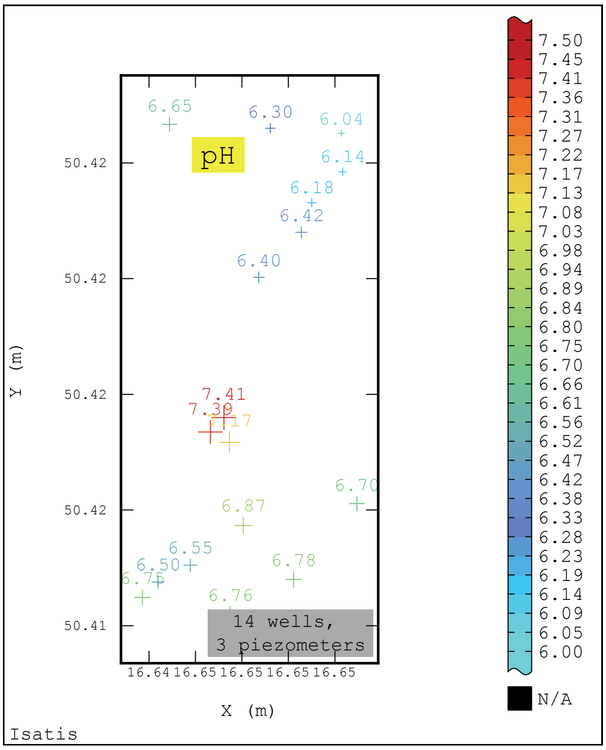

Fig. 2c. Base map of oxidation-reduction potential pH in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

The basic statistics of the underground water quality parameters, such as minima $X_{\min}$, maxima $X_{\max}$, averages $\overline{X}$, standard deviations S and variation coefficients V, were evaluated on the basis of the data for the 14 wells and then the 14 wells, including the 3 piezometers (Tables 1–2). For comparison, also the estimates of the statistical parameters of Fe^{++} content and Mn^{++} content, which were presented in earlier papers [7]–[10], [13], [14], are included in Table 1.

In the underground water coming from 14 wells located in the area of the intake Kłodzko, studied on 15.11.2011, there were found the limit permissible values by min, max values and average contents of manganese Mn^{++}, as well as the max and the average content of iron Fe^{++} and as the max NH_4^+ ion content approaches the limit value of this parameter (Table 1).

However, in the 3 piezometers made in water intake area in Kłodzko on 23.01.2012, extremely high Fe^{++} content was recorded, which refers to the min, max and average of this parameter (Table 2). These statistics of Mn^{++} content also greatly exceed the limit values of this element. There can be observed extremely higher pH of the water analyzed for 3 piezometers (Table 2), compared with the results of chemical analyses concerning the 14 wells (Table 1).

Table 1. Basic statistics of quality parameters of underground water in the intake area in the region of Kłodzko (14 wells) (year 2011)

Parameter analyzed	Sample size n	Minimal value $X_{\min}$	Maximal value $X_{\max}$	Average value $\overline{X}$	Standard deviation S	Variation coefficient V [%]
Oxidation-reduction potential pH	14	6.04	6.87	6.50	0.25	3.92
Temperature [°C] [degrees]	14	7.30	9.80	7.97	0.63	7.88
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	14	0.08	0.47	0.15	0.11	71.80
Nitrate ion NO_3^- content [g NO_3^-/m^3]	14	0.13	3.48	0.88	0.82	93.74
Phosphate ion PO_4^{-3} content [g PO_4^{-3}/m^3]	14	0.06	0.24	0.11	0.05	43.75
Total organic coal C (OWO) content C [g C/m^3]	14	0.71	1.54	1.09	0.18	16.69
Iron Fe^{++} content [g Fe^{++}/m^3]	14	0.05	0.93	0.27	0.30	109.50
Manganese Mn^{++} content [g Mn^{++}/m^3]	14	0.19	1.28	0.37	0.26	71.75

Permissible values of quality parameters of water: Ammonium ion NH_4^+ content <0.50 [g NH_4^+/m^3], Nitrate ion NO_3^- content NO_3^- [50 g NO_3^-/m^3], Phosphate ion PO_4^{-3} content – in non-normalized drinking water, Total organic coal C (OWO) content [5 g C/m^3], Iron Fe^{++} content < 0.20 [g Fe^{++}/m^3], Manganese Mn^{++} content < 0.05 [g Mn^{++}/m^3].

Table 2. Basic statistics of quality parameters of underground water in the intake area in the region of Kłodzko (3 piezometers) (year 2012)

Parameter analyzed	Sample size *n*	Minimal value X_{min}	Maximal value X_{max}	Average value $\overline{X}$	Standard deviation *S*	Variation coefficient *V* [%]
Iron Fe^{++} content [g Fe^{++}/m^3]	3	3.9900	6.1200	5.1300	0.8760	17.08
Manganese Mn^{++} content [g Mn^{++}/m^3]	3	0.2100	0.4600	0.3433	0.1027	29.92
Oxidation-reduction pH	3	7.1700	7.4100	7.3233	0.1087	1.48

Permissible values of quality parameters of water: Ammonium ion NH_4^+ content <0.500 [g NH_4^+/m^3], Nitrate ion NO_3^- content NO_3^- [50 g NO_3^-/m^3], Phosphate ion PO_4^{-3} content – in non-normalized drinking water, – Total organic coal C (OWO) content [5 g C/m^3], Iron Fe^{++} content <0.200 [g Fe^{++}/m^3], Manganese Mn^{++} content <0.050 [g Mn^{++}/m^3].

Table 3. Basic statistics of quality parameters of underground water in the intake area in the region of Kłodzko (14 wells + 3 piezometers) (years: 2011–2012)

Parameter analyzed	Sample size *n*	Minimal value X_{min}	Maximal value X_{max}	Average value $\overline{X}$	Standard deviation *S*	Variation coefficient *V* [%]
Oxidation-reduction potential pH	14+3	6.04	7.41	6.65	0.39	5.89
Iron Fe^{++} content [g Fe^{++}/m^3]	14+3	0.05	6.12	1.13	1.91	169.19
Manganese Mn^{++} content [g Mn^{++}/m^3]	14+3	0.19	1.28	0.36	0.24	67.00

Permissible values of quality parameters of water: Ammonium ion NH_4^+ content <0.500 [g NH_4^+/m^3], Nitrate ion NO_3^- content NO_3^- [50 g NO_3^-/m^3], Phosphate ion PO_4^{-3} content – in non-normalized drinking water, Total organic coal C (OWO) content [5 g C/m^3], Iron Fe^{++} content <0.200 [g Fe^{++}/m^3], Manganese Mn^{++} content <0.050 [g Mn^{++}/m^3].

The results discussed above confirm the results of the calculations of statistical parameters, carried out for a total of 14 wells and 3 piezometers (Table 3).

Generally it can be said that in the Kłodzko water intake area there are significant exceedances of the permissible value by the Fe^{++} and Mn^{++} contents in groundwater. Other water quality parameters did not exceed the admissible values.

The results of chemical analyses of water pH, determined for the 14 wells located in the study area of water intake in Kłodzko, give evidence of water acidic pH (Table 1). The results of chemical determinations of water pH performed for the 3 piezometers occurring in the central part of intake area i.e., min, max and the average indicate an alkaline pH (Table 2) (Fig. 2c), which may be related to the agricultural potential, the use of these areas. When the evaluations of basic statistics are made jointly on the basis of data from 14 wells and 3 piezometers, then the pH redox potential value of max shows alkaline pH (Table 3). The temperature °C reaches the average value approximating 8° degrees, not exceeding 9.8° (Table 1).

An analysis of the values of the coefficients *V* of the particular quality parameters for the 14 wells shows that Fe^{++} content, nitrate ion NO_3^- content, ammonium ion NH_4^+ content and Mn^{++} content vary widely (Table 1). The highest variation coefficients *V* were obtained for Fe^{++} content, nitrate ion NO_3^- content and ammonium ion NH_4^+ content, indicating a great variation in these parameters, whereas pH potential and temperature °C were found to vary only slightly. The estimates of the maximum, average and minimum Fe^{++} content and Mn^{++} content indicate significant exceedances of the allowable values (15.11.2011). The maximum ammonium ion NH_4^+ content in the water is close to the standard value. In the case of the other analysed parameters, their maxima, minima and averages do not significantly exceed the standard values (Table 1).

The evaluations based on the determination of the water coming from the 14 wells and the 3 new piezometers carried out in the time of 22.01.2012 –23.01.2012 (Table 3), corroborate the results of the calculations done using the database containing only data for the 14 wells (Table 1).

The estimates of the basic statistics of the underground water quality parameters for the Kłodzko water intake area, based on the data for the 14 wells (Table 1) and jointly the 14 wells and the 3 piezometers (Table 3), indicate an extreme variation in Fe^{++} content, a great variation in Mn^{++} content and very small variation in potential pH (Tables 1–3).

The variation coefficients V calculated on the basis of the data for solely the 3 piezometers indicate a small variation in Fe^{++} content (17%) and an average

Table 4. Averages values of the analyzed quality parameters of underground water in the intake area in Kłodzko region (2011 year)

Parameter analyzed	Sample size n	Average size $\overline{X}$ (with a well collective leverage)	Sample size n	Average size $\overline{X}$ (without a well collective leverage)
Oxidation-reduction potential pH	14	6.50	13	6.49
Temperature °C [degrees]	14	7.97	13	8.00
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	14	0.15	13	0.15
Nitrate ion NO_3^- content [g NO_3^-/m^3]	14	0.88	13	0.86
Phosphate ion PO_4^{-3} content [g PO_4^{-3}/m^3]	14	0.11	13	0.10
Total organic coal C (OWO) content [gC/m^3]	14	1.09	13	1.07
Iron Fe^{++} content [gFe^{++}/m^3]	14	0.27	13	0.28
Manganese Mn^{++} content [gMn^{++}/m^3]	14	0.37	13	0.38

Table 5. A comparison of outlier values of quality parameters in the intake area of underground water in region of Kłodzko (2011 year)

Parameter analyzed	Sample size n	Outlier value
Oxidation-reduction potential pH	14 14+3	– 7.41, 7.39
Temperature °C [degrees]	14	9.80
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	14	0.28 0.47
Nitrate ion NO_3^- content [g NO_3^-/m^3]	14	3.48
Phosphate ion PO_4^{-3} content [g PO_4^{-3}/m^3]	14	0.24
Total organic coal C(OWO) content [gC/m3]	14	0.71 1.54
Iron Fe^{++} content [gFe^{++}/m^3]	14 14+3	– 6.12, 5.28, 3.99
Manganese Mn^{++} content [gMn^{++}/m^3]	14 14+3	1.28

variation in Mn^{++} content (30%) in the underground water and a very small variation in pH (Table 2). It should be noted that the min. and max. Fe^{++} and Mn^{++} contents in water in the 3 piezometers considerably exceed the permissible values.

Table 4 contains the mean values of the particular quality parameters calculated with and without the data for the collecting siphon well taken into account, assuming a similar sample size [6]. It emerges from the comparison that the respective values of the parameters are identical or the differences between them are statistically insignificant (negligible). This also applies to the Fe^{++} content and the Mn^{++} content in the underground water (Table 4). Thus the inclusion and exclusion of the data on the water quality parameters for the collecting siphon well in/from the analysis has no effect on the estimates of the basic statistics.

For the chemical determinations (collected in the databases) of the underground water quality parameters carried out on water samples taken from the 14 wells and the 14 wells and the 3 piezometers the outliers are presented in Table 5. No outliers were found for only two water quality parameters, i.e., Fe^{++} content and pH potential, analysed in the 14 wells (Table 5).

3. DISTRIBUTION HISTOGRAMS OF UNDERGROUND WATER QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA

The histograms of several analysed variables, i.e., water quality parameters were calculated, some of them are presented below (Figs. 3–8). There can traced diversified shapes of these histograms.

The variable range is divided into iso-width classes. To each class is associated a bar whose extension (along the vertical axis) is directly proportional to the frequency of the class, that is the percentage of samples whose value belongs to the class [15]. The minimum and maximum values are also the boundaries of the graphic representation along the horizontal axis. The vertical axis is scaled on the class with the highest frequency to be displayed.

Generally, the distribution histograms of some of the analysed parameters, plotted on the basis of the data for the 14 wells or 14 wells + 3 piezometers, are strongly asymmetric (single-winged), with lower or higher frequency classes occurring (Figs. 3, 6, 7) [6]. This type of distribution characterized such parameters as Fe^{++} content (Fig. 3), ammonium ion NH_4^+ content (Fig. 6) and nitrate ion NO_3^- content (Fig. 7). The histograms of the other investigated parameters are bimodal, as e.g., manganese Mn^{++} content (Fig. 4), also phosphate anion PO_4^{-3} content (Fig. 8) or multimodal for pH redox potential (Fig. 5). Moreover, there can be observed unimodal type of distribution as in the case of temperature °C and bimodal for total organic carbon (TOC) [6].

Also the shapes of the distribution histograms for the 3 quality parameters calculated using the data for the 14 wells (year 2011), including data coming from the 3 piezometers (year 2012) located in the Kłodzko water intake area, were studied [6]. The distribution histograms of Fe^{++} content, Mn^{++} content and pH potential were calculated taking into account the data for the period 15.11.2011–23.01.2012.

The Fe^{++} content histogram is asymmetric (single-winged) and includes secondary classes of high Fe^{++} content values, but the percentage of these classes is low (Fig. 3), in contrast to the Fe^{++} content histogram calculated on the basis of data from the 14 wells [6]. The Mn^{++} content histogram is bimodal (Fig. 4) while the pH distribution histogram is multimodal (Fig. 5).

The distribution histograms of the investigated quality parameters are characterized by a smaller or greater positive skewness coefficient g_1, except for the pH potential histogram, exhibiting slight negative skewness g_1 (Tables 6, 7). The highest values of skewness g_1 were calculated for Mn^{++} content, nitrate anion NO_3^- con-tent and ammonium anion NH_4^+ content, while the lowest values of g_1 were obtained for total organic carbon (TOC). From among the analysed histograms the one showing the distribution of Mn^{++} content is the slenderest but at the same time it is characterized by the highest kurtosis coefficient g_2.

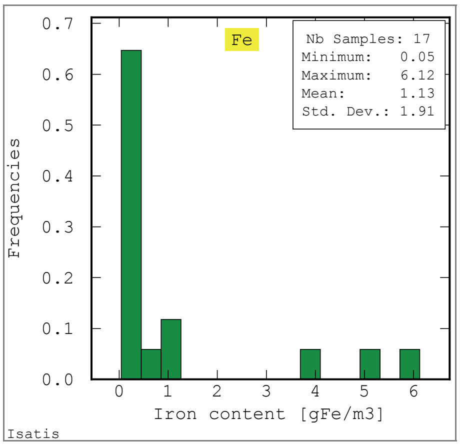

Fig. 3. Histogram of distribution of iron Fe^{++} content [g Fe^{++}/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

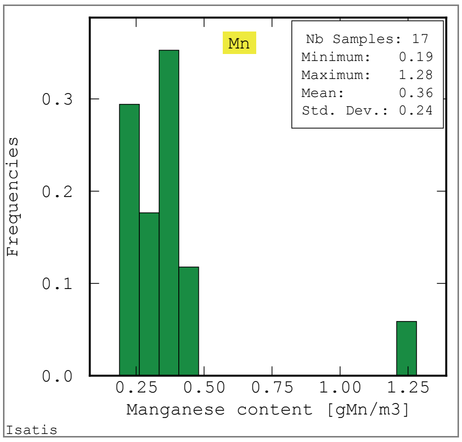

Fig. 4. Histogram of distribution of manganese Mn^{++} content [g Mn^{++}/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

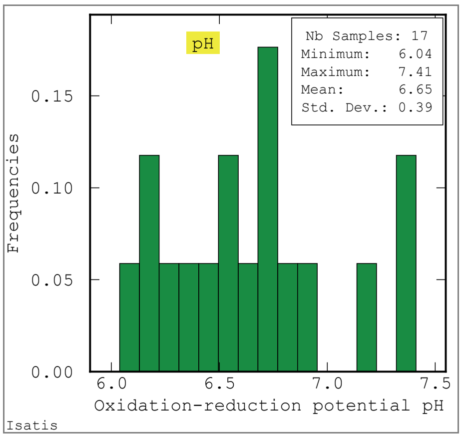

Fig. 5. Histogram of distribution of oxidation-reduction potential pH in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells + 3 piezometers

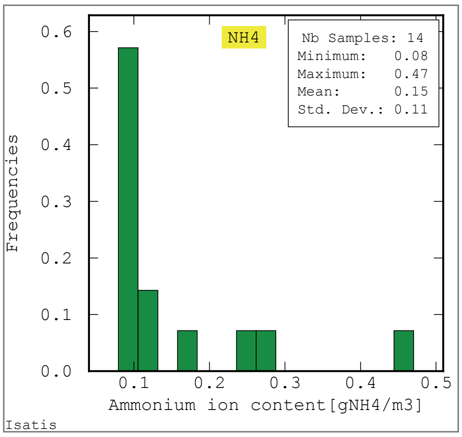

Fig. 6. Histogram of distribution of ammonium NH_4^+ ion content [g NH_4^+/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells

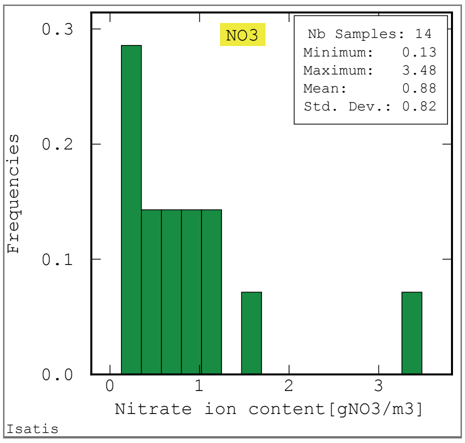

Fig. 7. Histogram of distribution of nitrate NO_3^- ion content [g NO_3^-/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells

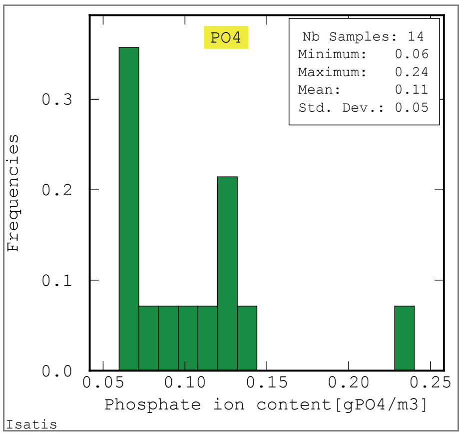

Fig. 8. Histogram of distribution of phosphate ion PO_4^- content [g PO_4^-/m^3] in underground water for water intake area of Kłodzko (SW part of Poland); data coming from 14 wells

Table 6. A comparison of values of skewness g_1 and kurtosis g_2 of distributions histograms of quality parameters in the intake area of underground water in region of Kłodzko (14 wells) (year 2011)

Parameter analyzed	Skewness g_1	Kurtosis g_2
Oxidation-reduction potential pH	–0.33	1.86
Temperature °C	1.55	5.41
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	1.94	5.84
Nitrate ion NO_3^- content [g NO_3^-/m^3]	2.13	7.37
Phosphate ion PO_4^{-3} content [g PO_4^{-3}/m^3]	1.56	5.34
Total organic coal C(OWO) content [g C/m^3]	0.39	4.33
Iron Fe^{++} content [g Fe^{++}/m^3]	1.42	3.58
Manganese Mn^{++} content [g Mn^{++}/m^3]	2.87	10.24

Table 7. A comparison of values of skewness g_1 and kurtosis g_2 of distributions histograms of quality parameters of underground water in region of Kłodzko (14 wells + 3 piezometers) (year 2012)

Parameter analyzed	Skewness g_1	Kurtosis g_2
pH	0.4697	2.4755
Iron Fe^{++} content [g Fe^{++}/m^3]	1.7619	4.4271
Manganese Mn^{++} content [g Mn^{++}/m^3]	3.0446	11.8570

4. CORRELATION BETWEEN UNDERGROUND WATER QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA

In the next stage of the investigations the correlation r between the original values of the particular underground water quality parameters, taking into account the data obtained from the chemical analyses carried out on 15.11.2011 for the 14 selected wells located in the Kłodzko water intake area, was studied [6], [10], [14].

The scatter diagram allows the plotting of a scatter plot between any pair of variables among the selected ones, that is the representation of two variables in an X–Y diagram [15]. Each sample, where both variables are defined is represented by a symbol whose coordinates correspond to the values of each variable. The two variables of the pair do not play a symmetrical role. The target variable (Y) is displayed along the vertical axis, whereas the horizontal axis corresponds to the conditioning variable (X). The linear regression Y/X was drawn in scatter plot (the regression line of the target variable Y as a linear function of the conditioning variable X).

A correlation coefficient has been determined, according to the formula expressed below

$$r = \frac{\sum_{i=1}^{1/N} w_i \left[\sum_{i=1}^{N} w_i (Z_i - m_z^w)^4 \right]}{\sigma_z^{w^4}}, \tag{1}$$

where

m_z^w – weighted arithmetic mean,

$$m_z^w = \frac{\sum_{i=1}^{N} w_i Z}{\sum_{i=1}^{N} w_i}, \tag{2}$$

$\sigma_z^{w^2}$ – weighted variance,

$$\sigma_z^{w^2} = \frac{\sum_{i=1}^{N} w_i (Z_i - m_z^w)^2}{\sum_{i=1}^{N} w_i}, \tag{3}$$

N – the total number of points,
Z_i – the value of the variable at a given point,
w_i – the weight assigned to a given point (sample),
σ_z^w – the weighted standard deviation.

The exemplary scatter diagrams of water quality parameters, shown in Figs. 9–16, with plotted regression lines, illustrate the interdependences between the values of some of the water quality parameters for which a distinct correlation became apparent and higher coefficient values r were obtained.

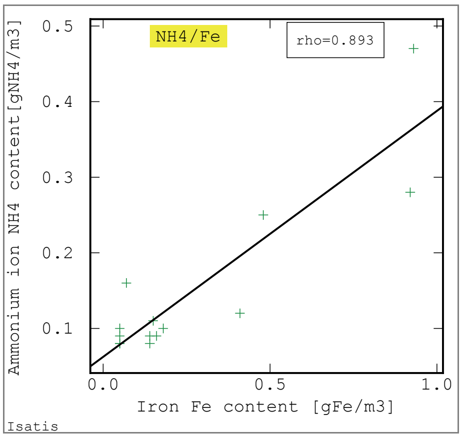

Fig. 9. Diagram correlation of Fe^{++} iron content [g Fe^{++}/m^3] and NH_4^+ ammonium ion content [g NH_4^+/m^3] in underground water, with the marked regression line Y/X in the area of water intake in the region of Kłodzko (14 wells)

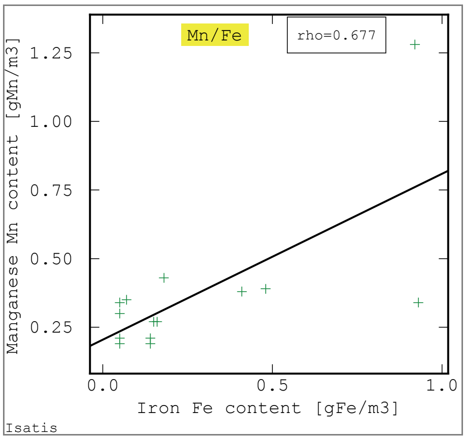

Fig. 10. Diagram correlation of iron Fe^{++} content [g Fe^{++}/m^3] and manganese Mn^{++} content [g Mn^{++}/m^3] in underground water, with the marked regression line Y/X in the area of water intake in the region of Kłodzko (14 wells)

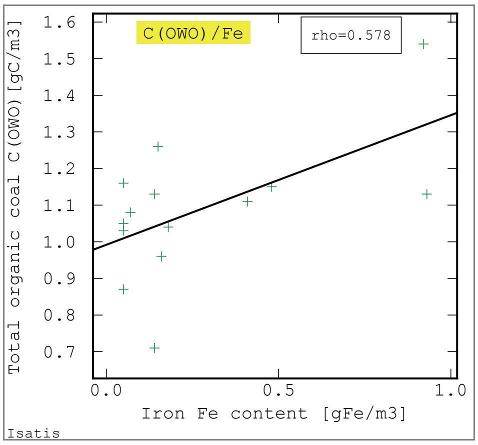

Fig. 11. Diagram correlation of iron Fe^{++} content [g Fe^{++}/m^3] and total organic coal C (OWO) [g C/m^3] in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

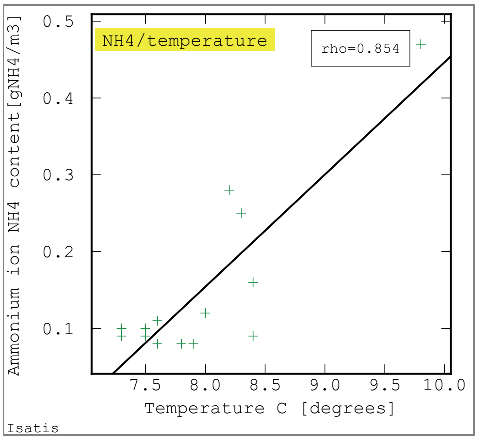

Fig. 14. Diagram correlation of temperature °C [degrees] and ammonium ion NH_4^+ content [g NH_4^+/m^3] in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

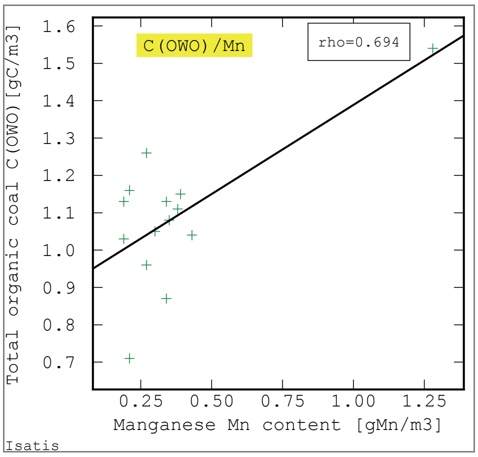

Fig. 12. Diagram correlation of manganese Mn^{++} content [g Mn^{++}/m^3] and total organic coal C (OWO) [gC/m^3] in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

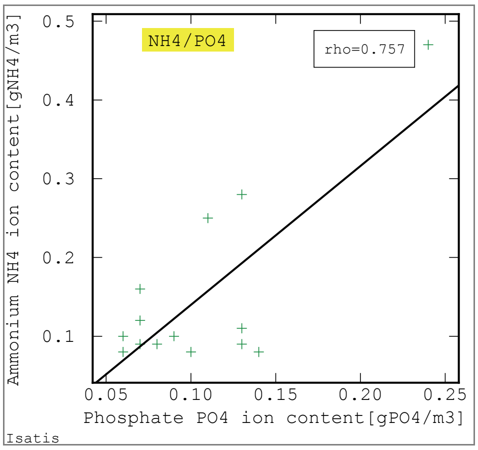

Fig. 15. Diagram correlation of phosphate ion PO_4^- content [g PO_4^-/m^3] and ammonium ion NH_4^+ content [g NH_4^+/m^3] in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

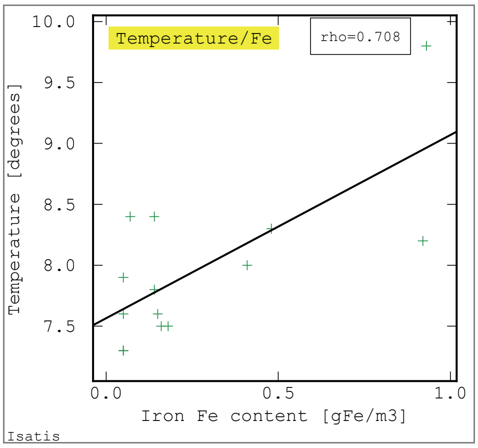

Fig. 13. Diagram correlation of iron Fe^{++} content [g Fe^{++}/m^3] and temperature °C [degrees] in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

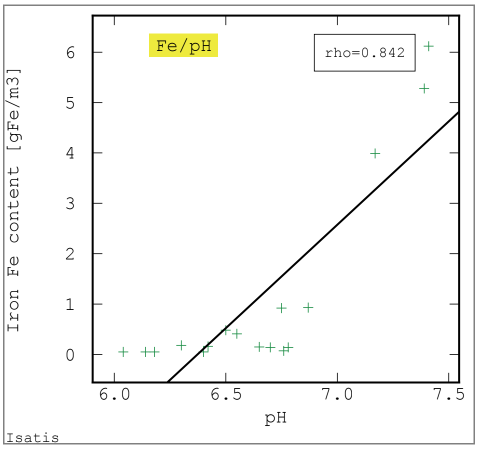

Fig. 16. Diagram correlation of iron Fe^{++} content [gFe^{++}/m^3] and potential pH in underground water, with the marked regression line *Y*/*X* in the area of water intake in the region of Kłodzko (14 wells)

The highest positive correlation coefficients *r* values were found between respectively: Fe^{++} content and ammonium ion NH_4^+ content ($r = 0.89$) (Fig. 9), Fe^{++} content and Mn^{++} content ($r = 0.68$) (Fig. 10), Fe^{++} content and total organic carbon C ($r = 0.69$) (Fig. 11), Mn^{++} content and total organic carbon C ($r = 0.69$) (Fig. 12), Fe^{++} content and temperature °C ($r = 0.71$) (Fig. 13), ion NH_4^+ content and temperature °C ($r = 0.85$) (Fig. 14), ion NH_4^+ content and phosphate PO_4^{-3} ion content ($r = 0.76$) (Fig. 15).

It can be noticed that very high correlation coefficient value *r* was obtained for the correlation between Fe^{++} content and pH for 14 wells and 3 piezometers $r = 0.842$ (Fig. 16). High values of Fe^{++} content and pH were observed in the same places in the middle of the study area, showing a character of underground water environment (Figs. 2a, 2c).

A slightly weaker, but distinct, positive correlation coefficients *r* values were found between respectively: Fe^{++} content and phosphate anion PO_4^{-3} content ($r = 0.60$), anion PO_4^{-3} content and temperature °C ($r = 0.61$), temperature °C and pH redox potential ($r = 0.64$) [6].

The observed relationships between individual quality parameters, first of all Fe^{++} content, NH_4^+ content and PO_4^{-3} content seem to prove a similar source of underground water pollution connected first of all with farming, improper fertilization of agricultural land in this area.

5. ANALYSIS OF DIRECTIONAL SEMIVARIOGRAMS OF UNDERGROUND WATER QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA

In order to estimate the spatial variation of underground water quality parameters geostatistical methods were used, such as the variogram function and then estimation technique – ordinary kriging [1], [3], [5], [15]–[17].

Empirical variogram describes correlation of the studied variables, i.e., underground water quality parameter values over an area considered (in 2D, 3D). In practice most often applied empirical measure of variability is semivariogram, determined and represented by the following formula [17]:

$$\gamma^*(h) = \frac{1}{2n_h}\sum_{i=1}^{n_h}[z(x_i + h) - z(x_i)]^2 \tag{4}$$

where $z(x_i + h)$, $z(x_i)$ – values of the regionalized variable under study at points x_i and $x_i + h$, and therefore spaced by distance h; n_h – number of pairs $(x_i, x_i + h)$ of a given regionalized variable at points spaced by distance h, used in the calculation of semivariogram function $\gamma^*(h)$; $\gamma^*(h)$ – values of semivariogram function.

Empirical variograms courses describe the nature and degree of variation of the regionalised variables under consideration, i.e., underground water quality parameter values. A graph of semivariogram function $\gamma^*(h)$ is named the empirical or experimental semivariogram.

Various analytical functions, named "geostatistical models" can be used for the approximation of empirical semivariogram courses [1], [3], [5], [15], [16]. Theoretical semivariogram is a characteristic of topoprobabilistic model which is usually referred to as a semivariogram, for short. In geostatistics, the representation of a regionalized variable by a random function is a topoprobabilistic model (any approach using the notation of probability to describe a phenomenon varying in space).

A semivariogram is a measure traditionally defined as half of the quadratic mean of the difference between two values of a measurable characteristic (the regionalized variable), separated by approximately distance *h* (vector *h*). A variogram is equal to twice the semivariogram. Half of the variogram of order 2 is the semivariogram. Variogram is sometimes used as a synonym for semivariogram.

A spherical model is a commonly applied model of variogram of the following shape: almost linear rising, increasing up to a certain distance, but stabilizing [17]. This model is determined by real (actual) range of influence of variogram *a*, a positive value of part of sill variance *C*, and nugget variance C_0

$$\begin{aligned}\gamma(h) = CSph\left(\frac{h}{a}\right) &= C\left[1.5\frac{h}{a} - 0.5\left(\frac{h}{a}\right)^3\right] + C_0 \quad \text{if} \quad h \le a \\ &= C + C_0 \quad \text{if} \quad h \ge a\end{aligned} \tag{5}$$

$$\gamma(h) = 0 \quad \text{if} \quad h = 0. \tag{6}$$

Different geostatistical parameters of fitted theoretical models such as total sill variance *C*, nugget effect C_0 and range of influence *a* have been determined.

The C_0 nugget effect is a visible discontinuity in the course of empirical semivariogram (at the starting point of the graph $\gamma(h)$ [1], [3], [5], [15]–[17]. The effect C_0 is the variation process' random factor. This effect is caused by measurement errors or micro-nest structures smaller than the sampling distance, or by both causes. At the beginning of the semivariogram graph the value of function $\gamma(h)$ is always 0, however, in the absence of C_0 effect it aims to a positive value of C_0, significantly greater than 0. C_0 effect indicates the presence of the effect on the occurrence of local variation, which means rapid fluctuation in the quality parameters under study.

The total sill variance C is the upper limit of the adopted variogram model, possible to achieve at long distances, for the large arguments transitive variogram type [1], [3], [5], [15]–[17]. The C_0 effect and partial variance C' taken together give the total sill variance C that represents the overall variation of the analyzed variable.

The range of influence a for a spherical model variogram is the distance at which the model reaches its maximum – the sill variance C [1], [3], [5], [15]–[17]. The range a means that up to this distance there is a measurable correlation with adjacent sample values.

As part of the structural analysis the courses of the directional semivariograms (D-90) of 8 underground water quality parameters were examined downwards the wells depth in the Kłodzko water intake area (Figs. 17–22). The semivariograms had been calculated on the basis of the results of the chemical analyses of water samples taken from the selected 14 wells, including the siphon well, located in the water intake area, carried out on 15.11.2011 [6]. The shapes of the directional semivariograms determined for the 14 wells selected from among the 22 wells located in the water intake area were studied [6], [10], [13], [14]. The database established for the 14 wells in November 2011 was expanded to include additionally the results of the chemical analyses of the water samples taken from the 3 piezometers in the Kłodzko water intake area carried out in January 2012 [6].

Periodic variation can be discerned in the three semivariograms: of Fe^{++} content and Mn^{++} content [6] and also ammonium ion NH_4^+ content (Fig. 20). A less distinct regularity, i.e., merely a tendency towards periodic variation, can be discerned in the semivariograms of nitrate anion NO_3^- content (Fig. 21), phosphate anion PO_4^{-3} content (Fig. 22) and total organic carbon C (TOC) [6]. A strong growing variation trend is evident in the directional semivariogram of pH potential (Fig. 19a), indicating distinct directional changes in this parameter along the depth of the wells. A similar tendency, but weaker, is visible in the directional semivariogram of temperature °C [6].

Also the directional semivariograms of three underground water quality parameters, i.e., Fe^{++} content (Fig. 17), Mn^{++} content (Fig. 18) and pH (Fig. 19b), determined on the basis of samples coming from the 14 wells including the 3 piezometers in the period of 15.11.11–23.01.12 were analysed. However, no distinct regularities in the variation of the parameters along the wells depth can be discerned in the semivariograms. A very strong short-periodic variation in function $\gamma(h)$ is observed. The most distinct changes of this kind are observed in the semivariogram of Mn^{++} content (Fig. 18).

Over the longer period (years 1977–2012) an increasing trend in the variation of Fe^{++} content and Mn^{++} content in the underground water in the Kłodzko water intake area clearly emerges. It is gentler for Fe^{++} and steeper for Mn^{++} [9], [10], [13], [14].

Generally, it is supposed that the quality of both the network water and the treated water can be the resultant of the quality of underground water in the Kłodzko water intake area, i.e., of the changes in Fe^{++} and Mn^{++} content taking place in the years 1977–2012 [11], [12]. In the analysed shorter period (2007–2011) towards 2011 a clearly downward trend in Fe^{++} content in Kłodzko water supply system, accompanied by a tendency towards periodic variation, became clearly apparent [11], [12]. The Mn^{++} content in the network water was characterized by an opposite behaviour, showing an upward trend in its variation towards 2011.

Tables 8, 9 show the values of the geostatistical parameters of the theoretical models adopted to approximate the courses of empirical semivariograms of the water quality parameters.

The directional semivariograms of the quality parameters of the water coming from the 14 wells were approximated with a single spherical model and in three cases with a composite model being a combination of respectively two spherical models and the nugget effect, a spherical model and the nugget effect or a spherical model, cubic model and the nugget effect (Table 8).

The very short influence ranges a of the semivariograms of Fe^{++} content, Mn^{++} content [6] and ammonium ion NH_4^+ content (Fig. 20) are conspicuous. Longer ranges a are observed in the semivariograms of nitrate ion NO_3^- content (Fig. 21), total organic carbon C and temperature °C (Table 8) [6]. A particularly long range of influence a is visible in the pH semivariogram (Fig. 19a). No nugget effect C_0 was found in the Fe^{++}, Mn^{++} [6], NH_4^+, NO_3^- (Figs. 20–21) and temperature °C semivariograms [6]. The C_0 effect occurred in the semivariograms of water pH (Fig. 19a), anion

PO_4^{-3} content (Fig. 22) and total organic carbon C [6], which is evidence of a marked variation in the values of these parameters along the depth of the wells.

The directional semivariograms of the three quality parameters: Fe^{++} content (Fig. 17), Mn^{++} content (Fig. 18) and pH (Fig. 19b), determined on samples from the 14 wells and the 3 piezometers over the very short test period of 15.11.11–23.01.12 were analysed. The semivariograms were approximated using a composite model consisting of the two spherical models and the nugget effect (Table 9).

There can noticed the relatively long ranges of influence *a* of semivariograms of Fe^{++} and Mn^{++} content in groundwater (Table 9), in comparison with the results obtained, taking into account the data related to the 14 wells, i.e., showing extremely short ranges *a* (Table 8). However, in these conditions resulting in very short ranges *a* of pH semivariograms (14 wells + 3 piezometers) (Table 9), compared to very long ranges *a* of pH semivariograms calculated using data deriving from 14 wells (Table 8).

Table 8. Comparison of values of geostatistical models of directional semivariograms D-90 of quality parameters of underground water in area of water intake in the region of Kłodzko; (14 wells) (year 2011)

Parameter analyzed	Nugget effect C_0 $[g/m^3]^2$	Partial sill variance C' $[g/m^3]^2$	Total sill variance C $[g/m^3]^2$	Range of influence *a* [m]	Basic model structures
Iron Fe^{++} content $[g\ Fe^{++}/m^3]$	–	–	0.13867	0.13	spherical
Manganese Mn^{++} content $[g\ Mn^{++}/m^3]$	–	–	0.10875859	0.14	spherical
Ammonium ion NH_4^+ content $[g\ NH_4^+/m^3]$	–	0.015885 0.002276	0.018161	0.13 0.13	spherical spherical
Nitrate ion NO_3^- content $[g\ NO_3^-/m^3]$	–	0.491955 0.545665	1.037620	0.54 0.74	spherical spherical
Phosphate ion content PO_4^{-3} $[g\ PO_4^{-3}/m^3]$	0.001086	0.002002	0.003088	0.35	nugget effect spherical
Total organic coal C(OWO) content C $[g\ C/m^3]$	0.025273	0.020672	0.045945	0.44	nugget effect spherical
Oxidation-reduction potential pH	0.025830	5.330109 0.212198	5.568137	189.52 227.48	nugget effect cubic, spherical
Temperature [°C] [degrees]	–	0.103170 0.468727	0.57187	0.56 1.48	spherical spherical

Table 9. Comparison of values of geostatistical models of directional semivariograms D-90 of quality parameters of underground water in area of water intake in the region of Kłodzko; (14 wells + 3 piezometers) (year 2012)

Parameter analyzed	Nugget effect C_0 $[g/m^3]^2$	Partial sill variance C' $[g/m^3]^2$	Total sill variance C $[g/m^3]^2$	Range of influence *a* [m]	Basic model structures
Iron Fe^{++} content $[g\ Fe^{++}/m^3]$	0.36400	1.6380 1.6380	3.64000	0.22 0.88	nugget effect spherical spherical
Manganese Mn^{++} content $[g\ Mn^{++}/m^3]$	0.005932 –	0.029389 0.049880	0.095201	0.43 1.14	nugget effect spherical spherical
Oxidation-reduction potential pH	0.015346	0.069059 0.062716	0.131775	0.22 0.90	nugget effect spherical spherical

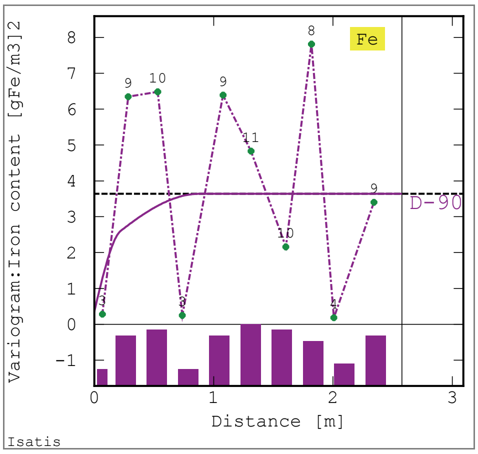

Fig. 17. Directional semivariogram (D-90) of iron Fe^{++} content [g Fe^{++}/m^3]^2 in underground water in Kłodzko intake area; 14 wells + 3 piezometers

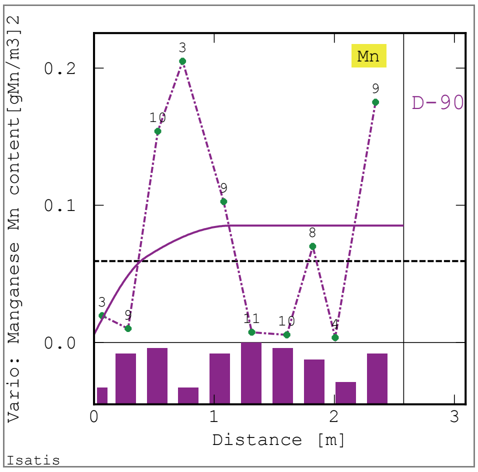

Fig. 18. Directional semivariogram (D-90) of manganese Mn content [g Mn^{++}/m^3]^2 in underground water in Kłodzko intake area; 14 wells + 3 piezometers

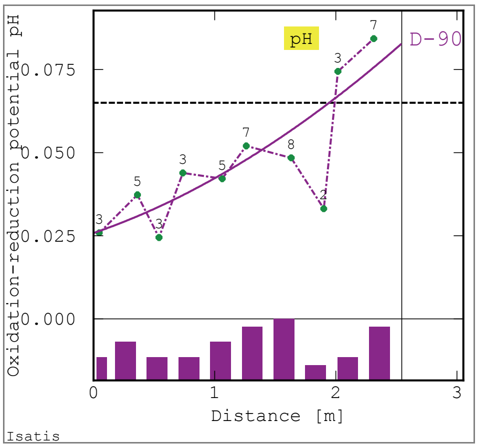

Fig. 19a. Directional semivariogram (D-90) of oxidation-reduction potential pH in underground water in Kłodzko intake area; 14 wells

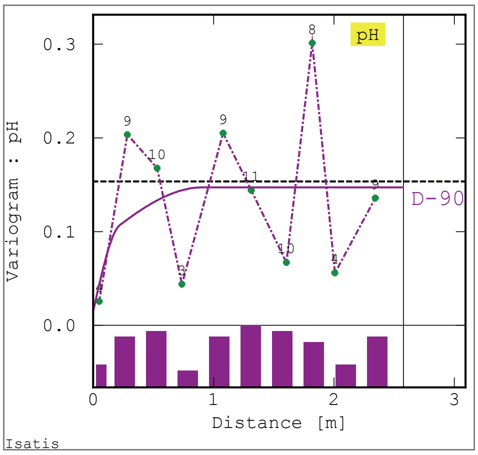

Fig. 19b. Directional semivariogram (D-90) of oxidation-reduction potential pH in underground water in Kłodzko intake area; 14 wells + 3 piezometers

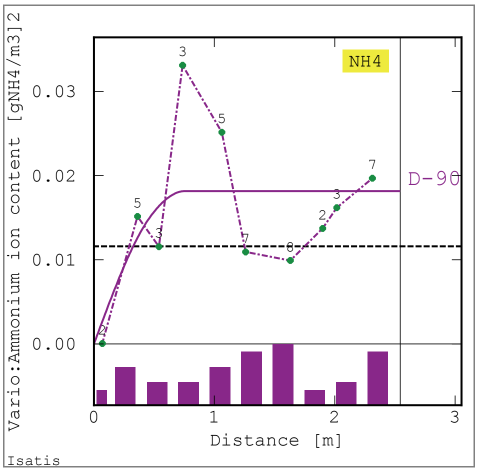

Fig. 20. Directional semivariogram (D-90) of ammonium ion NH_4^+ content [g NH_4^+/m^3]^2 in underground water in Kłodzko intake area; 14 wells

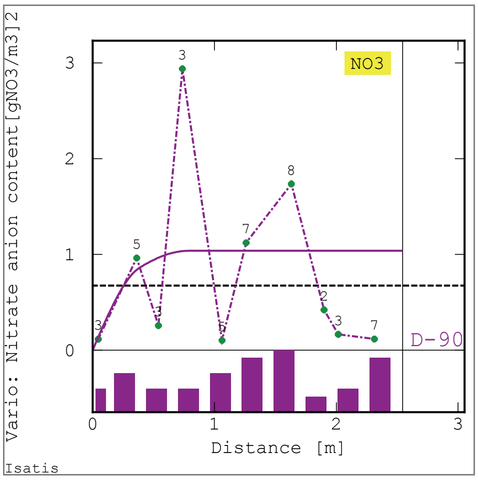

Fig. 21. Directional semivariogram (D-90) of nitrate ion NO_3^- content [g NO_3^-/m^3]^2 in underground water in Kłodzko intake area; 14 wells

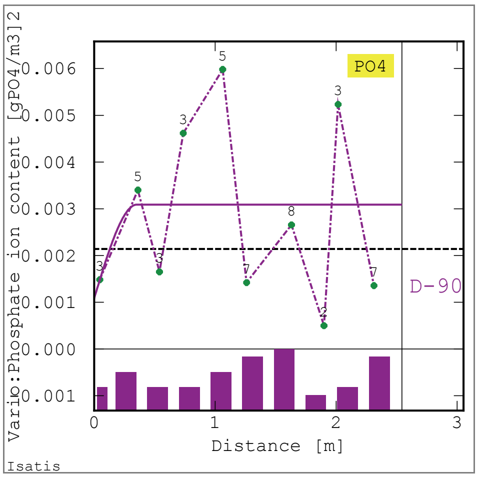

Fig. 22. Directional semivariogram (D-90) of phosphate anion PO_4^{-3} content [g $PO_4^{-3}/m^3]^2$ in underground water in Kłodzko intake area; 14 wells

6. RESULTS OF ESTIMATION OF UNDERGROUND WATER QUALITY PARAMETERS IN KŁODZKO WATER INTAKE AREA USING ORDINARY KRIGING TECHNIQUE

Estimated averages Z^* and standard deviation of estimation σ_k in the block centres of a 3D grid covering the Kłodzko water intake area were estimated using ordinary (block) kriging [1], [3], [5], [15], [16].

In the estimation procedure the ordinary kriging was used, which serves to estimate the average Z^* in a point location (ordinary point kriging) or in the centre of a block (ordinary block kriging) [1], [3], [5], [15], [16]. This technique allows us to estimate the point or block average in a node of the elementary square or rectangular grid (block centre) as the weighted average Z^*, calculated on the basis of values measured in its local neighbourhood, i.e., in the sample search area (*moving neighbourhood*), for the centre of an ellipse or circle placed in the node within the block or of all available values occurring in the study area (*unique neighbourhood*). At the same time, with each estimated average Z^* (kriging estimate), the standard (kriging) estimation deviation σ_k or kriging variance σ_k^2 is calculated.

Weighted (moving) average Z^* is estimated using the following formula

$$Z_k^* = \sum_{i=1}^{n} w_{ik} z_i \qquad (7)$$

where z_i – analysed parameter, i.e., underground quality parameter, at point i, for $i = 1, ..., n$; kriging weighting factor (weight) assigned to sample i.

With the so called kriging system of equations (estimations) [1], [3], [5], [15], [16] it becomes possible to determine the weighting factors w_{ik}, assigned to data sampled within an estimated area and in its vicinity. Then they allow us to calculate the average error, called kriging error, the variance of which is given by

$$\sigma_k^2 = \Sigma w_{ik} \bar{\gamma}(S_i, A) + \lambda - \bar{\gamma}(A, A) \qquad (8)$$

where w_{ik} – kriging weighting factor (weight) assigned to sample i; $\bar{\gamma}(A, A)$ – average of the variogram function between any two points in block A; $\bar{\gamma}(S_i, A)$ – average of the variogram function between sampled values S_i and points in block A, λ – Lagrange multiplier.

Kriging variance σ_k^2 depends on the sample positions relative to the location to be estimated, and the parameters of the adopted empirical variogram theoretical model.

Kriging calculations were made taking into account the unique “neighbourhood”. This means that all data from an analysed area are taken into account when estimating the estimated averages Z^* in each elementary block centre. The dimensions of this grid were 58 × 46 × 108 along the X-axis, the Y-axis and the Z-axis, respectively (which corresponded to the wells depth). The respective total number of grid nodes was 291104. The mesh of assumed grid amounted to the dimensions of 0.0001 m × 0.00025 m × 0.1 m.

All results of the conducted estimation of the underground water quality parameters are presented in the same Tables 10–11, in order to compare the results related to data coming from the 14 wells (year 2011) and jointly from the 14 wells and 3 piezometers (years 2011–2012), and moreover the data are connected with the period of the years of 1977–2011 [6], [10], [13].

The highest coefficients of the variation coefficients V of estimated averages Z^* were obtained for Fe^{++} content and nitrate anion NO_3^- content, followed by ammonium anion NH_4^+ content (Table 10). In the case of the other parameters, coefficients V were low, reaching the lowest values for temperature °C and pH.

The highest average values ($\bar{X}$) of averages Z^* of iron Fe^{++} content (max value of Z^* and average $\bar{X}$ of Z^*) were obtained if basic statistics had been taken in the calculations, including additional data deriving from 3 piezometers (a total of 14 wells and

Table 10. Global statistics of estimated averages Z^* of quality parameters of underground water; results of ordinary block kriging (year 2011*; years 2011–2012**; years 1977–2011***)

Parameter analyzed	Number of grid nodes n	Minimal value $X_{\min}$ [g/m^3]	Maximal value $X_{\max}$ [g/m^3]	Average value $\overline{X}$ [g/m^3]	Standard deviation S [g/m^3]	Variation coefficient V [%]
Iron Fe^{++} content [g Fe^{++}/m^3]	277200* 293480** 51840***	0.0502 0.0728 0.0500	0.9166 5.7107 0.4100	0.2573 0.8409 0.1900	0.1510 1.1265 0.1200	58.70 133.97 64.10
Manganese Mn^{++} content [g Mn^{++}/m^3]	277200* 293480** 51840***	0.1905 0.2290 0.35	1.2753 0.7883 0.61	0.3391 0.3522 0.46	0.0781 0.0788 0.09	23.05 22.37 18.75
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	277200	0.0822	04543	0.1512	0.0669	44.22
Nitrate ion NO_3^- content [g NO_3^-/m^3]	277200	0.1746	3.2647	0.8802	0.4387	49.84
Phosphate PO_4^{-3} content [g PO_4^{-3}/m^3]	277200	0.0791	0.1800	0.1052	0.0125	11.92
Organic coal C (OWO) content [g C/m^3]	277200	0.7328	1.3479	1.0883	0.0975	8.96
Temperature [°C] [degrees]	277200	7.3378	9.6972	7.9949	0.4416	5.52
pH	277200* 293480**	6.0853 6.0581	6.7652 7.3623	6.5134 6.6263	0.1976 0.2366	3.03 3.57

Iron Fe^{++}, manganese Mn^{++} (year 2011*; years 2011–2012**; years 1977–2011***); pH (year 2011, years 2011–2012)**; ammonium ion NH_4^+, nitrate ion NO_3^-, phosphate ion PO_4^{-3}, content of organic coal C(OWO), temperature °C (year 2011*).

Table 11. Global statistics of estimation standard deviation σ_k of quality parameters of underground water; results of ordinary block kriging (year 2011*; years 2011–2012**; years 1977–2011***)

Parameter analyzed	Number of grid nodes n	Minimal value $X_{\min}$ [g/m^3]	Maximal value $X_{\max}$ [g/m^3]	Average value $\overline{X}$ [g/m^3]	Standard deviation S [g/m^3]	Variation coefficient V [%]
Iron Fe^{++} content [g Fe^{++}/m^3]	277200* 293480** 51840***	0.0104 0.1930 0.0600	0.3930 2.5034 0.0700	0.2964 1.5413 0.0600	0.0935 0.7010 0.0000	31.54 45.48 6.87
Manganese Mn^{++} content [g Mn^{++}/m^3]	277200* 293480** 51840***	0.0088 0.0616 0.1300	0.3500 0.2993 0.2200	0.2464 0.2325 0.1800	0.0863 0.0740 0.0200	35.02 31.84 13.54
Ammonium ion NH_4^+ content [g NH_4^+/m^3]	277200	0.0161	0.1490	0.0940	0.0427	45.43
Nitrate ion NO_3^- content [g NO_3^-/m^3]	277200	0.1818	1.0223	0.8145	0.2574	31.61
Phosphate ion PO_4^{-3} content [g PO_4^{-3}/m^3]	277200	0.0220	0.0445	0.0405	0.0060	14.71
Organic coal C (OWO) content [gC/m^3]	277200	0.7328	1.3479	1.0883	0.0975	8.96
Temperature [°C] [degrees]	277200	0.0554	0.7222	0.3620	0.1985	54.85
pH	277200* 293480**	0.0639 0.0293	0.2429 0.4257	0.1421 0.2580	0.0537 0.1271	37.79 49.26

Iron Fe^{++}, manganese Mn^{++} (year 2011*; years 2011–2012**; years 1977–2011***); pH (year 2011*, years 2011–2012**); ammonium ion NH_4^+, nitrate ion NO_3^-, phosphate ion PO_4^{-3} content of organic coal C (OWO), temperature °C (year 2011*).

3 piezometers) (Table 10). The coefficient of variation *V* proves extremely large changes in the content of iron Fe^{++} in the area of Kłodzko.

If the basis for calculation is the data associated with a longer period of years 1977–2011, max value Z^* exceeds the permissible value for this element, while the average value Z^* ($\overline{X}$) reaches a similar level, and the coefficient *V* indicates a large variation in the iron Fe^{++} content (Table 10).

The min and max estimated values Z^* and mean averages Z^* ($\overline{X}$) of manganese Mn^{++} content exceed the permitted value of this parameter, regardless of the variant considered in the analysis (14 wells + 3 piezometers, the years 1977–2011) (Table 10). The variation coefficients *V* indicate low variation of Mn^{++} content, a slightly higher for variant of wells 14 + 3 piezometers.

In the case of potential pH higher max values of Z^* and average $\overline{X}$ were obtained on the basis of data coming from 14 wells and 3 piezometers (Table 10). The max values of Z^* for pH and coefficient *V* are a little higher for this variant of calculations.

Analysing the values of variation coefficients *V* of estimation standard deviation σ_k one can notice that the highest coefficients *V* characterize ammonium ion NH_4^+ content and temperature °C, followed by pH, Fe^{++} content, Mn^{++} content, NO_3^- and NH_4^+ anion content (Table 11).

The high values of coefficients *V* are due to, among other things, the short-term changes in the investigated parameters, evident in the vertical direction (along the wells depth), and difficulties in selecting appropriate analytical functions for the directional semivariograms.

The highest values of min and max of st. deviation of σ_k, as well as, the average value $\overline{X}$, st. deviation and coefficient of variation *V* for iron Fe^{++} content were obtained for the variant of calculation, comprising 14 wells and 3 piezometers (Table 11). The lowest values of the relevant basic statistics were obtained for data related to the years of 1977–2011.

In the case of the Mn^{++} content the lowest values of max Z^*, average $\overline{X}$ and coefficient of variation *V*, st. deviation of estimation σ_k characterize the results of the calculations conducted for data connected with the period of years 1977–2011 (Table 11).

The max value Z^*, average $\overline{X}$, st. deviation σ_k and coefficient *V* for pH are higher if the calculations have been performed taking data from 14 wells + 3 piezometers into account (Table 11).

The results of the estimation based on the data for the 14 wells (first variant of the study) and next 14 wells + 3 piezometers (second variant of the study), by means of ordinary kriging are evidence of the existence of levels of elevated values of the different underground water quality parameters (Figs. 23–28) [6], [9], [10], [13], [14].

In the first variant of the calculations the highest averages Z^* of Fe^{++} content in the underground water occur in the SW part of the water intake area and within the elevation interval of 290.55–291.45 m a.s.l. (the levels 50 and 60), while the Fe^{++} content maximum (0.70–0.90 gFe^{++}/m^3) occurs at level 50 [6]. In the second variant of the study we notice two levels with the increased averages Z^* of Fe^{++} content, lower level more distinct outlined (~ 290 m a.s.l.) and upper weaker (~ 293 m a.s.l.) (4.1–4.6 gFe^{++}/m^3 at level 60 with surrounding envelope of Fe^{++} contents to 3.6–4.1 gFe^{++}/m^3 and 3.1–3.6 gFe^{++}/m^3 (S and SW part of area) (Fig. 23).

In the first variant of the studies the maximum estimated averages Z^* of Mn^{++} content in the underground water are found mostly in the SW part of the water intake area within the elevation interval of 290.55–291.45 m a.s.l., while the Mn^{++} content maximum (0.80–0.95 gMn^{++}/m^3) is observed at level 60 [6]. In the second variant of the analysis the level with elevated averages Z^* is more distinct delineated (~ 293 m a.s.l.) (0.76–0.81 gMn^{++}/m^3 at level 60, with an envelope of Mn^{++} contents to 0.66–0.76 gMn^{++}/m^3) (central and SW part of area) (Fig. 24).

The maximum estimated averages Z^* of ammonium ion NH_4^+ content (0.35–0.43 $g\,NH_4^+/m^3$) in the underground water occur mostly in the SW part of the water intake area at the elevation of 290.55 m a.s.l., at level 50 (Fig. 25).

The maximum estimated averages Z^* of nitrate anion NO_3^- content (2.4–3.1 $g\,NO_3^-/m^3$) in the underground water occur mostly in the NW part of the water intake area within the elevation interval of 291.45–292.36 m a.s.l., at levels 60 and 70 (Fig. 26).

The maximum estimated averages Z^* of phosphate anion PO_4^{-3} content (0.15–0.18 $g\,PO_4^{-3}/m^3$) in the underground water occur mostly in the S and SW parts and less often in the E and SE parts of the water intake area at the elevation of 290.55 m a.s.l., at level 50 (Fig. 27).

The maximum estimated averages Z^* of total organic carbon C (1.25–1.35 gC/m^3) in the underground water occur mostly in the SW and S parts and less often in the E and SE parts of the water intake area at the elevation of 291.45 m a.s.l., at level 60 [6], [14]. High averages Z^* of carbon C (1.20–1.27 gC/m^3) were also found at levels 30 (288.73 m a.s.l.) and 50 (290.55 m a.s.l.).

In the first variant of the studies the maximum estimated averages Z^* of underground water pH occur in the N and S parts of the water intake area at elevations of 290.55 and 292.36 m a.s.l. – at levels 50 and 70 (6.63–6.73 and 6.53–6.63 pH) [6]. In the second variant of analysis two levels of elevated averages Z^* of pH are observed at levels 60 and 70, more outlined upper level with values ranging from: 7.2–7.3 and 6.9–7.2 (293 m a.s.l.) and lower weakly delineated (290 m a.s.l.), with values of pH 6.9–7.2 (central and SW part of area) (Fig. 28).

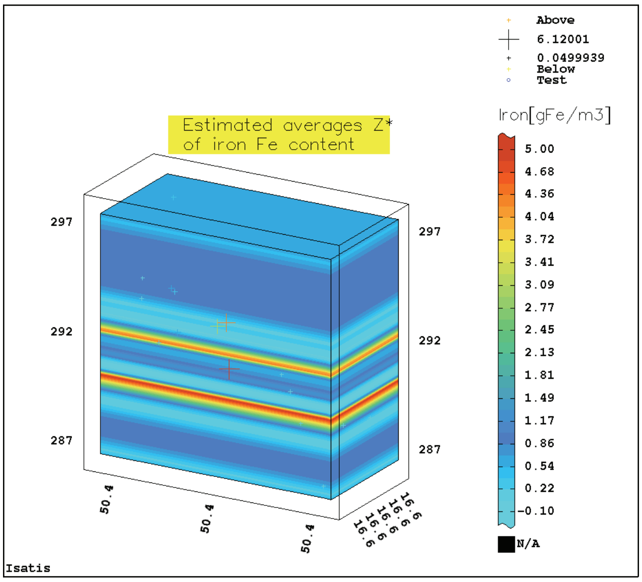

Fig. 23. Block diagram of estimated averages Z^* distribution of iron Fe^{++} content [gFe^{++}/m^3] in underground water in Kłodzko intake area; 14 wells + 3 piezometers

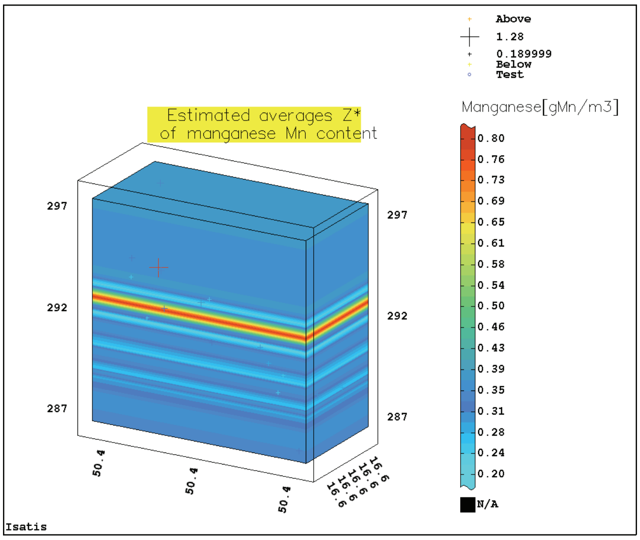

Fig. 24. Block diagram of estimated averages Z^* distribution of manganese Mn^{++} content [gMn^{++}/m^3] in underground water in Kłodzko intake area; 14 wells + 3 piezometers

The maximum averages Z^* of underground water temperature °C (9.1–9.3 °C and 9.3–9.5 °C) occur in the N, NE and S parts of the intake area at the elevation of 290.55 m a.s.l., at level 50 [6], [14].

The results of the estimation based on the data for the 14 wells and the 3 piezometers, by means of ordinary kriging, indicate the occurrence of depth levels with elevated (increased) values of the three water quality parameters, thereby extending and specifying the knowledge of their variation for Kłodzko water intake area [6], [10], [13], [14].

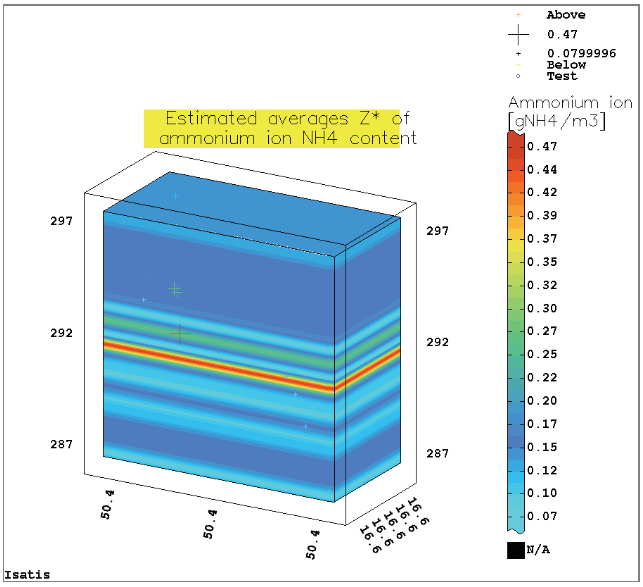

Fig. 25. Block diagram of estimated averages Z^* distribution of ammonium ion NH_4^+ content [g NH_4^+/m^3] in underground water in Kłodzko intake area; 14 wells

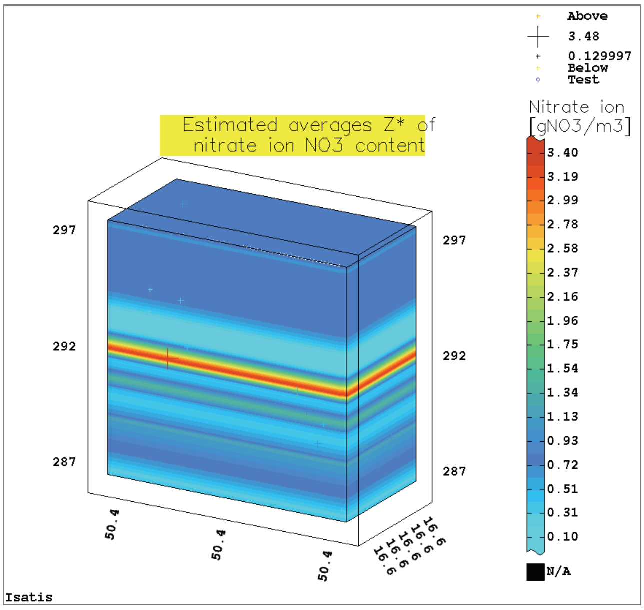

Fig. 26. Block diagram of estimated averages Z^* distribution of nitrate ion content [g NO_3^-/m^3] in underground water in Kłodzko intake area; 14 wells

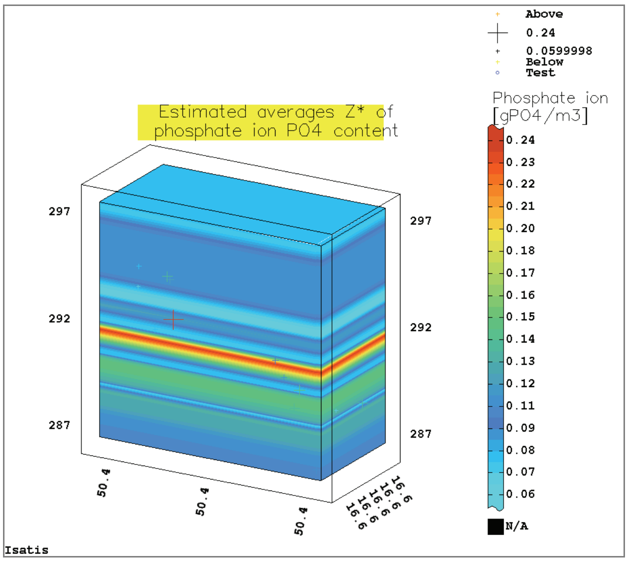

Fig. 27. Block diagram of estimated averages Z^* distribution of phosphate anion content $[\mathrm{g\,PO_4^{-3}/m^3}]$ in underground water in Kłodzko intake area; 14 wells

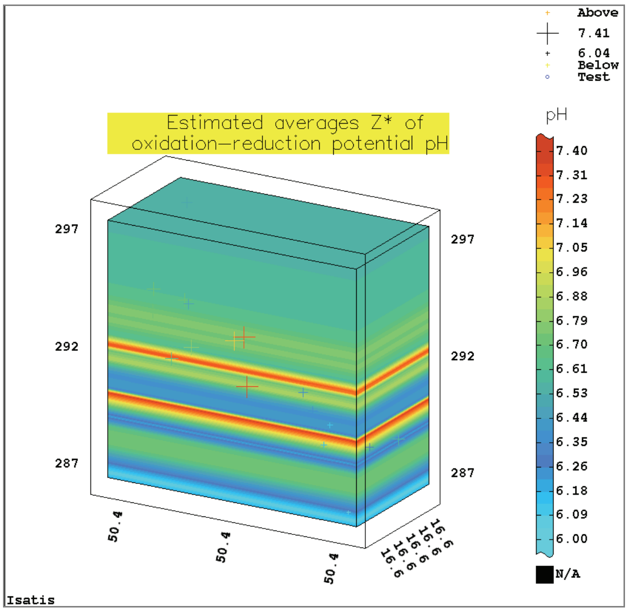

Fig. 28. Block diagram of estimated averages Z^* distribution of oxidation-reduction potential pH in underground water in Kłodzko intake area; 14 wells + 3 piezometers

7. RECAPITULATION

The levels of pollution of groundwater aquifers were determined and characterized in area around the town of Kłodzko and in the vertical profile of the wells analysed, according to the depth of the wells.

It was found that the greatest impact on groundwater quality had the kind of land development located near the wells. At the most important values of indicators of chemical composition, found in the underground water in some wells, it can be influenced the proximity of land used for agriculture and the smallest output (efficiency) of these wells.

For the region of Kłodzko under study, sources of the increased contents of Fe^{++} and Mn^{++}, in lesser degree of NH_4^+, are connected, first of all with agriculture, i.e., farming, improper fertilization of agricultural land and also caused by the factors of geochemical origin (rockbase in Kłodzko water intake area). The Fe^{++} and Mn^{++} compounds from the rocks and the soil are leached into the deep waters. The Fe^{++} may come from metallurgical wastes while the Mn^{++} may originate from the mining, smelting, ceramic and artificial fertilizer industries. The elevated content of Fe^{++} and Mn^{++} can be derived from weathering of bedrock, namely of greenstone rocks representing Old Paleozoic.

The adopted (3D) geostatistical model enables researchers and practitioners to determine averages Z^* (together with estimation standard deviation σ_k) in the individual nodes of the 3D grid covering the area of the Kłodzko Catchment and at selected points of the area. The content of the databases used to construct the 3D model enables one to estimate averages Z^*, modelling of their variation and so to analyse the quality of underground water in an area defined by researchers and users.

8. CONCLUSION

A hydrogeochemical model of the Kłodzko Catchment in the Kłodzko town underground water intake area was developed. Thanks to the 3D geostatistical model of the variation in water quality parameters it was possible to precisely characterize this variation in the whole water intake area under study consideration in the years 2011–2012, analysed for the years 1977–2012. Spatial analyses showed different behaviours of the water quality parameters and certain regularities in their variability

Mostly there can be noticed a very strong short-periodic variation in semivariogram function $\gamma(h)$ values of water quality parameters, expressed along the wells depth, rarely more distinct or even directional variation.

The essential water quality parameters are: Fe^{++} content, Mn^{++} content, nitrate anion NO_3^- content and ammonium anion NH_4^+ content. These parameters should be continuously monitored out of concern for the health of the local population (of inhabitants, animals and plants).

Based on the estimation carried out using ordinary kriging and data for the 14 wells and for the 14 wells and the 3 piezometers it was possible to identify levels with elevated water quality parameters. The maximum averages Z^* of the parameters would be found mostly at levels 50 and 60 and less often at levels 60 and 70, within the terrain elevation range of 290.55–292.36 m a.s.l., mostly in the SW part and less often in the N, NW and NE parts of the Kłodzko water intake area.

Owing to the enrichment of the databases with the results of the chemical determinations of Fe^{++}, Mn^{++} and pH carried out for the 3 piezometers, it became possible to obtain a more accurate picture of the concentration of the elements (14 wells + 3 piezometers) and so to verify the results obtained previously only on the basis of the data for the 14 wells, chosen from the 22 wells.

The results of the spatial analyses carried out for the Kłodzko water intake area in the years 2011–2012 add to the previous picture of the variation in the water quality parameters, related to years 1977–1999.

The results of the geostatistical studies can well be used in further spatial analyses to describe the state of water quality.

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