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Space-Temporal Variation in Underground Water Some Quality Parameters in Klodzko Water Intake Area Using Statistical and Geostatistical Methods (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 Klodzko Drainage Basin, dedicated to the spatial and time variation in the selected quality parameters of underground water in the Klodzko water intake area (SW part of Poland) [1-6]. The research covers the period 1977-2012. Spatial analyses of the variation in different quality parameters, between others, Fe [gFe/m^3], Mn [gMn/m^3], ammonium ion [gNH_4^+/m^3] contents and oxidation capacity [gO_2/m^3], 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 [2-4]. Spatial and time variation in the parameters was analyzed on the basis of archival data (period 1977-1999) for 22 (pump and siphon) wells, later data obtained (November 2011) from tests of water taken from 14 existing wells and the latest data (January 2012) acquired from 3 new piezometers, which were made in other locations in the relevant area. Thematic databases, containing original data on coordinates X, Y (latitude, longitude) and Z (terrain elevation and time–years) and on regionalized variables, i.e. the underground water quality parameters in the Klodzko water intake area determined for different analytical configurations (22 wells, 14 wells, 14 wells + 3 piezometers), were created [2]. Both archival data (acquired in the years 1977-1999) and the latest data (collected in 2011-2012) were analyzed. These data were subjected to spatial analyses [2-6] using statistical and geostatistical methods [7-12]. The evaluation of basic statistics of the investigated quality parameters, including their histograms of distributions, scatter diagrams between these parameters and also correlation coefficients r, were presented in this article. The directional semivariogram function 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 studied water quality parameters, calculated along the time interval and the well depth (taking into account the terrain elevation), were used in the ordinary (block) kriging estimation. The obtained results of estimation, allowed to determine the levels of increased values Z* of studied underground water quality parameters [2, 4-6]. Generally, the behaviour of the underground water quality parameters has been found to vary in space and time. Thanks to the spatial analyses of the variation in the quality parameters in the Klodzko underground water intake area some regularities (trends) in the variation in water quality have been identified.

Key words: Underground water, quality parameters, space-time variation, geo-statistics, directional semivariogram, ordinary kriging, hydrogeochemical model (3D).

1. Introduction

A 3D hydrogeochemical model of the variation in water quality parameters in the Klodzko Quaternary ground water intake area near Klodzko (the Klodzko Neisse and Bystrzyca Dusznicka drainage area), which includes the terrain topography, is presented[1].

Geostatistical methods, i.e. the directional

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semivariogram function and estimation techniques: ordinary (block) kriging were used to build the 3D hydrogeochemical model [2-6]. In order to present a general background for the variation in the quality parameters the quick (inverse distance squared) interpolation technique was used in the grant work [2].

The results of geostatistical studies of Fe iron content and Mn content space-temporal variation in a treated water in Klodzko town area and in Klodzko water supply system were presented at the EUROPEAN GEOSCIENCES UNION EGU General Assembly in Vienna, Austria, in April 12-17, 2015 [13] and in the article published in Ref. [14].

Geostatistics is the primary (top) solution when it comes to modeling spatial data in an accurate and intelligent way, guaranteeing precision and reliability in results [7-12]. Geostatistics has been applied, among others, in hydrogeology, geology of mineral deposits, applied geology, environmental geology, mining geology, mining, environmental studies, agriculture, geochemistry, epidemiology, oceanography, meteorology and forestry.

Geostatistics in hydrogeology is used for the modeling of the water-bearing reservoir (i.e., the permeability, porosity), the modeling the geometry and hydraulic layer (disposable) height and the estimating of water pollution, together with its uncertainty [11].

Model of permeability is connected with:

- estimating the data in order to insure the quality of the data;
- optimization sampling strategies and costs of the study;
- multiple use of heterogeneous data sources;
- obtain an accurate and reliable mapping;
- quantification and risk assessment;
- automatic update of communication data.

The inhabitants of Klodzko are supplied with water by a central water main drawing off water from underground intakes in Quaternary formations [1, 3, 15, 16]. Water is drawn off (siphoned or pumped) via dug and drilled wells located on both sides of the Klodzko Neisse river. Generally, the depth of the wells ranges from 9.5 m to 38.0 m. The Quaternary formations are deposited directly on crystalline metamorphic rocks. These are Pleistocene deposits dating back to the Cracow and Central Poland glaciation period, consisting of fluvioglacial accumulation sands and gravels and river accumulation gravels and sands forming well-preserved sand-gravel terraces, boulder clays, varved clays and loess-like clays. The younger Quaternary (Holocen) formations, i.e. silts, sands and gravels, are deposited in the river valleys and in streams.

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. This means that the roof forms the uneven below-Quaternary surface of the Klodzko Neisse valley.

In the N part of the water-bearing area the permeable layer floor is situated at a depth of 18.5-21.5 m b.g.l. The layer is made up of pebbles, gravels and sands. Whereas in the S part of this area the poorly permeable layer roof (Old Palaeozoic greenstone weathering waste) lies at a depth of 34.5-38 m b.g.l. The aquifer is made up of sands with an admixture of river accumulation gravels and pebbles. The hydrogeochemical characteristics of environments of river valleys were presented in the work [15, 16].

In this article the subject of the spatial analyses[2] was the variation evaluation (in the horizontal and vertical extents and in time) in the values of some water quality parameters, i.e. iron Fe content, manganese Mn content, ammonium ion content NH_4^+ and oxidation capacity in the area of ground water intakes near the town of Klodzko.

[2] The geostatistical studies were conducted using statistical software package ISATIS (the Isatis version 2015) made by Geovariances Firm, Avon Cedex—Fontainebleau, France.

2. Subject and Range of the Studies

The input for the geostatistical studies were the results of chemical analyses of underground water samples (including water quality parameters) carried out for the wells in the water intake area in different periods of time, and moreover heavy metal content determinations for the town of Klodzko (Fig. 1) [2-4].

The water quality data included: archival data acquired in the 1970s, data acquired in the period 1977-1999 and recent data collected on 15.11.2011 and 22-23.01.2012. Various thematic databases, containing values of coordinates X, Y (latitude and longitude) and Z (terrain elevation, and time–years) and regionalized variables, i.e. the topographic parameter and hydrogeological and underground water quality parameters, were created. Spatial and space-time analyses were carried out for several analytical variants, taking into account data from 22 wells, 14 wells, 14 wells + 3 piezometers and from 3 piezometers in the Klodzko water intake area, using the computing programmes included in the ISATIS software package.

First data from 22 (pump and siphon) wells built in the years 1954-1998 in the Klodzko water intake area were analyzed. Fourteen wells plus a collector siphon well (15.11.2011) were selected for further analyses aimed at determining the current underground water condition. At a later date (22-23.01.2012) 3 new piezometers were made in other locations, in the water intake area whereby the existing databases of boreholes (wells) and so the set of chemical determination results could be expanded.

The variation in the values of the topographic parameter (terrain elevation), hydrogeological parameters (water abstraction level Z with and without the landform features and the water table depth taken into account) and various water quality parameters (in space and time) was studied on the basis of the data coming from 22, 14 and 14 wells and 3 piezometers [2]. Also the variation in the heavy metal contents in water coming from the 3 piezometers was investigated.

Initially, data coming from chemical determinations carried out for the 22 wells with terrain elevations in a range of 287.22-297.70 m a.s.l. were analyzed.

Spatial analyses of the variation in:

- the topographic parameter (terrain elevation m a.s.l, min. = 287.22 m a.s.l., max. = 297.70 m a.s.l., average = 291.68 m a.s.l.);
- hydrogeological parameters: water abstraction level Z (m a.s.l)—the dynamic water table (min. = 276 m a.s.l., max. = 286 m a.s.l., average = 282.05 m a.s.l.) and the depth of occurrence of the underground water table (m b.g.l.) (min. = 6.22 m b.g.l., max. = 16.44 m b.g.l., average = 9.64 m b.g.l.);
- water quality parameters: Fe content [gFe/m^3], Mn content [gMn/m^3], NH_4^+ (ammonium ion) content [gNH_4^+/m^3] and oxidation capacity [gO_2/m^3];
- within the underground water intake area were carried out [2].

Then the data on the water samples taken from only the 14 wells, and also from the collector siphon well located in the Klodzko water intake area, were studied. Spatial analyses of the selected underground water quality parameters were carried out, among others: Fe content [gFe/m^3], Mn content [gMn/m^3] and ammonium ion content [gNH_4^+/m^3] [2].

Then chemical analyses of underground water samples taken from the three piezometers (P1, P2, P3) with a depth of 9-10 m were performed whereby the set of the existing test results was expanded [2], two above mentioned parameters were, such as: manganese Mn content < 0.05 [g/m^3], total iron Fe content < 0.20 [g/m^3] and added also heavy metals contents: zinc Zn [g/m^3], copper Cu—2.00 [g/m^3], total chromium Cr—0.05 [g/m^3], cadmium Cd—0.005 [g/m^3] and lead Pb—0.025 [g/m^3].

The data coming from both the 3 piezometers and the 14 holes (14 wells + 3 piezometers) (water determinations for the 3 piezometers located in the Klodzko intake area (Fig. 1) were added to the database for the 14 wells) were subjected to analysis [2].

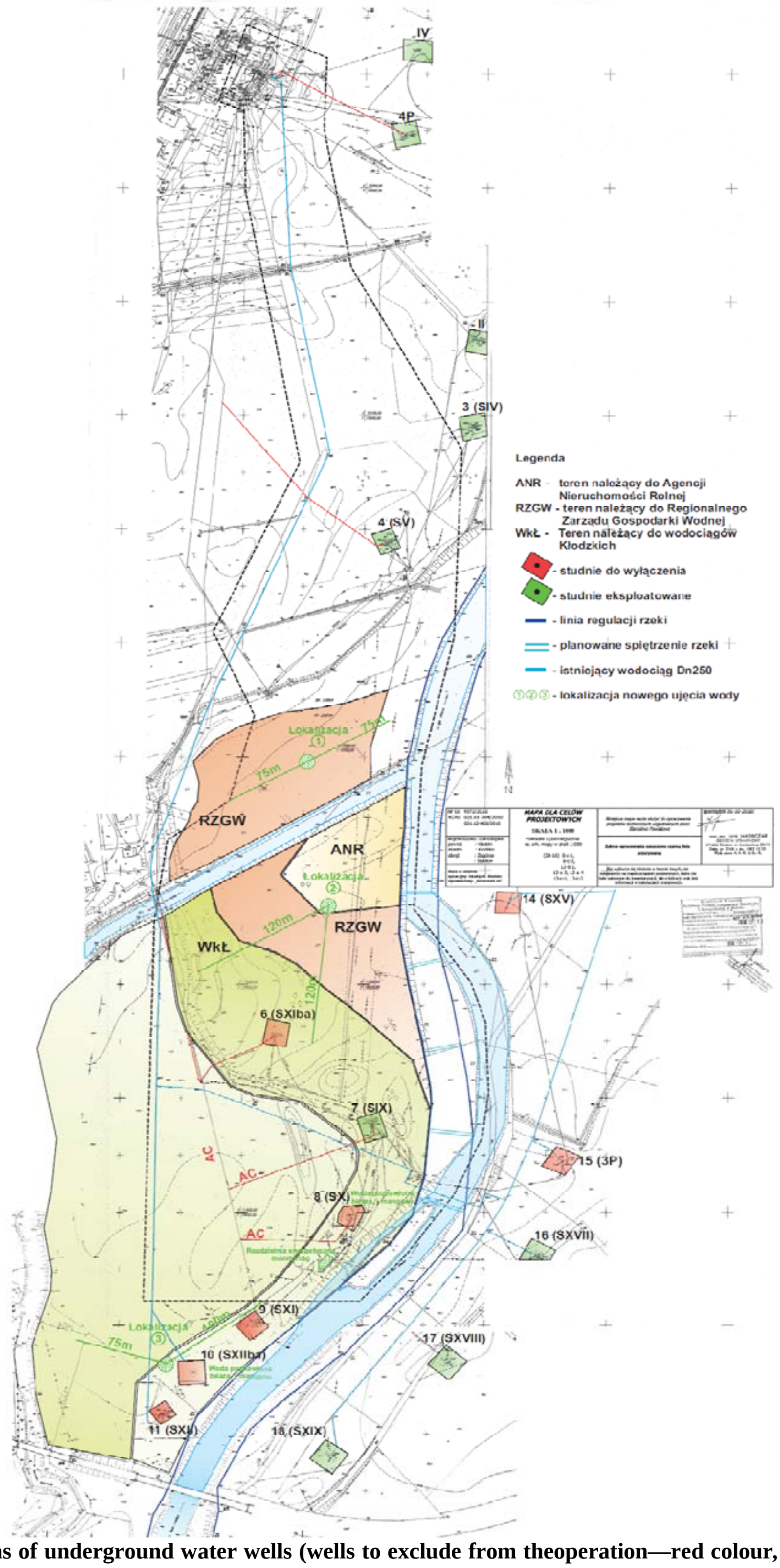

Fig. 1 A map locations of underground water wells (wells to exclude from theoperation—red colour, wellsoperated—green colour) in Klodzko water intake area (SW part of Poland); map for design purposes; District Office Klodzko, Waterworks Klodzkie [2].

In the presented article the results of the statistical and geostatistical investigations of variation of iron Fe content, manganese Mn content, ammonium ion NH_4^+ content [gNH_4^+/m^3] and oxidation capacity [gO_2/m^3], conducted for various variants of the study, were presented.

3. Results of Statistical Evaluation

The basic statistics were evaluated and histograms of various water quality parameters distribution were calculated [2, 3]. Moreover, the degree of correlation between the values of the particular parameters was established by determining the values of linear correlation coefficients r.

The shapes of asymmetrical histograms of two parameters analyzed—Fe and Mn, calculated on the basis of data deriving from spatio-time databases confirm described tendency of variation (Figs. 2 and 3), observed also using data from 14 wells (Figs. 5-7) and from 14 wells and 3 piezometers (Figs. 8 and 9). The histogram of Fe content is 1-sided, with a long tail classes of lower frequencies (Fig. 2), and a one modal histogram of the Mn content—with the marked positive skewness, with other classes of lower Mn content of various percentage shares (Fig. 3). Histogram of oxidation capacity distribution is 1-modal, with very clearly noticeable on the different subpopulations (Fig. 4).

Shapes of distribution histograms of quality parameters studied for other variants of study are varied. If data coming from 14 wells and 14 wells and 3 piezometers have been taken in the calculations, histograms of Fe iron content distribution are 1—winger with visible classes of higher Fe content, with bigger (14 wells) (Fig. 5) or small percentages of Fe content (14 wells + 3 piezometers), but richer Fe content (Fig. 8), dependently on the variant of study. For this latter variant of analysis only one modal class dominates. In contrast, the Mn content histograms are bi-modal, percentage modal shares of both classes are weakly diversified and comparable for both variants of study (Figs. 6 and 9). Histogram of NH_4^+ ammonium ion content distribution (14 wells) has 1-sided character, with the marked lower shares of classes of higher content (Fig. 7).

The statistical analyses of the variation in the quality parameters indicated certain regularities in the variation of underground water quality and made it possible to determine the trends in this variation [2-4]. When analyzing the behaviour of the averages of the parameters in the years 1977-1999 one can notice random fluctuations in Fe content and discern a tendency

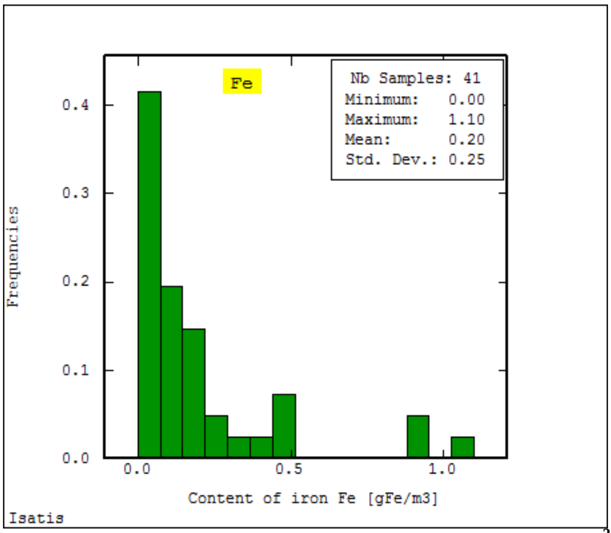

Fig. 2 Histogram of distribution of iron Fe content [gFe/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

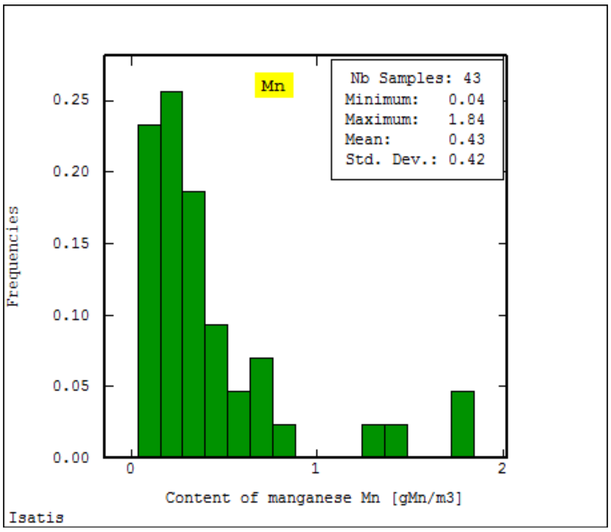

Fig. 3 Histogram of distribution of manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

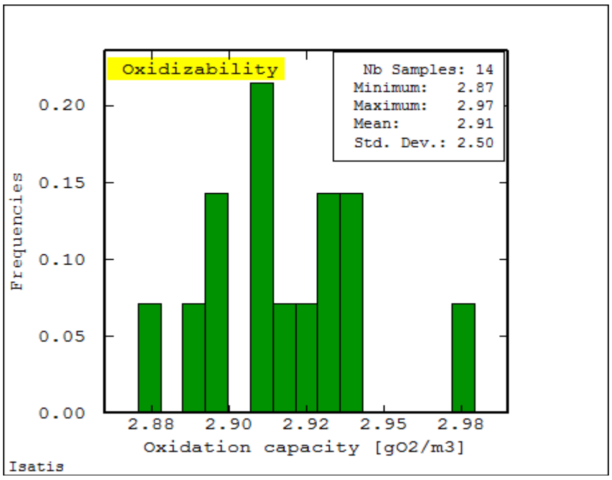

Fig. 4 Histogram of distribution of oxidation capacity [gO_2/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

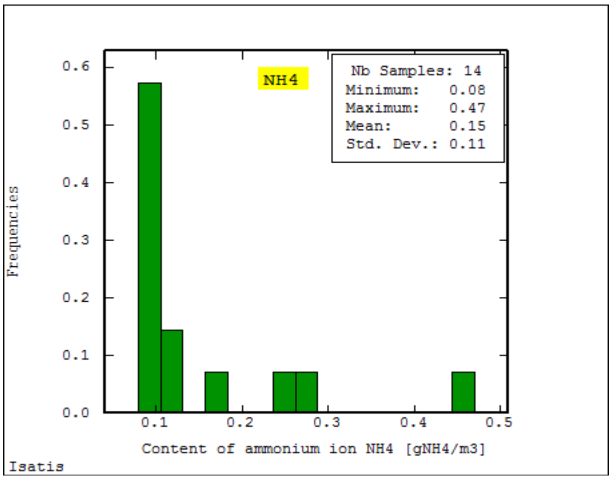

Fig. 7 Histogram of distribution of ammonium NH_4 content [gNH_4^+/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

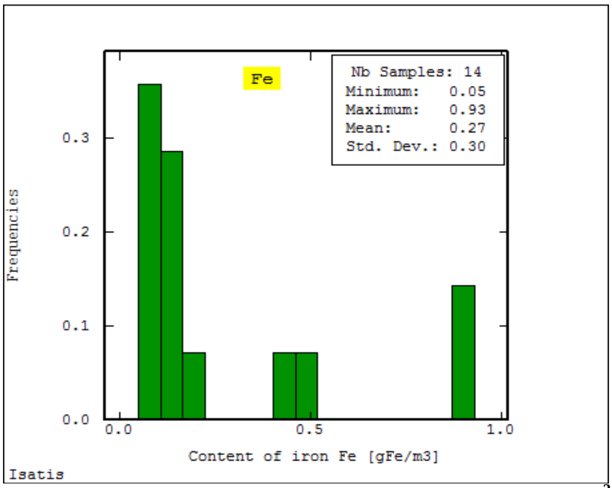

Fig. 5 Histogram of distribution of iron Fe content [gFe/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

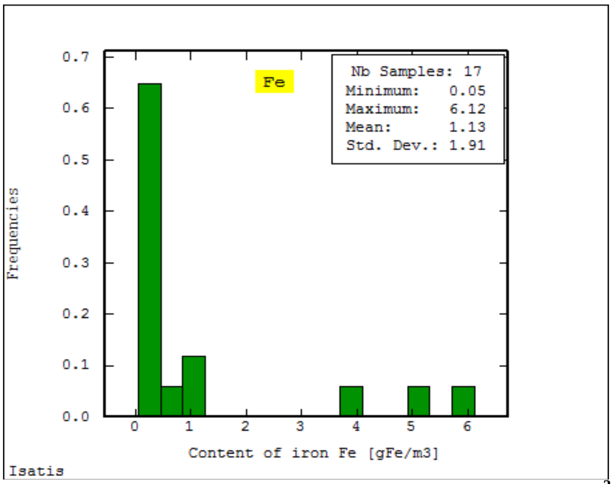

Fig. 8 Histogram of distribution of iron Fe content [gFe/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells + 3 piezometers.

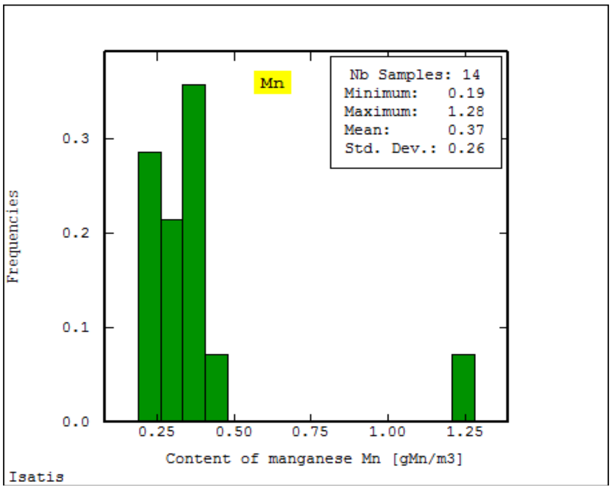

Fig. 6 Histogram of distribution of manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

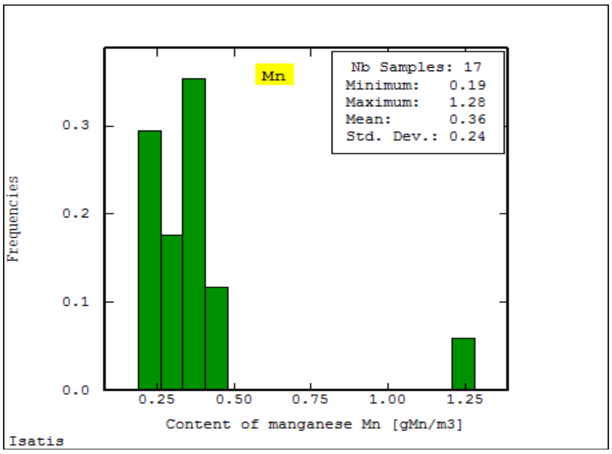

Fig. 9 Histogram of distribution of manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells + 3 piezometers.

towards periodic changes in Mn content and oxidation capacity [2, 3].

According to the adopted evaluation variants, iron and manganese concentrations on the whole exceeded the allowable values or were close or equal to them (Tables 1-4). It has been found that the average Fe and Mn content in the underground water in the water intake area near Klodzko in the years 1977-1999 significantly exceeded the standard values for these parameters, i.e. Fe content < 0.20 [g/m^3] and Mn content < 0.05 [g/m^3]. An analysis of the underground water oxidation capacity determinations shows no exceedance of the allowable value (Tables 1 and 3). As regards Fe content, its maximum and average values exceeded the allowable levels. The highest Fe concentrations were recorded in 2012 in water coming from the three piezometers drilled in new locations in the water intake area (Table 3). The minimum, maximum and average Fe concentrations were exceeded in that year. As regards Mn concentrations, the minimum, maximum and average values exceeded the values allowable for this element or were close to them (Table 3). This behaviour of Mn content was observed for all the analysed variants (Tables 1-4).

One should note the relatively low values of variation coefficients V: the low variation in Fe content and the moderate variation in Mn content (Table 3). In 2012 no so large increase in Mn content (Table 3), in comparison with the estimates for 2011 (Table 2), as that recorded for Fe content (Tables 2 and 3) was noticed in the water coming from the three piezometers.

The estimates of the basic statistics for the underground water quality parameters determined on the basis of the data for the 22 wells located in the water intake area for the period 1977-1999 indicate extremely high variation in Fe content, very high variation in Mn content and high variation in oxidation capacity (Table 1). An analysis of the values of variation coefficients V for the particular parameters shows very high variation in Fe content [2]. Also high variation in Mn content and ammonium ion NH_4^+ content, for which identical values of coefficients V were obtained, is notable. The estimates of maximum, average and minimum Fe and Mn content values for the 14 wells (2011 year) (Table 2) indicate that the standard values for these parameters (Fe content < 0.20 [g/m^3]. Mn content < 0.05 [g/m^3]) are significantly exceeded [2]. The maximum ammonium anion NH_4^+ content in the water is close to the standard value, i.e. < 0.50 [g/m^3].

The permissible iron content (Fe > 0.20 [gFe/m^3]) and manganese content (Mn > 0.05 [gMn/m^3]) were found to be considerably exceeded in underground water coming from the 3 new piezometers (2012 year) in the Klodzko water intake area [2]. The minimum X_{min}—3.99 [gFe/m^3], maximum X_{max}—6.12 [gFe/m^3] and average—5.13 [gFe/m^3] Fe content values and also the minimum X_{min}—0.21 [gMn/m^3], maximum X_{max}—0.46 [gMn/m^3] and average—0.34 [gMn/m^3] Mn content values were very high (Table 3). The variation coefficients V calculated on the basis of the data for only the 3 piezometers indicate low variation in Fe content (V—17.08%) and average variation in Mn content (V—29.92%). The coefficient V of oxidation capacity (oxidizability) shows low variation (V: 16.26-17.96%) (Table 3).

The estimates of the basic statistics for the quality parameters of the underground water in the intake area near Klodzko, based on the data for jointly the 14 wells and the 3 piezometers, indicate the extremely high variation in Fe content (V: 169.19%), high or average variation in Mn content (V: 67.00%) (Table 3) [2, 3]. The maximum Fe content of 6.12 [gFe/m^3] and the average Fe content of 1.13 [gFe/m^3] are considerably exceeded and in the case of Mn content, not only the above statistics—X_{max} = 1.28 [gMn/m^3] and average = 0.36 [gMn/m^3], but even the minimum value of 0.19 [gMn/m^3] is exceeded. The estimates of the statistical parameters, based on the data for jointly the 14 wells and the 3 piezometers, were undoubtedly influenced by the results of the chemical analyses of Fe and Mn

Table 1 Basic statistical parameters of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

Chemical element	Size n	X_{min}	X_{max}	Average $\overline{X}$	Standard deviation S	Variation coefficient V [%]
Iron Fe [gFe/m^3]	41	0.00	1.10	0.20	0.25	128.36
Manganese Mn [gMn/m^3]	43	0.06	1.84	0.49	0.42	96.21
Oxidation capacity [gO_2/m^3]	24	0.48	3.60	1.79	0.88	49.26

Correlation (Fe/Mn) coefficient $r = 0.3297$ ($n = 41$);

Correlation (Fe/oxidation capacity) coefficient $r = 0.2102$ ($n = 22$);

Correlation (Mn/oxidation capacity) coefficient $r = 0.3194$ ($n = 22$).

Table 2 Basic statistical parameters of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

Chemical element	Size n	X_{min}	X_{max}	Average $\overline{X}$	Standard deviation S	Variation coefficient V [%]
Iron Fe [gFe/m^3]	14	0.05	0.93	0.27	0.29	109.50
Manganese Mn [gMn/m^3]	14	0.19	1.28	0.37	0.26	71.75
Ammonium ion [gNH_4^+/m^3]	14	0.08	0.47	0.15	0.11	71.80

Correlation Fe/Mn coefficient $r = 0.6773$;

Correlation Fe/NH_4^+ coefficient $r = 0.8934$;

Correlation Mn/NH_4^+ coefficient $r = 0.4196$.

Table 3 Basic statistical parameters of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); data coming from 3 piezometers.

Chemical element	Size n	X_{min}	X_{max}	Average $\overline{X}$	Standard deviation S	Variation coefficient V [%]
Iron Fe [gFe/m^3]	3	3.99	6.12	5.13	0.88	17.08
Manganese Mn [gMn/m^3]	3	0.21	0.46	0.34	0.10	29.92
Oxidation capacity [gO_2/m^3]	3	0.93	1.46	1.22	0.22	17.96

Correlation Fe/Mn coefficient $r = - 0.5055$;

Correlation (Fe/oxidation capacity) coefficient $r = 0.9998$.

Table 4 Basic statistical parameters of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells + 3 piezometers.

Chemical element	Size n	X_{min}	X_{max}	Average $\overline{X}$	Standard deviation S	Variation coefficient V [%]
Iron Fe [gFe/m^3]	14 + 3	0.05	6.12	1.13	1.91	169.19
Manganese Mn [gMn/m^3]	14 + 3	0.19	1.28	0.36	0.24	67.00

Correlation Fe/Mn coefficient $r = 0.0391$.

content in the water, performed only for the 3 piezometers (2012 year) [2].

When the correlation between the Fe content and the Mn content for the years 1977-2011 (the space-time data base) is analysed, taking into account the sample sizes of 41 and 43, the correlation is found to be weaker, but still distinct (Fig. 10). The correlation coefficient (r) reaches values above 0.3 (Table 1). A similar value of coefficient r was obtained for the correlation between oxidation capacity and Mn content (Fig. 12), whereas alow value of coefficient r describes the correlation between oxidation capacity and Fe content (Fig. 11) (Table 1).

In the case of the 2011 data, the high values of coefficients r characterizing the correlations between Fe, Mn and ion NH_4^+ concentrations, particularly high for the Fe/NH_4^+ content correlation, are notable (Table 2). The correlation coefficients r were calculated on the basis of data obtained from underground water chemical analyses carried out for the 14 wells (Figs. 13-15). The results seem to point to a common source of the elevated concentrations of the chemical elements, determined in 2011. This particularly applies to the correlation between the Fe content and the NH_4^+ content.

When the data from the three piezometers drilled in new locations in the analysed water intake area in 2012 are added to the data on the Fe and Mn concentrations determined in the water coming from the 14 wells, no correlation between the concentrations of the above elements is found (Fig. 16) (Table 4). The very high Fe and Mn concentrations in the water coming from the 3 piezometers could have contributed to this result.

The investigations of the correlation between the underground water quality parameters, based on data for 2011 year, indicate that the highest positive correlation value r is between the contents of the individual elements (in the following order): Fe and ammonium ion NH_4^+ contents (r = 0.89) (Fig. 14), Fe and Mn contents (r = 0.68) (Fig. 13), Fe content and temperature °C (r = 0.71), Mn and total organic carbon

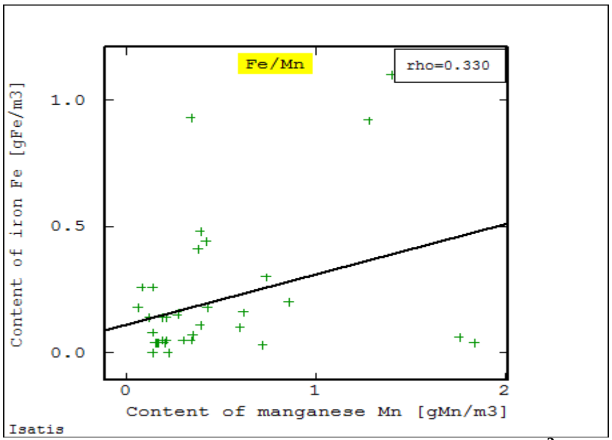

Fig. 10 Scatter diagram of iron Fe content [gFe/m^3] and manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

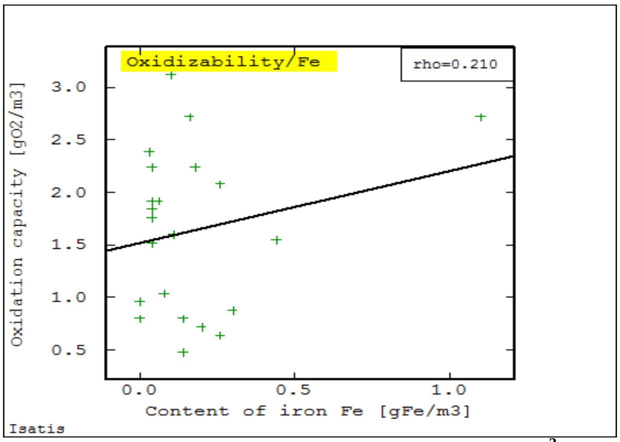

Fig. 11 Scatter diagram of iron Fe content [gFe/m^3] and oxidation capacity [gO_2/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

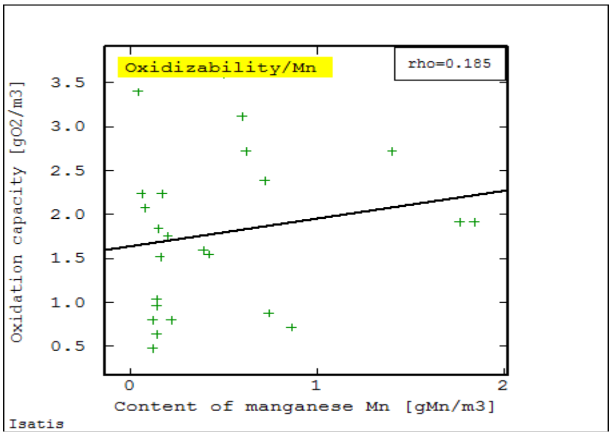

Fig. 12 Scatter diagram of manganese Mn content [gMn/m^3] and oxidation capacity [gO_2/m^3] in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

content C (r = 0.69), ammonium ion NH_4^+ content and temperature °C (r = 0.85), and ammonium ion $NH_4^+$and phosphate anion PO_4^{-3} content (r = 0.76) [2, 3]. A correlation between Mn and NH_4^+ contents is weaker but clear (r = 0.4196) (Fig. 15), than in case of correlation between Fe and NH_4^+ elements contents (Fig. 14) and between Fe and Mn elements contents (Fig. 13).

A slightly weaker positive correlation value r exists between: Fe content and phosphate anion PO_4^{-3} content (r = 0.60), phosphate PO_4^{-3} anion content and temperature °C (r = 0.61), Fe content total and carbon content C (r = 0.58), temperature °C and pH (r = 0.64), as well as Fe content and pH, ammonium ion NH_4^+ content and pH (r = 0.55) [2]. The highest positive coefficients (r) of linear correlation between the different underground water quality parameters for the 3 piezometers were obtained for the correlations between: K content and Fe content (0.9979), K content and solute content (0.8264), Mg content and Pb content (0.9999), Mn content and Zn content (0.8806), Fe content and pH (0.9470), Fe content and solute content (0.7884), and K content and pH (0.9657) (2012 year) [2]. The highest negative correlation coefficients (r) characterize the correlations between: Mg content and Zn content (-0.9975), Mn content and Mg content (-0.8447), Mn content and Pb content (-0.8515), Pb content and Zn content (-0.9983), Mn content and solute content (-0.9294), Zn content and solute content (-0.6435), and Mn content and pH (-0.7559) (2012 year) [2].

Comparison of the results of chemical analyses of underground water for wells and piezometers with the results of chemical determinations carried out for the two rivers, i.e. the surface waters in the Bystrzyca Dusznicka river and the Klodzko Neisse river (performed in 22-23.01.2012) [2], is interesting and amazing, prompting to take vigorous, effective action in order to restore the original state of water quality. These latter results indicate that the total Fe content (the Bystrzyca: Fe—2.76 [gFe/m^3], the Neisse: 4.18

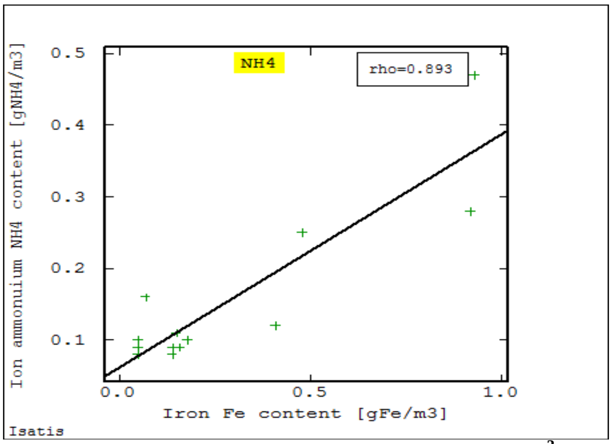

Fig. 13 Scatter diagram of iron Fe content [gFe/m^3] and manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

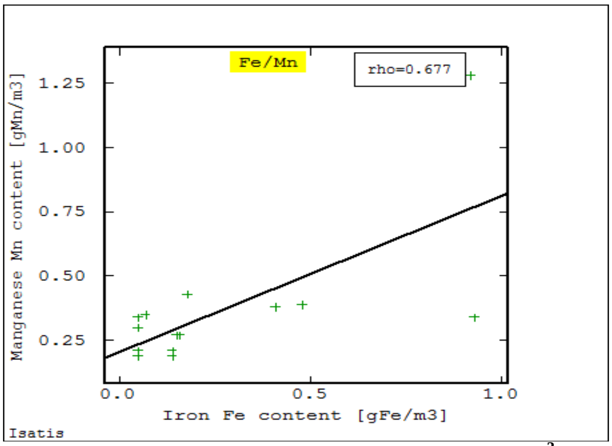

Fig. 14 Scatter diagram of iron Fe content [gFe/m^3] and ammonium ion NH_4 content [gNH_4^+/m^3] and in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

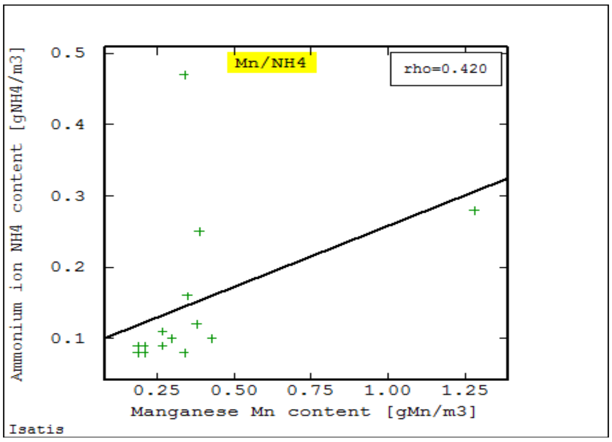

Fig. 15 Scatter diagram of manganese Mn content [gMn/m^3] and ammonium ion NH_4^+ content [gNH_4^+/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

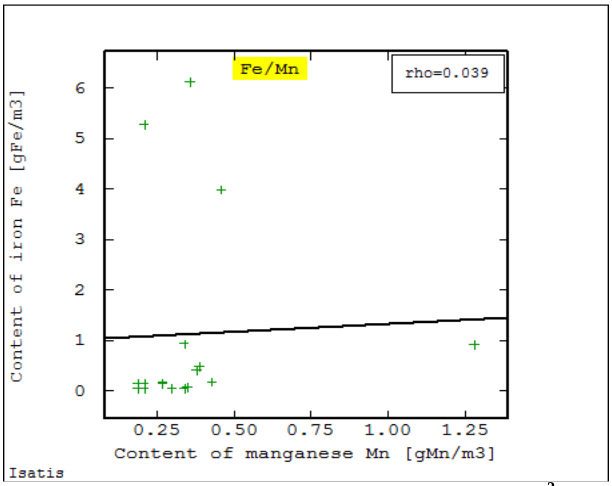

Fig. 16 Scatter diagram of iron Fe content [gFe/m^3] and manganese Mn content [gMn/m^3] in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells + piezometers.

[gFe/m^3] exceeds very much the permissible value (Fe < 0.20 [g/m^3]) in both rivers [2]. One should note the extremely high Fe exceedances in the Neisse water.

The Mn content (the Bystrzyca: Mn—0.06 [g/m^3], the Neisse—0.05 [g/m^3]) in the Neisse water is the almost same as the permissible value or only slight exceed this value (Mn < 0.05 [g/m^3]).

The values of the heavy metal content in the surface waters of the two rivers (the Klodzko Neisse and the Bystrzyca Dusznicka), i.e. Cu content (0.0011-0.0014 [g/m^3]), Pb content (0.0096-0.0098 [g/m^3]), Cd content (0.0011-0.0013 [g/m^3]) and total Cr content (0.0094-0.0095 [g/m^3]) [2], are substantially lower than the permissible values, what should be regarded as satisfactory optimistic of research results.

4. Results of Semivariograms Analysis

Then empirical directional semivariograms showing the variation in the water quality parameters along the well depth, taking into account the terrain elevation and longer time periods (whereby the character and degree of the variation could be comprehensively described), were determined [2], in the analysed area near Klodzko. The approximation of the directional semivariograms was performed by means of theoretical analytical functions (called geostatistical models) [2, 4]. The results of the conducted approximation are shown in Tables 5-7. The empirical semivariograms over the years 1977-2011 were approximated using a composite model consisting of the nugget effect, the cubic model and the spherical model (Table 5). In the Fe and Mn content semivariograms the nugget effect C_0 amounted to about ½ of the overall variation of C, but it predominated in the oxidation capacity semivariogram.

The influence ranges were different for the Fe content and the Mn content, i.e. 1-3.65 years for Mn and 3-3.3 years for Fe. The influence range of the oxidation capacity semivariogram was 2 years.

The directional variation in the semivariogram function γ(h) values of the parameters becomes visible only over a longer study period. The directional semivariograms of Fe and Mn content, calculated along the time period (the years: 1977-2011) for the underground water intake area near Klodzko show clear upward trends in the values of semivariogram function γ(h) (Figs. 17 and 18) [2]. In the case of the Fe content semivariogram, the increase in the value of γ(h) is slower, but clear (Fig. 17). Stronger variation is visible in the Mn content semivariogram and the latter is much steeper (Fig. 18). However the increase in the semivariogram function value of γ(h) of the oxidation

Table 5 Comparison of geostatistical parameters for models of directional semivariograms of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

Chemical element	Nugget effect C_0	Partial sill variance C’	Total sill variance C	Range of influence a [year]	Basic model structures
Iron Fe [gFe/m^3]	0.024914	0.006807 0.010254	0.041975	3.29 2.98	nugget effect cubic spherical
Manganese Mn [gMn/m^3]	0.137079	0.042028 0.098106	0.278213	1.11 3.65	nugget effect cubic spherical
Oxidation capacity [gO_2/m^3]	0.623281	0.066641	0.689922	2.16	nugget effect spherical

Table 6 Comparison of geostatistical parameters for models of directional semivariograms of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells.

Chemical element	Nugget effect C_0	Partial sill variance C'	Total sill variance C	Range of influence a [m]	Basic model structures
Iron Fe [gFe/m^3]	0.035246	0.026740 0.103321	0.165307	1.04 3.27	nugget effect cubic spherical
Manganese Mn [gMn/m^3]	0.006966	0.031347 0.031347	0.069660	0.22 0.88	nugget effect cubic spherical
Ammonium ion NH_4^+ [gNH_4^+/m^3]	-	0.009486 0.005703	0.015189	0.46 0.58	cubic spherical

Table 7 Comparison of geostatistical parameters for models of directional semivariograms of chemical elements (quality parameters) in underground water for water intake area of Klodzko (SW part of Poland); data coming from 14 wells + 3 piezometers.

Chemical element	Nugget effect C_0	Partial sill variance C'	Total sill variance C	Range of influence A [m]	Basic model structures
Iron Fe [gFe/m^3]^2	0.222192	1.638008 2.205247	4.065447	0.22 0.56	nugget effect cubic spherical
Manganese Mn [gMn/m^3]^2	0.007010	0.025075 0.047727	0.079812	0.49 0.75	nugget effect spherical spherical

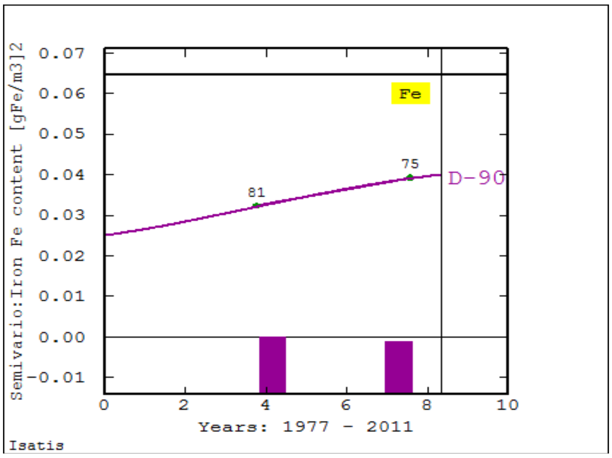

Fig. 17 Directional semivariogram (D-90) of iron Fe content [gFe/m^3]^2 in underground water in Klodzko intake area; years 1977-2011.

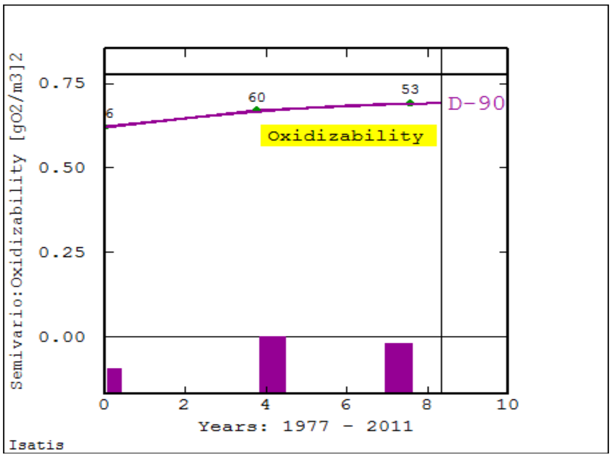

Fig. 19 Directional semivariogram (D-90) of oxidation capacity [gO_2/m^3] in underground water in Klodzko intake area; years 1977-2011.

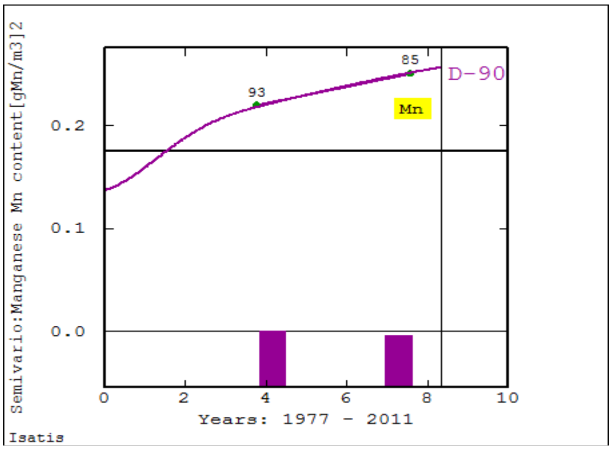

Fig. 18 Directional semivariogram (D-90) of manganese Mn content [gMn/m^3]^2 in underground water in Klodzko intake area; years 1977-2011.

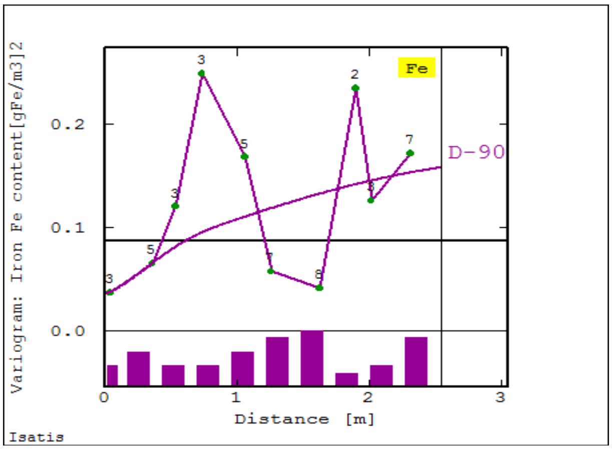

Fig. 20 Directional semivariogram (D-90) of iron Fe content [gFe/m^3]^2 in underground water in Klodzko intake area; 14 wells.

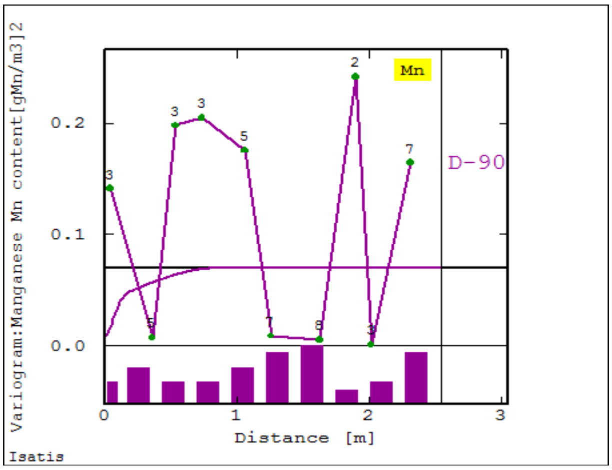

Fig. 21 Directional semivariogram (D-90) of manganese Mn content [gMn/m^3]^2 in underground water in Klodzko intake area; 14 wells.

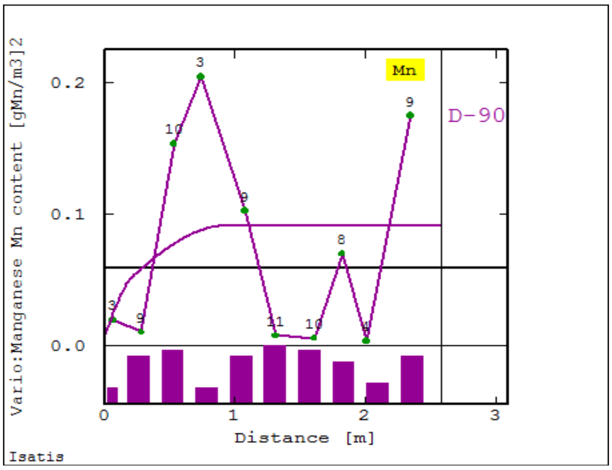

Fig. 24 Directional semivariogram (D-90) of manganese Mn content [gFe/m^3]^2 in underground water in Klodzko intake area; 14 wells + 3 piezometers.

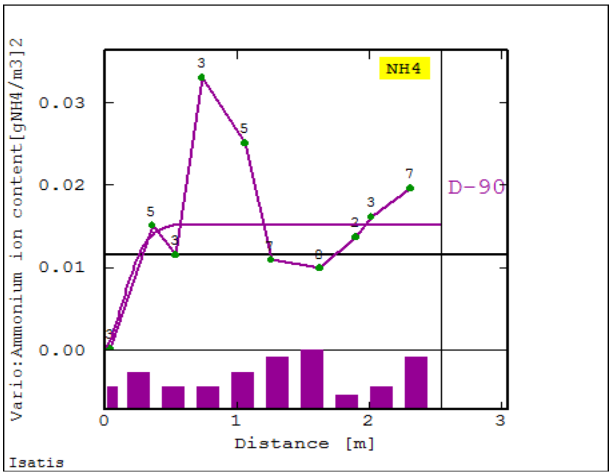

Fig. 22 Directional semivariogram (D-90) of ammonium ion NH_4^+ content [gNH$_4$/m^3]^2 in underground water in Klodzko intake area; 14 wells.

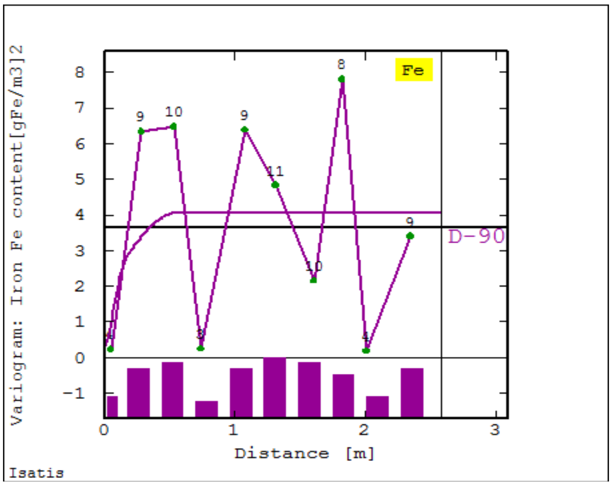

Fig. 23 Directional semivariogram (D-90) of iron Fe content [gFe/m^3]^2 in underground water in Klodzko intake area; 14 wells + 3 piezometers.

capacity semivariogram is slowest (Fig. 19).

A periodic nature, character of variation can be observed in the directional Fe and Mn content semivariograms (Figs. 20 and 21), if data coming only from 14 wells have been taken into calculations. A such tendency of clear periodic variability is observed in the ammonium ion NH_4^+ content semivariogram (Fig. 22).

Some traces of periodic variation (quasi-periodicity) can be discerned in the directional Fe and Mn content semivariograms (using data coming from 14 wells + 3 piezometers) (Figs. 23 and 24) calculated along the wells depth for the underground water intake area near Klodzko [2]. Generally, these are short-term variation in the value of semivariogram function $\gamma(h)$.

Both studied semivariograms courses confirm strong variation of the studied parameters values.

Also the empirical semivariograms of Fe and Mn concentrations, calculated taking into account the data from the 14 wells (analysed along their depth) in the Klodzko water intake area, were approximated using the combination of nugget effect C_0, the cubic model and the spherical model (Table 6). Since no nugget effect was present in the semivariogram of NH_4^+ content only the last two model components were used to calculate this semivariogram (Table 6). The share of nugget effect C_0 in the Fe and Mn content semivariograms was very small. Wider influence ranges (1-3.3 m) than those in the Mn (0.2-0.9 m) and

NH_4^+ content (0.5-0.6 m) semivariograms, were observed in the Fe content semivariograms (Table 6), which is evidence of the greater variation in Mn and NH_4^+ concentrations than in Fe concentration (Table 6).

Among the results of the approximation of the semivariograms calculated on the basis of the data obtained from the 14 wells and the 3 piezometers the narrow influence ranges (a) of the concentrations of two chemical elements, i.e. Fe: 0.22-0.56 m and Mn: 0.49-0.75 m are notable (narrower in the case of the Fe content semivariogram) (Table 7). They were approximated using a combination of spherical models or a combination of the spherical model and the cubic model (Table 7). The share nugget effect C_0 in the semivariograms of the considered elements can be described as negligible.

5. Results of Estimation

Thanks to the approximation of the directional semivariograms by means of theoretical analytical functions (called geostatistical models) ordinary (block) kriging could be applied to estimate averages Z* of the studied parameters, with minimum estimation variance σ_k^2 [2, 4]. The unique kriging neighbourhood, i.e. the sample searching subarea, was taken into account, due to the small number of analyzed data.

The investigated water intake area near Klodzko was covered with a grid of rectangular elementary blocks. Different elementary grid dimensions were used in the estimation of the underground water quality parameters. The total number of elementary fields for the centres for which estimated averages Z* were estimated ranged from 51,840 to 464,640, depending on the spatial analysis variant (Tables 8-10).

The selected results of estimation using ordinary block kriging and the calculated block diagrams with the determined levels of elevated values of studied underground water quality parameters were shown below.

Block diagrams showing estimated averages Z* distribution, calculated using directional semivariograms (taking time period into account) and ordinary kriging, were presented in the Figs. 25-27.

The highest estimated averages Z* of Fe content in the highest estimated averages Z* of Fe content in the underground water characterize the years: 1977 —0.30614-0.30629 [gFe/m^3], 2005 —0.308925-0.308940

Table 8 Global statistics of estimated averages Z* of chemical elements (quality parameters) in the nodes of spatial grid in underground water for water intake area of Klodzko (SW part of Poland); space-time data base.

Chemical element	Size of grid nodes N	Z^*_{min}	Z^*_{max}	Average $\overline{\overline{Z^*}}$	Standard deviation	Variation coefficient V [%]
Estimated average Z* of iron Fe [gFe/m^3]	51,840	0.08	0.32	0.18	0.08	44.81
Standard deviation of estimation σ_k [gFe/m^3]	51,840	0.05	0.09	0.07	0.01	12.88
Estimated average Z* of manganese Mn [gMn/m^3]	51,840	0.36	0.61	0.46	0.08	18.39
Standard deviation of estimation σ_k [gMn/m^3]	51,840	0.13	0.23	0.18	0.02	13.96
Estimated average Z* of oxidization capacity [gO$_2$/m^3]	51,840	1.45	2.07	1.77	0.16	8.90
Standard deviation of estimation σ_k [gO$_2$/m^3]	51,840	0.23	0.33	0.28	0.03	10.19

Table 9 Global statistics of estimated averages Z* of chemical elements (quality parameters) in the nodes of spatial grid in underground water for water intake area of Klodzko; (data coming from 14 wells).

Chemical element	Size of grid nodes N	Z^*_{min}	Z^*_{max}	Average $\overline{\overline{Z^*}}$	Standard deviation	Variation coefficient V [%]
Estimated average Z* of iron Fe [gFe/m^3]	277,200	0.10	0.69	0.27	0.12	45.91
Standard deviation of estimation σ_k [gFe/m^3]	277,200	0.12	0.32	0.24	0.06	25.35
Estimated average Z*of manganese Mn [gMn/m^3]	277,200	0.21	0.79	0.35	0.09	25.15
Standard deviation of estimation σ_k [gMn/m^3]	277,200	0.07	0.28	0.21	0.07	31.64

Table 10 Global statistics of estimated averages Z* of chemical elements (quality parameters) in the nodes of spatial grid in underground water for water intake area of Klodzko; data coming from 14 wells + 3 piezometers.

Chemical element	Size of grid nodes N	Z^*_{min}	Z^*_{max}	Average $\overline{\overline{Z^*}}$	Standard deviation	Variation coefficient V [%]
Estimated average Z* of iron Fe [gFe/m^3]	293,480	-0.03	4.99	0.99	0.98	99.15
Standard deviation of estimation σ_k [gFe/m^3]	293,480	0.44	2.03	1.49	0.51	34.37
Estimated average Z* of manganese Mn [gMn/m^3]	293,480	0.22	0.79	0.36	0.08	23.63
Standard deviation of estimation σ_k [gMn/m^3]	293,480	0.06	0.29	0.21	0.07	35.93

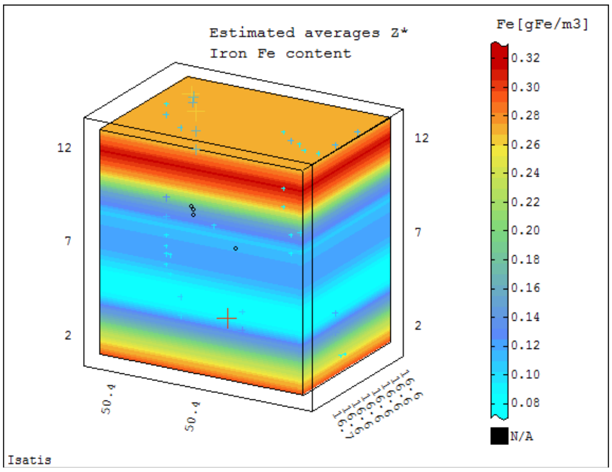

Fig. 25 Block diagram of estimated averages Z* distribution of iron Fe content [gFe/m^3] in underground water in Klodzko intake area; years 1977-2011.

[gFe/m^3], 2008—0.34220-0.34226 [gFe/m^3], while the lowest averages Z* are connected with the years: 1988—0.084819-0.084834 [gFe/m^3] and 1991—0.075627-0.075633 [gFe/m^3] [2] (Fig. 25).

The maximum estimated averages Z* of Mn content in the underground water characterize the years: 1977—0.52935-0.5259 [gMn/m3], 1988—0.60760-0.60766 [gMn/m^3], 1991—0.60785-0.60791 [gMn/m^3] and 2002—0.50202-0.50205 [gMn/m^3], while the lowest averages Z* characterize the years: 1994—0.362709-0.362724 [gMn/m^3] and 1997—0.365084-0.365099 [gMn/m^3] [2] (Fig. 26).

The highest estimated averages Z* of oxidation capacity in the underground water are related to the years: 1984—1.873899-1.873905 [gO_2/m^3], 1988—1.896985-1.897000 [gO_2/m^3] and 1998—1.807260-1.807263 [gO_2/m^3], while the lowest averages Z* characterize the year: 1981—1.501546-1.501561 [gO_2/m^3] [2] (Fig. 27).

One elevated Fe content level: a stronger one (0.80-0.90) and a weaker making an envelope of Fe content reaching 0.60-0.70 [gFe/m^3], have been identified (Fig. 25). In the case of Mn content, only one level of elevated Mn content, ranging from 0.64 to 0.74 [gMn/m^3], has been identified (Fig. 26). One elevated oxidation capacity level: a stronger one (1.95-2.00, 1.90-2.00 [gO_2/m^3]) and a weaker making an envelope of oxidizability gaining 1.85-1.90 [gO_2/m^3], have been distinguished (Fig. 27).

In the light of the estimates made using ordinary kriging it becomes apparent that maximum estimated averages Z* of Fe and Mn content in the underground water generally occur in the SW part of the considered water intake area in Klodzko, in the elevation range of 290.55-291.45 m a.s.l. [2].

If data coming only from 14 wells have been taken into calculations, one elevated Fe content level: a stronger one (0.80-0.90) and a weaker making an envelope of Fe content reaching 0.60-0.70 [gFe/m^3], have been identified (Fig. 28). In the case of Mn content, only one level of elevated Mn content, ranging from 0.64 to 0.74 [gMn/m^3], has been identified (Fig. 29). In case of ammonium ion NH_4^+ content, one elevated level: more intensive one (> 0.42 [gNH_4^+/m^3]) and a weaker making an envelope of ion NH_4^+ content reaching 0.32-0.37 [gNH_4^+/m^3], have been noticed (Fig. 30).

Maximum estimated averages Z* of ion NH_4^+ content are connected with the different parts (NW, W, SW) of the water intake area, in the range of 292-293 m a.s.l [2].

Using data coming from 14 wells + 3 piezometers two elevated Fe content levels can be distinguished: a weaker one (3.50-4.50) and a stronger one (4.50-5.00) [gFe/m^3], with an envelope of Fe content reaching 3.50-4.50 [gFe/m^3], have been identified (Fig. 31). In the case of Mn content, only one level of elevated Mn content, ranging from 0.75 to 0.80, with an envelope of Mn content reaching 0.65-0.75 [gMn/m^3] has been identified (Fig. 32).

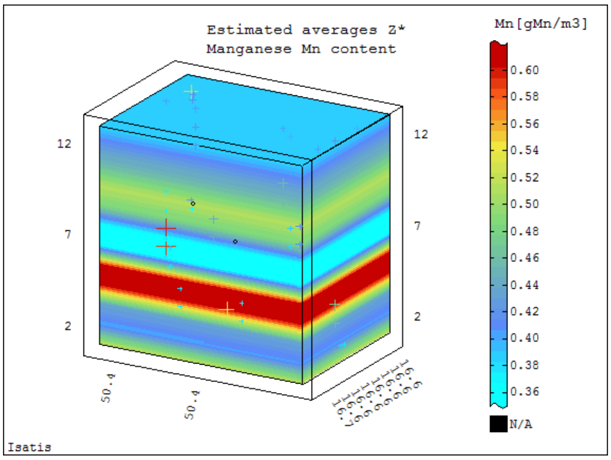

Fig. 26 Block diagram of estimated averages Z* distribution of manganese Mn content [gMn/m^3] in underground water in Klodzko intake area; years 1977-2011.

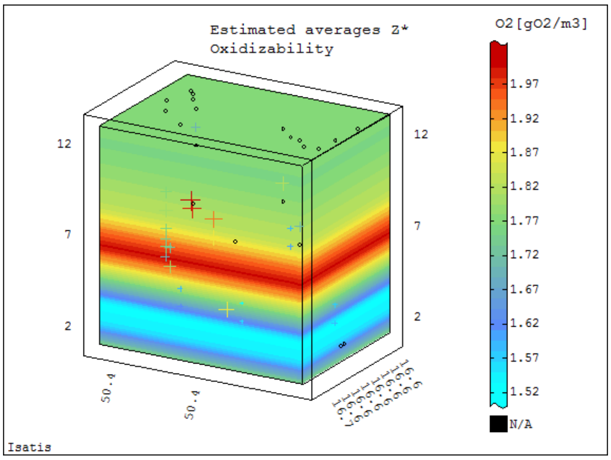

Fig. 27 Block diagram of estimated averages Z* distribution of oxidation capacity [gO_2/m^3] in underground water in Klodzko intake area; years 1977-2011.

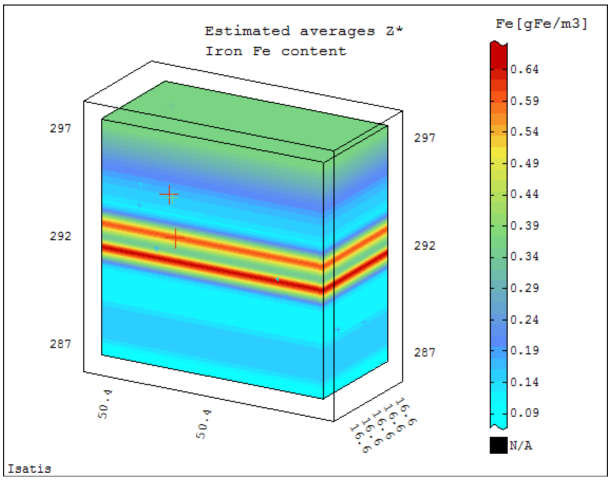

Fig. 28 Block diagram of estimated averages Z* distribution of iron Fe content [gFe/m^3] in underground water in Klodzko intake area; 14 wells.

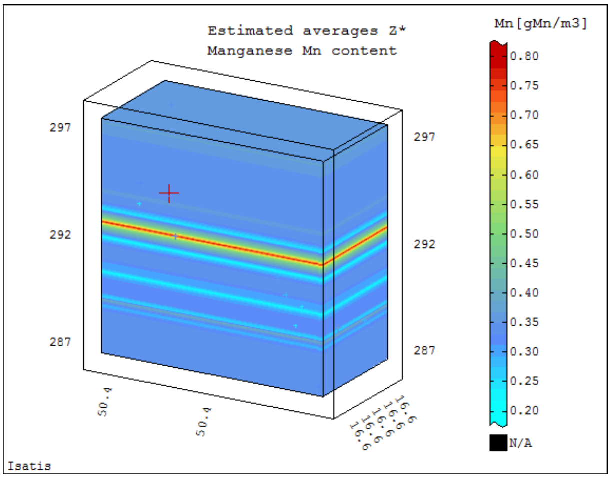

Fig. 29 Block diagram of estimated averages Z* distribution of manganese Mn content [gMn/m^3] in underground water in Klodzko intake area; 14 wells.

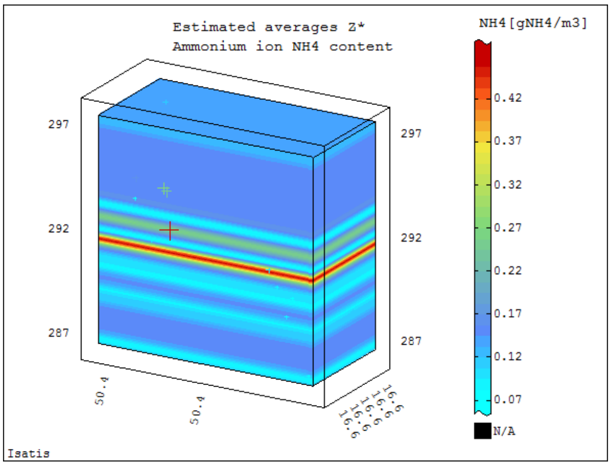

Fig. 30 Block diagram of estimated averages Z* distribution of ammonium ion content [gNH_4^+/m^3] in underground water in Klodzko intake area; 14 wells.

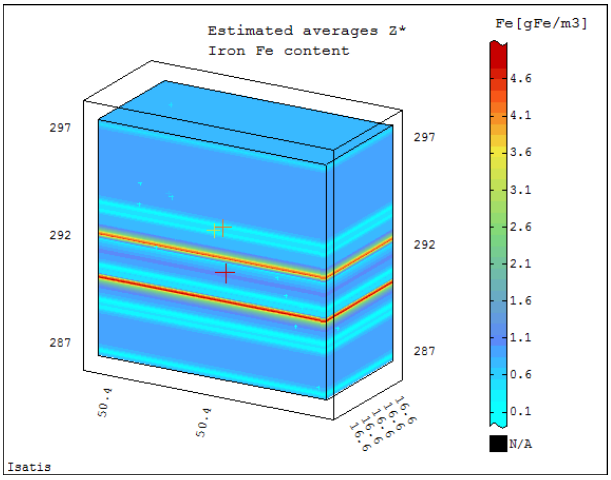

Fig. 31 Block diagram of estimated averages Z* distribution of iron Fe content [gFe/m^3] in underground water in Klodzko intake area; 14 wells + 3 piezometers.

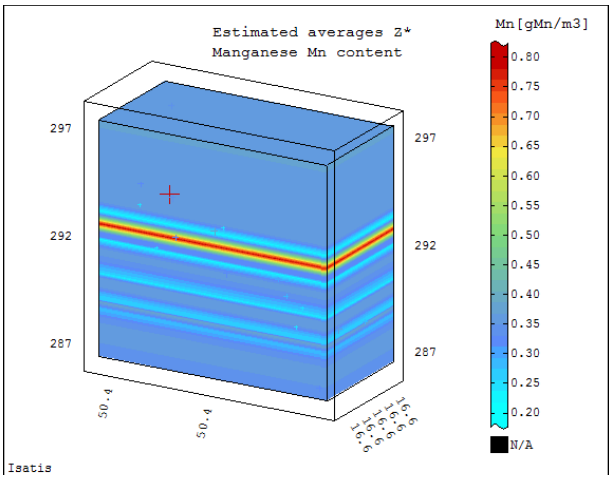

Fig. 32 Block diagram of estimated averages Z* distribution of manganese Mn content [gMn/m^3] in underground water in Klodzko intake area; 14 wells + 3 piezometers.

When an estimation with the space-time data base taken into account was carried out, variation coefficients V indicating a high variation in estimated Fe content averages Z*, a small variation in Mn content averages Z* and a very small variation in oxidation capacity averages Z* were obtained (Table 8). Low coefficients V of estimation standard deviation σ_k were obtained for the three analysed quality parameters.

In the next analytical variant the data on the 14 wells were included in the calculations. Then the variation coefficients V of the geostatistical parameters were slightly higher, except for the coefficient V of Fe content averages Z*, reaching similar values (Table 9) as the ones obtained on the basis of the space-time database (Table 8). This applies to both averages Z* and estimation standard deviation σ_k.

When the analysis was carried out for the data from the 14 wells and the 3 piezometers, very high variation in Fe content averages Z* and relatively low variation in Mn content averages Z* and estimation standard deviation σ_k of Fe content became evident (Table 10). The variation in standard deviation σ_k of Mn content was found to be slightly higher.

Databases containing the grid data yielded by the spatial analyses conducted, e.g. the values of coordinates X, Y and Z, estimated averages Z*, estimation standard deviation σ_k and other geostatistical parameters making efficiency (effectiveness) measure calculated in the nodes of the spatial elementary network, were created [2]. The content of the databases can be used in further analyses, e.g. to obtain grid cross sections.

Effectiveness of geostatistical techniques in determining estimated averages Z* of the underground water quality parameters was assessed and the advantages of the ordinary (block) kriging procedure used for this purpose became clearly apparent [2].

6. Results Discussion

This article is the fragment of the realized big research grant work [2]. The basis for spatial analyses was a sample of data on chemical determinations of underground water for selected water quality parameters, among others, iron Fe, manganese Mn, ammonium ion $NH4^+$ content and oxidizability of this water. These data were determined in the period 1977-2012, but not numerously, then statistical size (number) was rather poor. Unfortunately, it was caused by lack of possibilities to obtain a bigger amount of data concerning underground water, i.e. the results of chemical analyses of underground water in Klodzko area. For this reason I have had a few samples in my disposal to conduct detailed geostatistical analyses.

Basic statistical evaluation was carried out, before geostatistical studies, and then directional semivariograms and an ordinary kriging were calculated.

A standard geostatistical application (using Isatis software) was applied with regard to used not rich size of samples, therefore it was not any need to apply advanced geostatistical methods in these studies.

When spatially-time variation in groundwater quality parameters over the years 1977-2012 were analyzed, richer data samples in the analysis were included. The obtained results of analyses indicate trends in variation of these two parameters in the considered period of time, particularly of manganese Mn content, further of iron Fe content, much less expressed in the case of oxidizability. Calculated block diagrams of these elements show clearly defined, elevated levels of the studied groundwater parameters in this period.

It turned out that clear regularities of the changes in the content of Mn and content of NH_4^+ in the years 1977 to 2012 persist in the water supply, but also are noticed in a treated water [13, 14]. However, the changes of Fe content, both in the water supply system, as well as in a treated water rather should be considered as a periodical.

The subject of analysis was also the spatial variability of some water quality parameters of underground water in the Klodzko area. Then the poor sample analysed, which was resulted with a small size of wells and piezometers occurring in the area (14 wells; 14 wells + 3 piezometers). These data were connected with chemical determinations of water quality parameters, made in 2011 (November) and 2012 (January).

As a result, we observed a very large diversity of function $\gamma(h)$ values in semivariograms courses, their violent fluctuations. The results of 3D estimating—the raster maps (in perspective) (3D Box—3D Grid Contents) for this variant of study give a general idea of the extent and nature of changes in the content of Fe, Mn and NH_4^+ ion in the water intakes Klodzko area.

7. Conclusion

Owing to the use of the hydrogeochemical space-time model of the variation in the quality parameters of the underground water in the Quaternary formations precise characteristics of the parameters have been obtained for the entire water intake area for the years 1977-2012 [2-4].

Over the longer period (1977-2012) an increasing trend in the variation of Fe content and Mn content in the underground water in the Klodzko water intake area clearly emerges. It is gentler for Fe and steeper for Mn. The considerable exceedance of the allowable concentrations of these elements in the tested (2011) water from the 14 wells in the water intake area and in the tested (2012) water from the 3 new piezometers drilled in the new locations is evidence of the deteriorating quality of the water over time and so of the deteriorating condition of the environment as a result of its pollution. This may pose a long-term hazard to the health of the local population. The changes in iron (Fe) content, manganese (Mn) content and ammonium ion (NH_4^+) content in the Klodzko water intake area, analysed along the depth of the 14 wells and the 3 piezometers have a quasi-periodic character.

The 3D geostatistical model enables the modelling and estimation of averages Z*, i.e. the analysis of the quality condition of underground water in a given researcher-defined area over a short and long time span. It becomes possible to determine estimated averages Z* (in a particular space-time point) in the nodes of the 3D grid covering the drainage area of the Klodzko Region.

The obtained results of estimation, allowed to determine the levels of elevated values of studied underground water quality parameters [2, 4-6]. Frequently maximum average values of Z* parameters were found at levels of 50 or 60, rarely 70, related to the height of the terrain interval from 290.55-292.36 m a.s.l., from the SW part of the area in question intakes (less of N, NW and NE parts).

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