

# Application of ICP-MS and various computational methods for drinking water quality assessment from the Silesian District (Southern Poland)

Research Article

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**Abstract:** In this study, more than 200 samples of drinking water from taps in the Silesian District (southern Poland) were analyzed. Concentrations of As, Bi, Cd, Co, Cr, Mo, Ni, Pb, Rb, Sb, Se, Te, Tl and V were measured using inductively coupled plasma-mass spectrometry technique (ICP-MS). The levels of the tested elements generally met European Union regulations. All analytical results were processed using computational methods, including the Pearson and Gini coefficients with the Lorenz curves, one-way ANOVA, the Kruskal-Wallis one-way analysis of variance, the Mann-Whitney U test, the variance correlation test and the Spearman's test. In addition, Principal Component Analysis (PCA) with Varimax and Cluster Analysis with Ward's Method were applied. It was shown, that some parameters (e.g. hardness and alkalinity) were highly correlated. The score plot described the degree of mineralization of water samples, so the origin of water could be easily determined. In turn, based on the created dendrogram, the division of samples into several groups (with soft, medium and highly mineralized water) could be deduced.

**Keywords:** Trace elements • Tap water • Environmental analysis • PCA • CA

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## 1. Introduction

Nowadays, high quality of drinking water is very important. Good drinking water should be tasty, clean and deprived of sediments and bad smell. Concentration of some macro- and microelements should be at the appropriate level. However, presence of dangerous bacteria, bad smell or toxic and harmful compounds of heavy metals or phenols disqualifies drinking water. The permissible levels of dangerous compounds are regulated by law in many countries all over the world [1]. In European Union, the Council Directive from 3 November 1998 is now in force [2]. Also, the World Health Organization issued some recommendations about harmful

substances in drinking water. Poland, as a member state of the European Union, has to conform to the EU Council Directive, so the Decree of the Health Minister from 29 March 2007 [3] is now in force.

Surface water or groundwater intakes may be used for producing drinking water. Before sending it to consumers' taps, raw water should undergo several treatment steps. The kind of water, pipelines, treatment method, and disinfection materials used may have large influence on the quality of the product [4]. Every day, all waterworks monitor many physico-chemical parameters, such as conductivity, pH, hardness, oxidability and concentration of many organic and inorganic compounds before sending treated water to consumers. But, in the homes of

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the consumers, such studies are rarely conducted at the request and expense of the customer and in the case of emergency - accident or contamination of water in water mains. However, some metals from an old pipeline may be rinsed and carried with water [5,6]. Therefore, it is also important to verify whether the water in the consumer's house meets specific conditions regulated by law. It may be essential information about the state of a pipeline.

Some of the elements investigated in this study have highly toxic properties, such as As, Bi, Cd, Pb, Rb, Sb, Te, Tl. Large quantities of these elements may damage the nervous system (Bi, Pb, Tl), or certain organs of living organisms (Cd). It may be also a factor in carcinogenicity and teratogenicity (As). Some of these elements (Bi, Pb) may disturb the metabolism of important microelements. Others may accumulate in some tissues, including liver, bone, kidney and brain - Pb, Sb, Te [7]. Other elements, such as: Co, Cr, Mo, Ni, Se and V in small quantities are necessary for the proper functioning of the human body [8,9]. For example, Co is a part of the vitamin B<sub>12</sub> molecule. On the other hand, too high concentrations of these elements may be harmful and, for example, may cause damage to the nervous system (vanadium) [10].

Inductively coupled plasma-mass spectrometry (ICP-MS) constitutes a leading technique among the many analytical techniques used in quantitative analysis of trace elements. It was also demonstrated that the ICP-MS technique, due to low levels of detection (even ppt), allows the determination of elements present in very small quantities in various environmental samples, such as different types of drinking water [11,12]. Analysis of water using an ICP-MS spectrometer is fast, does not require mineralization (in addition to acidification of the sample), and it allows for simultaneous analysis of isotopes of many elements [13,14].

The main purpose of this work was the application of many various techniques for large amount of data processing. Several statistical and chemometric methods were applied to evaluate the quality of drinking water and the identification of its origin. A large set of data was received, which was then treated with statistical methods (Pearson and Gini coefficients with Lorenz curves, ANOVA, the Kruskal-Wallis test, the Mann-Witney U test the variance correlation test and the Spearman's test). It allowed the determination of some similarities and differences between regions and selected parameters. Principal Component Analysis (PCA) with Varimax rotation mode and Cluster Analysis with Ward method were also applied. These chemometric techniques were widely used for processing large environmental data sets, e.g. from air, soil [15,16], geochemical data [17] or especially from surface water analysis [18-22].

PCA allowed the understanding of some dependences about analyzed parameters. Resulting score plots showed some similarities and differences between individual samples and helped in determining the origin of each water sample (surface or groundwater). In turn, CA was very helpful in finding similarities between all investigated samples.

## 2. Experimental procedure

### 2.1. Sampling

Drinking water in the Silesian District taps comes from various sources: surface reservoirs and underground intakes. In the central part of the region (GOP: Gornoslaski Okreg Przemyslowy - Upper-Silesian Industrial Region) Upper-Silesian Waterworks Plc. Company (Gornoslaskie Przedsiębiorstwo Wodociagow) is the main supplier. Drinking water is taken here mainly from some surface reservoirs (such as Goczalkowice Reservoir), rivers or from groundwater supplies [23,24]. Besides that – many cities have their own groundwater supplies (such as in northern part of the province). There are also some other suppliers, such as Aqua in its southern part.

All samples of drinking water (shown in Fig. 1) were collected from 201 domestic taps and some water treatment plants from many poviats and cities in the Silesian District. The sampling campaign lasted in the summer of 2008. Before taking the sample, water was flown from the tap for at least 15 min. The sample containers were rinsed twice with analyzed water and then filled up carefully without air bubbles. One part of each sample was kept in 5 L capacity plastic storage tank for some basic analysis. The other part (for trace elements analysis) was collected into brand-new 100 mL PET tube and acidified with ultrapure 10% HNO<sub>3</sub> (Merck, Germany).

### 2.2. Analysis and methods

After transportation into the laboratory, each sample was immediately analyzed for some basic parameters, such as pH, conductivity, alkalinity, and total hardness. Tubes with water were stored in temperature of 4°C until trace elements determination.

Conductivity was measured according to the requirements of PN-EN standard [25], using Radelkis Conductivity Meter (type OK-102/1). Then, an Elwro 5170 pH-meter was used for measurement of pH according to PN Standard [26]. The total hardness of water mainly defines the presence of bivalent cations such as calcium and magnesium. It was measured according to the PN-ISO standard, by

a versenic method [27]. Alkalinity is the ability of water to neutralize strong acids added, and it is caused mainly by dissolved carbonates and hydrogen carbonates. It was analyzed according to the PN-EN ISO standard by the titration acidimetric method [28].

Some trace elements, such as As, Bi, Cd, Co, Cr, Mo, Ni, Pb, Rb, Sb, Se, Te, Tl, and V were analyzed using the inductively coupled plasma mass spectrometry technique (ICP-MS), according to PN-EN ISO standard [29].

**Table 1.** Measurement conditions for ICP-MS (Perkin-Elmer Sciex ELAN 6100).

<b>f power, W</b>	1200
<b>Plasma gas flow, L min<sup>-1</sup></b>	15
<b>Nebulizer gas flow, L min<sup>-1</sup></b>	0.82-0.86
<b>Auxiliary gas flow, L min<sup>-1</sup></b>	1.15
<b>Nebulizer</b>	Cross flow
<b>Plasma torch</b>	quartz
<b>Sample uptake mL min<sup>-1</sup></b>	1
<b>Scanning mode</b>	Peak hop
<b>Dwell time, ms</b>	100
<b>Sweeps/Reading</b>	20
<b>Number of replicates</b>	3
<b>Read delay time, s</b>	15
<b>Cell gas</b>	CH <sub>4</sub>
<b>DRC gas flow, mL min<sup>-1</sup></b>	0.7
<b>RPq (rejection Parameter q)</b>	0.65

**Table 2.** Limits of detection and recovery of NIST 1643e reference material.

Isotope	LOD (µg L <sup>-1</sup> )	NIST CRM 1643e (µg L <sup>-1</sup> )	Result (µg L <sup>-1</sup> )	Recovery [%]
<sup>75</sup> As	0.20	60.450 ± 0.720	61.160	101.2
<sup>209</sup> Bi	0.10	14.090 ± 0.150	15.110	107.2
<sup>114</sup> Cd	0.03	6.568 ± 0.073	6.680	101.7
<sup>59</sup> Co	0.01	27.060 ± 0.320	27.360	101.1
<sup>52</sup> Cr	0.02	20.400 ± 0.240	19.870	97.4
<sup>85</sup> Rb	0.01	14.140 ± 0.180	13.950	98.7
<sup>123</sup> Sb	0.01	58.300 ± 0.610	59.320	101.7
<sup>78</sup> Se	0.02	11.970 ± 0.140	11.630	102.9
<sup>88</sup> Sr	0.02	323.100 ± 3.600	330.200	102.2
<sup>130</sup> Te	0.02	1.090 ± 0.110	1.111	101.9
<sup>205</sup> Tl	0.03	7.445 ± 0.096	7.601	102.1
<sup>98</sup> Mo	0.01	121.400 ± 1.300	124.000	102.1
<sup>60</sup> Ni	0.05	62.410 ± 0.690	67.200	107.7
<sup>208</sup> Pb	0.03	19.630 ± 0.210	19.350	98.6
<sup>51</sup> V	0.03	37.860 ± 0.590	38.640	102.1

The Perkin-Elmer Sciex ELAN 6100 DRC-e quadrupole spectrometer was used. The system was equipped with a Cetax 500 autosampler and a cross flow nebulizer. The spectrometer was optimized to provide maximal intensity for <sup>24</sup>Mg, <sup>115</sup>In, <sup>238</sup>U, and minimal values for CeO/Ce (below 3%) and Ba<sup>2+</sup>/Ba (below 3%). The optimum measurement conditions are presented in Table 1. The detection limits of analyzed elements are shown in Table 2. Chromium and selenium were measured using DRC-e conditions. Due to the extremely high levels of macroelements such as Ca, Mg, K and Na (especially in groundwaters), all water samples were diluted 1:1 with high purity water.

### 2.3. Reagents

All reagents used for titration were analytically pure. High purity double-distilled and deionized water for dilution and all titration reagents preparation were obtained using a Millipore's Milli-Q system. All solutions of multielemental (Merck, Germany) and mono-elemental (Sb 1000 µg L<sup>-1</sup>) standards were prepared daily by the dissolution reference materials (Merck, Germany) in water obtained from Milli-Q System (Millipore, USA) and used for the calibration. Standards, blanks and samples were measured using <sup>103</sup>Rh as internal standard (10 µg L<sup>-1</sup>, Merck, Germany). Solution of 10 µg L<sup>-1</sup> Rh was introduced into all solutions on line, by second tubing on peristaltic pump. Ultrapure concentrated nitric acid (60%, Merck, Germany) was used for adjusting samples and standard solutions acidity.

## 2.4. Quality control

The 1643e NIST (Trace elements in water, USA) reference material was used to verify the quality of the measurements. Certified values of concentration from this reference material are available for all analyzed elements in this work. Recovery experiments of CRM NIST 1643e and limits of detection are presented in Table 2. The determined values agreed well with these certified values.

## 2.5. Data processing methods

Kurtosis is a measure of flattening the distribution of characteristics. Probability distributions can be divided by the value of kurtosis for distributions: mesokurtotic - kurtosis value is 0, the flattening of the distribution is similar to the flattening of the normal distribution (for which the kurtosis is exactly 0); leptokurtotic - kurtosis is positive, the values of features more concentrated than the normal distribution; platykurtotic - kurtosis is negative, the feature value less concentrated than the normal distribution. If the probability density function (for continuous distributions) or probability mass function (discrete distributions) on the right side of its maximum decreases more slowly than the left (the distribution has "the right long tail"), the distribution is called the upward slant, positively inclined, asymmetric upward or right-sided asymmetry. Distribution of this is the expected value (average) greater than the median. An analogous situation is defined as left-skewed distribution. Kurtosis and skewness are subjected in this article to a full consideration of descriptive statistical evaluation of physico-chemical parameters [30].

The information in a Lorenz curve may be summarized by the Gini coefficient and the Lorenz asymmetry coefficient. The Gini coefficient is a measure of statistical dispersion of the data. It can be thought of as the ratio of the area that lies between the line of equality and the Lorenz curve over the total area under the line of equality. Lower (or near zero) value of the Gini coefficient indicates smaller dispersion of analyzed data. The Lorenz curve is a graphical representation of the cumulative distribution function. The Lorenz curve always starts at (0,0) and ends at (1,1) [30].

Then, the diversity of the analyzed parameters in all regions using one-way ANOVA and the Kruskal-Wallis one-way analysis of variance were examined. The Kruskal-Wallis one-way analysis of variance by ranks is a non-parametric method for testing the equality of population medians among groups. It is identical to a one-way analysis of variance with the data replaced by their ranks. The null hypothesis ( $H_0$ ) implies that there are no statistical differences in the parameter across all

regions. Opposite hypothesis ( $H_1$ ) means that the test parameter is varied across all regions [31,32].

In statistics, the Mann-Whitney U test is a non-parametric statistical hypothesis test for assessing whether two independent samples of observations have equally large values. This test can be used to investigate the differences between any two regions for all analyzed parameters [31].

Analysis of the interdependence of variables was carried out by calculating the linear Pearson correlation coefficients. The values of correlation coefficients for all sampling points are summarized in the table of correlation (Table 3). It was assumed that the regression modeling of the potential usefulness of the selected variable (explanatory) to model another variable (explained variable) determines the absolute value of the high correlation coefficient between these two variables. The statistical analysis usually assumes that if the correlation coefficient is  $>0.9$ , it means a very strong linear dependence;  $0.7-0.9$  - significant linear dependence;  $0.4-0.7$  - moderate linear dependence;  $0.2-0.4$  - distinct linear dependence, but low;  $<0.2$  - no linear dependence [30].

Measurement series were obtained by statistical correlation analysis using variance correlation test and Spearman's test. Spearman's rank correlation coefficient is a non-parametric measure of statistical dependence between two variables. If there are no repeated data values, a perfect Spearman correlation of  $+1$  or  $-1$  occurs when each of the variables is a perfect monotone function of the other. The Spearman correlation coefficient is often thought of as being the Pearson correlation coefficient between the ranked variables. The variance correlation test was used to compare the variance associated with linear regression to the residual variance. Estimated variance was compared with the array distribution critical values (F). If the absolute value of Spearman's rank correlation coefficient is greater than the critical value [33], the alternative hypothesis by correlating results of determination of elements must be accepted. If the estimation of the variance is greater or equal than the critical value, the alternative hypothesis by correlating results of determination of elements must be accepted. Otherwise, the null hypothesis of no such correlation must be accepted [34].

Also, Principal Component Analysis (PCA) was used for processing data. PCA is one of the most often applied dimensionality reduction techniques used for data compression and visualization. It could reveal similarity between large amount of samples and the relationship among the measured parameters [24,35].

Interpretation of the loadings was much easier after applying the Varimax rotation method. This very popular algorithm was proposed by H. Kaiser in 1985. The aim of the Varimax method is to find the angle that maximizes the sum of the variances of loadings. More technical details concerning these methods, together with example programs in Matlab, can be found in [36-38]. At the end of this study Cluster Analysis with the Ward technique was applied. It is quite popular clustering algorithm, which computes the Euclidean distances between samples. The aim of this method is to unify groups such that the variation inside these groups does not increase too much. As a result, homogenous groups are obtained. The calculation results can be seen on a figure, called dendrogram [27].

## 2.6. Software

All calculations were performed using Microsoft Excel 2007 and Matlab 2010a. All figures were prepared in Matlab 2010a and Corel Draw X4.

## 3. Results and discussion

### 3.1. Summary results

All 201 tap water samples were analyzed for 18 physicochemical parameters. Table 3 shows dependences on analyzed parameters as the Pearson correlation coefficients. The results are given in Table 4 together with European Union and WHO guidelines.

The permissible concentration levels of analyzed elements meet the European Council Directive. WHO recommendations [39] are generally met, except for slightly higher concentration of Cd (max. measured value:  $3.24 \mu\text{g L}^{-1}$ ; EU standard:  $3 \mu\text{g L}^{-1}$ , WHO standard:  $3 \mu\text{g L}^{-1}$ ) in some samples. The permissible level for Pb now meets EU regulations (max. measured value:  $24.8 \mu\text{g L}^{-1}$ , EU standard:  $25 \mu\text{g L}^{-1}$ ). Higher Pb content could be caused by presence of leaden connections of pipes in some old, not modernized pipelines. For some elements, such as As, Ni, Se and Sb, the obtained values are near the permissible levels.

### 3.2. Groups of samples

Better correlation coefficients were obtained when all samples were grouped into 12 sub-regions, based on the origin of the water. All groups and results are given in Supplementary Table 1. Each sample, belonging to a group, is shown as a point in a different shape in Fig. 1. Sub-region 1 is the mountainous part of the Silesian District, where soft, surface water from mountain springs

predominates. Main cities supplied with that water are: Zywiec, Bielsko-Biala, Pszczyna, Cieszyn. One part of Bedzin Poviát (with main cities: Bedzin, Czeladz, Siewierz) is provided with water from Czarna Przemsza river (sub-region 2). The other part is provided with groundwater (sub-region 3). Dabrowa Gornicza city, as the sub-region 4, is supplied with groundwater.

Drinking water for the central part of the Province is taken mainly from some surface reservoirs, such as Dzieckowice (marked in Fig. 1 as 'D'), Czaniec ('C'), and the biggest in the Province – Goczalkowice ('G'), built on the Vistula River. Some cities, such as: Tychy, Myslowice, Pszczyna, and a part of Katowice (sub-region 5) are provided with a mixture of water from Goczalkowice and Dzieckowice Water Plant. The other cities have water from Goczalkowice Water Plant with Go-Cza system (water taken from Goczalkowice and Czaniec reservoirs). The cities in GOP are supplied with water from Go-Cza system via two different pipelines. The first one runs from Murcki storage reservoir to receivers in Katowice, Chorzow, Ruda Slaska, Siemianowice and part of Sosnowiec (sub-region 6). The second pipeline runs from Mikolow reservoir, and then to consumers in Ruda Slaska, Chorzow, Mikolow, part of Katowice and Swietochlowice (sub-region 7).

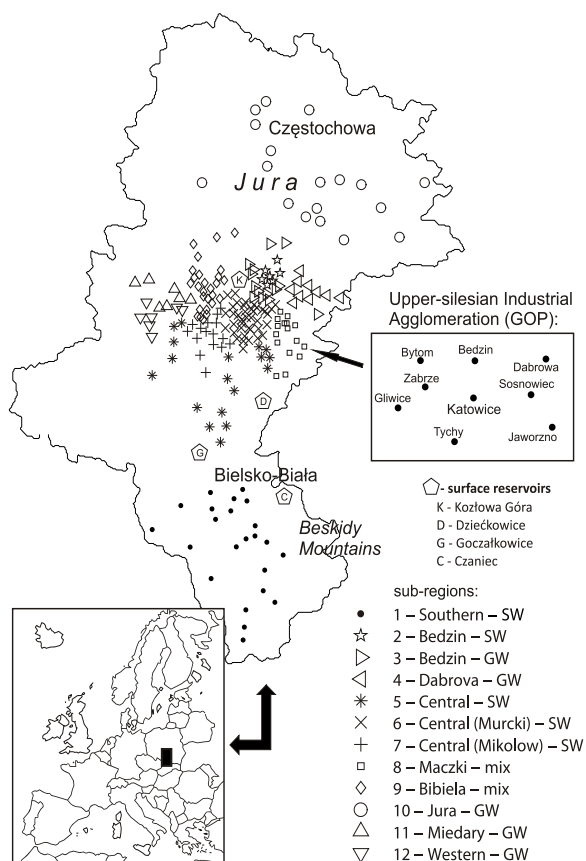
In eastern part of Sosnowiec, citizens use surface water from Maczki Water Plant (sub-region 8). In Jaworzno – drinking water from Maczki is partly mixed with groundwater. Next cities: Bytom, Piekary Slaskie and Tarnowskie Gory (sub-region 9) are provided with a mixture of groundwater from Bibiela Water Plant and surface water from Kozłowa Gora reservoir (marked as 'K' in Fig. 1). Cities in the northern part of the district: Czestochowa, Zawiercie, Myszkow (sub-region 10 - Jura) are provided with groundwater from their own supplies. Western GOP cities, such as Gliwice, Zabrze and Pyskowice are provided with groundwater from Miedary water plant (sub-region 11) or from their own supplies (sub-region 12).

All investigated groundwater samples have generally higher conductivity than surface water. Hardness, alkalinity, and pH are also higher. The hardest water is in Gliwice, Zabrze and Bedzin (sub-regions 3 and 12). The softest water comes from mountain springs in the hilly part of the province (sub-region 1). The highest mean content of arsenic ( $3.0 \mu\text{g L}^{-1}$  As) was found in groundwater from western sub-region 12 (Gliwice) and the lowest one ( $0.95 \mu\text{g L}^{-1}$  As) – in groundwater from Jura (sub-region 10). In the case of cadmium, it was observed that in the deep waters samples its concentration is generally higher than in surface waters. The highest concentration of Cd was observed



**Table 3.** Pearson correlation coefficients for all water samples (cond – conductivity, alk – alkalinity, hard - total hardness); \* values below 0.35 were omitted

pH	alk	hard	As	Bi	Cd	Co	Cr	Mo	Ni	Pb	Rb	Sb	Se	Te	TI	V	*
0.45	0.92	0.97				0.56		0.58	0.59		0.64		0.69		0.58	0.45	cond
	0.51	0.48															pH
		0.96				0.47		0.60	0.50		0.48		0.61		0.54		alk
						0.52		0.62	0.53		0.58		0.65		0.57	0.39	hard
														0.66		0.42	As
																	Bi
						0.36							0.43				Cd
								0.38	0.53		0.49		0.44		0.50	0.56	Co
										0.47			0.45		0.60		Cr
											0.51		0.45		0.60		Mo
											0.59		0.71		0.54	0.51	Ni
														0.47	0.49	0.48	Pb
																	Rb
																	Sb
															0.52	0.40	Se
																	Te
																	TI



**Figure 1.** Arrangement of 201 sampling places, mainly cities and reservoirs in the Silesian District contour map; SW – water from surface reservoirs and rivers, GW – groundwater supply, mix – a mixture of surface and groundwater.

in groundwater samples from sub-regions: 4 (Dabrowa: 1.5 µg L<sup>-1</sup>), 10 (northern - Jura: 1.3 µg L<sup>-1</sup>), and 11 (western - Miedary: 1.5 µg L<sup>-1</sup>).

This work has shown that the quality of water in the Silesian District is generally good. Most concentrations of trace elements are in agreement with Polish, European and WHO regulations. Slightly higher concentrations of some elements (such as Cd) in samples indicate the need for the systematic conduct of such research.

### 3.3. Other statistical methods

In this part of the statistical analysis the dispersion of the parameters has been shown. The results of the analysis of the Gini coefficients for all parameters are shown in Table 5. Increased value of the Gini coefficient indicates greater dispersion of data so the parameters which are mostly distributed in all regions are TI, Se, Mo, hardness and conductivity, while the parameters characterizing the smallest dispersion are pH, Pb and Te. The parameters characterizing the extreme distribution illustrated the Lorenz curves (Fig. 2). This agrees with obtained results - the highest concentration range was observed for TI - the lowest content of this metal is below 0.01 µg L<sup>-1</sup>, while the largest reaches nearly 1 µg L<sup>-1</sup>. The smallest range was found for pH (6.7 – 7.5).

Then, the diversity of the analyzed parameters in all regions using one-way ANOVA and the Kruskal-Wallis one-way analysis of variance was examined. The null hypothesis (H<sub>0</sub>) implies that there are no statistical differences in the parameter across all regions. Opposite hypothesis (H<sub>1</sub>) means that the test

**Table 4.** The results: mean, min and max  $\pm$  standard deviation for all 201 samples + WHO and EU regulations; \* - from 2014, the maximum concentration of Pb in drinking water will amount only to 10  $\mu\text{g L}^{-1}$ .

		median	mean $\pm$ SD n= 201	min	max	WHO limits	EU limits
<b>cond</b>	<b>(<math>\mu\text{S cm}^{-1}</math>)</b>	298.000	388.000 $\pm$ 257.000	81.200	1205.00	-	2500
<b>pH</b>		7.100	7.100 $\pm$ 0.300	5.900	7.90	-	6.5-9.4
<b>alk</b>	<b>(<math>\text{mg L}^{-1}</math>)</b>	2.390	2.550 $\pm$ 1.660	0.310	7.19	-	-
<b>hard</b>	<b>(<math>\text{mg CaCO}_3 \text{ L}^{-1}</math>)</b>	142.000	190.000 $\pm$ 134.000	28.400	591.00	-	60-500
<b>As</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	1.250	1.520 $\pm$ 0.850	0.390	7.48	10	10
<b>Bi</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.392	0.614 $\pm$ 0.641	< 0.100	2.88	-	-
<b>Cd</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.420	0.723 $\pm$ 0.746	< 0.030	3.24	3	5
<b>Co</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.150	0.211 $\pm$ 0.197	0.028	1.45	-	-
<b>Cr</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.742	0.885 $\pm$ 0.807	< 0.020	7.37	50	50
<b>Mo</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.358	0.602 $\pm$ 0.572	0.030	2.92	-	-
<b>Ni</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	3.630	4.220 $\pm$ 2.560	0.436	19.80	20	20
<b>Pb</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	6.720	8.310 $\pm$ 5.990	< 0.030	24.80	10	10 / 25*
<b>Rb</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	1.930	2.280 $\pm$ 1.440	0.132	11.20	-	-
<b>Sb</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.202	0.241 $\pm$ 0.167	0.044	1.09	20	5
<b>Se</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.412	0.929 $\pm$ 1.275	< 0.020	8.56	10	10
<b>Te</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	1.690	1.830 $\pm$ 0.780	0.380	4.17	-	-
<b>Tl</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.024	0.122 $\pm$ 0.278	< 0.030	1.78	-	-
<b>V</b>	<b>(<math>\mu\text{g L}^{-1}</math>)</b>	0.266	0.301 $\pm$ 0.172	< 0.030	1.16	-	-

**Table 5.** The Gini coefficients for all parameters.

pH	Pb	Te	As	Sb	Ni	V	Rb	Cr
0.0147	0.0808	0.0810	0.1410	0.1556	0.1976	0.2087	0.2356	0.2439
Bi	Co	Cd	alk	cond	hard	Mo	Se	Tl
0.2499	0.2616	0.2773	0.2862	0.3129	0.3153	0.3595	0.4732	0.6532

parameter is varied across all regions. The results are summarized in Table 6. The Kruskal-Wallis test gives similar results as a more powerful one-way ANOVA. Table 6 presents the value of F and chi, which are the critical values for the corresponding levels of significance (5% and 1%) for the F distribution and the distribution of chi-square. If the calculated value is greater than the F or chi critical we should reject the null hypothesis ( $H_0$ -no differences between the regions), assuming the alternative hypothesis ( $H_1$ ) of the statistical variation for the physico-chemical parameter in all 12 regions. The largest differences occur for conductivity and the lowest for Pb.

The results obtained with one-way ANOVA and the Kruskal-Wallis test suggested a detailed analysis for the most extreme parameters. Therefore, conductivity and Pb were tested by the Mann-Whitney U test (Table 7). Null hypothesis is no difference between the two regions from 12 ( $H_0$ ), while the alternative hypothesis

is differentiation of these considered two regions ( $H_1$ ). Since conductivity was the most varied parameter among all, therefore almost all of the two regions have statistically different conductivity. In turn, because Pb showed no differences in all regions, so usually every two regions do not differ in the concentration of Pb.

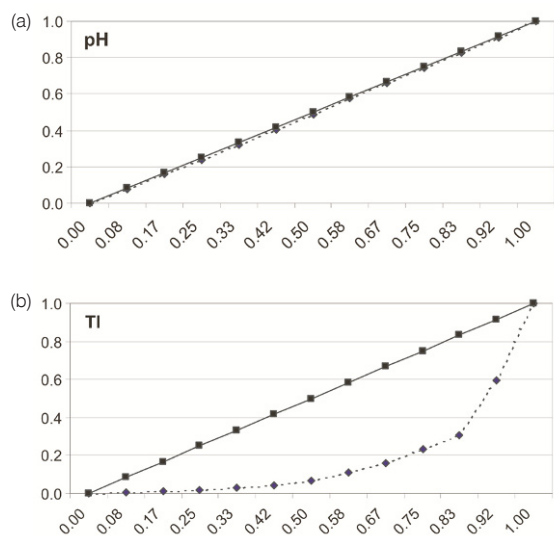
The Pearson correlation coefficients table allows to select the next variables modeled (explained variable) of the most important explanatory variables. The values of correlation coefficients are given in Supplementary Table 2. In turn, selected potential explanatory variables are summarized in Table 8. The overview allows to select specific physical and chemical parameters for explanatory variables repeated in various locations.

While examining cross-correlations between the physico-chemical parameters, the following conclusions were obtained: most of the existing correlation was observed for sub-regions 2, 3, 4, 11 and 12 (mainly for groundwaters). The strongest line correlations

depending on the level of the Pearson correlation coefficients  $r \geq 0.65$  are observed between Te and As (max: 0.94 for sub-regions 1 and 4). Tellurium is associated with sulphide minerals, mainly in the

gold, antimony, copper, mercury and arsenic zones of mineralization. Despite the fact that the migration of Te compounds into the aquatic environment is small, our study showed a strong correlation between the concentrations of Te and As occurring in the waters of the GOP. This is probably related to the processes of biological methylation of tellurium, which in this case behaves similarly to selenium and arsenic [7]. Large dependences were also observed between V, Se, Te and other elements and parameters.

In the next step, statistical correlation analysis using variance correlation test and Spearman's test were applied. The regions characterized by the highest correlation (for  $r_s > 0.9$ ) due to the physicochemical parameters studied are 6 and 7 (1.000), 5 and 6 (0.973), 5 and 7 (0.973), 3 and 4 (0.918), 3 and 8 (0.909) and 9 and 12 (0.909). However, sub-regions showing a low correlation (for  $r_s < 0.4$ ) are: 1 and 4, 1 and 11, 7 and 11. Similar conclusions as to the Spearman test were obtained using variance correlation test, e.g. maximum value = high correlation: 442 for sub-regions 7 and 6, minimum value = low correlation: 1.41 for sub-regions 11 and 7 (Table 9).



**Figure 2.** Graphical representation of the Lorenz curves for pH and TI.

**Table 6.** The results of ANOVA test and the Kruskal-Wallis (K.W.\*) one-way analysis of variance.

	cond	pH	alk	hard	As	Bi	Cd	Co	Cr	Mo	Ni	Pb	Rb	Sb	Se	Te	Tl	V
<b>ANOVA</b>	189	9.99	93.5	143	3.53	3.65	5.83	11.3	7.67	24.3	11.6	0.66	16.3	2.96	27.7	1.96	27.1	9.69
	<b><math>F=1.93</math> (5%), <math>2.37</math> (1%)</b>																	
<b>K.W.*</b>	177	85.4	161	169	33.2	21.3	33.8	70.2	15.7	102	76.9	13.9	78.8	40.2	141	21.7	113	60.9
	<b><math>chi=19.7</math> (5%), <math>24.7</math> (1%)</b>																	

**Table 7.** The Mann-Whitney U test; s-r –sub-region number,  $H_0$  – no differences between two regions,  $H_1$  – differences between two regions.

	Conductivity											
	s-r 1	s-r 2	s-r 3	s-r 4	s-r 5	s-r 6	s-r 7	s-r 8	s-r 9	s-r 10	s-r 11	s-r 12
<b>s-r 1</b>		$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$
<b>s-r 2</b>	$H_0$		$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_0$	$H_0$	$H_0$	$H_0$	$H_1$
<b>s-r 3</b>	$H_0$	$H_0$		$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_0$
<b>s-r 4</b>	$H_0$	$H_0$	$H_0$		$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_0$	$H_1$
<b>s-r 5</b>	$H_0$	$H_1$	$H_0$	$H_0$		$H_0$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$
<b>s-r 6</b>	$H_0$	$H_1$	$H_0$	$H_0$	$H_0$		$H_0$	$H_1$	$H_1$	$H_1$	$H_1$	$H_1$
<b>s-r 7</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_1$	$H_0$		$H_1$	$H_1$	$H_1$	$H_1$	$H_1$
<b>s-r 8</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$		$H_1$	$H_1$	$H_0$	$H_1$
<b>s-r 9</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$		$H_0$	$H_1$	$H_1$
<b>s-r 10</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_1$	$H_0$	$H_0$	$H_0$	$H_0$		$H_1$	$H_1$
<b>s-r 11</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$		$H_1$
<b>s-r 12</b>	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	$H_1$	$H_0$	$H_0$	$H_0$	$H_0$	$H_0$	

Concentration of Pb



**Table 8.** The most important explanatory variables selected on the basis of an analysis of the Pearson coefficients of correlation values ( $r \geq 0.65$ ); „-“ means no correlation, s-r – sub-region number.

	s-r 1	s-r 2	s-r 3	s-r 4	s-r 5	s-r 6	s-r 7	s-r 8	s-r 9	s-r 10	s-r 11	s-r 12
<b>As</b>	-	cond	-	-	-	-	alk	-	-	-	-	-
<b>Bi</b>	-	pH	-	cond	pH	-	-	-	-	pH	alk	pH
<b>Cd</b>	-	hard	-	-	-	-	-	-	-	-	cond, hard	As
<b>Co</b>	-	cond, As	-	-	-	-	-	-	-	-	cond, alk, hard, Bi, Cd	As, Cd
<b>Cr</b>	-	cond, As, Co	-	-	-	-	-	-	-	Co	cond, alk, Bi	Bi
<b>Mo</b>	-	cond, As, Co, Cr	-	-	-	-	-	-	-	cond	Bi, Cr	alk, Bi
<b>Ni</b>	As	cond, As, Co, Cr, Mo	-	-	-	-	-	Mo	-	-	cond, As	pH, As, Bi, Co, Cr
<b>Pb</b>	-	cond, hard, Cd	Ni	Cd, Co	-	-	-	-	-	-	Bi, Cd, Co	Mo
<b>Rb</b>	-	cond, As, Co, Cr, Mo, Ni	-	cond, hard	-	-	-	Mo, Ni	-	-	cond, alk, hard, Cd, Co	As, Cd, Co, Cr, Ni
<b>Sb</b>	-	cond, hard, Bi, Cr, Pb, Rb	Pb	Cd, Co, Pb	Rb	-	Mo	-	-	Mo	-	Cr
<b>Se</b>	-	As, Co, Mo, Ni	Pb, Sb	Cd, Co, Pb, Sb	-	-	Ni	Sb	Cd	As	cond, alk, Rb, Sb	hard, Bi, Cr, Ni, Sb
<b>Te</b>	As	Bi, Se	-	As, Rb	As	As	As	-	As	-	As, Ni	pH, As, Bi, Co, Cr, Ni, Rb, Se
<b>Tl</b>	Rb	cond, As, Co, Cr, Mo, Ni, Rb, Se, Tl	Ni	Rb	-	-	-	-	-	-	Mo	cond, pH, hard, Bi, Cr, Rb, Se, Te
<b>V</b>	-	cond, As, Co, Cr, Mo, Ni, Rb, Se, Tl	Co	As, Cr, Te, Tl	Cr	-	-	Ni, Rb	-	-	cond, alk, Cd, Co, Ni, Rb, Se	pH, As, Co, Ni, Te

### 3.4. Principal component analysis and cluster analysis

PCA chemometric technique was very helpful in finding the relationship among water samples. All analytical results were put together in one 201×18 matrix (*samples×parameters*) and were autoscaled. Then, the singular value decomposition (SVD) algorithm was used [35]. After calculating the cumulative percentage of variance it was possible to see the percentage of the variability, described by all principal components. The first principal component (PC1) is the most important, it describes most of the total variability of data (above 35%). The first two PCs describes above 50% of the total variance, the

first three PCs - about 60%, the first four PCs - almost 70% and the first five PCs – about 75%. The other main components explain less variance of data.

Then, the Varimax rotation method was applied and the plot of the main component weights (loadings), which shows all analyzed parameters, was drawn (Fig. 3).

If the angle between the vectors joining the point scales with the beginning of the coordinate system is close to 0 degrees, then the correlation between the parameters is very high (see Pearson correlation coefficients in Table 3, e.g. alkalinity-hardness: 0.96, conductivity-hardness: 0.97). In the case of 90 or 270 degree angles the dependencies are very small, e.g. Te-conductivity: 0.12). At angles close

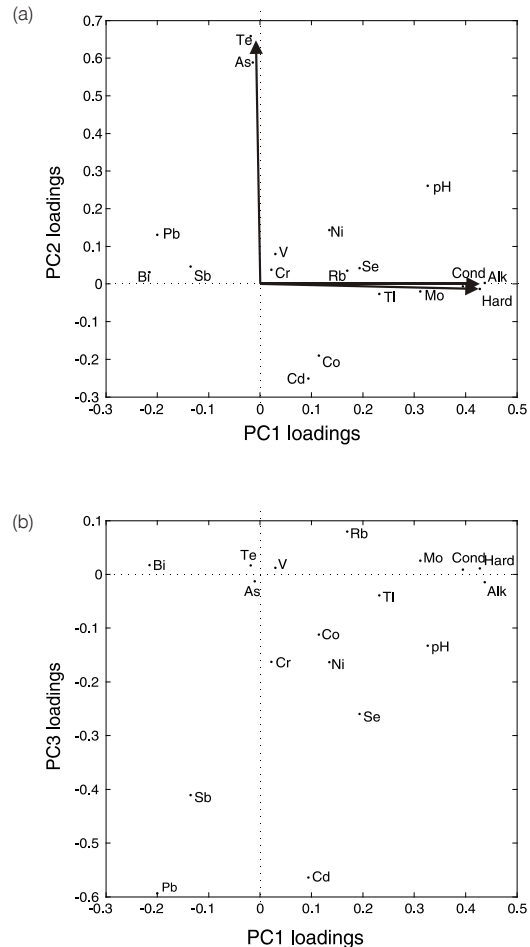
**Table 9.** Spearman's rank correlation coefficient and variance correlation test; s-r – sub-region number.

	s-r 1	s-r 2	s-r 3	s-r 4	s-r 5	s-r 6	s-r 7	s-r 8	s-r 9	s-r 10	s-r 11	s-r 12	Spearman's rank correlation coefficient ( $r_s$ ) critical values: $r_{s,0.05} = 0.618$ ; $r_{s,0.01} = 0.755$	
s-r 1		0.609	0.482	0.300	0.845	0.845	0.845	0.527	0.718	0.591	0.373	0.791		
s-r 2	8.32		0.827	0.736	0.736	0.691	0.691	0.709	0.864	0.600	0.564	0.773		
s-r 3	2.21	20.2		0.918	0.582	0.500	0.500	0.909	0.845	0.800	0.709	0.855		
s-r 4	3.46	10.9	50.7		0.445	0.409	0.409	0.855	0.755	0.809	0.745	0.682		
s-r 5	60.0	17.5	3.23	2.59		0.973	0.973	0.664	0.818	0.645	0.436	0.791		
s-r 6	26.0	18.8	3.19	2.05	99.1		1.000	0.618	0.764	0.582	0.355	0.718		
s-r 7	33.7	16.0	2.70	1.90	153	442		0.618	0.764	0.582	0.355	0.718		
s-r 8	9.70	29.4	36.5	41.8	9.39	10.6	8.62		0.864	0.773	0.618	0.864		
s-r 9	27.9	22.2	12.4	19.3	19.1	13.0	11.8	57.0		0.745	0.764	0.909		
s-r 10	6.10	10.1	21.2	45.8	3.44	3.11	2.93	36.8	25.3		0.800	0.800		
s-r 11	3.71	4.73	12.9	19.8	2.21	1.45	1.41	11.8	10.4	21.0		0.673		
s-r 12	9.05	35.4	42.3	22.0	11.6	9.64	8.43	51.8	47.2	29.1	12.4			
<b>Estimation of the variance</b> critical values: $F_{0.05} = 5.12$ ; $F_{0.01} = 10.56$														

to 180 degrees the values are inversely correlated. Points lying near the beginning of the coordinate system could not be taken into account, because their vectors are just the projection on this plane. Table 10 shows selected factor loadings obtained for the first five PCs. It may be assumed that the axis of PC1 will describe the degree of water mineralization, which is associated with the level of conductivity, alkalinity and hardness. PC1 axis can be conditionally named "water mineralization". Thus, the creation of PC2 is associated mainly with Te and As. The third PC is associated with Cd and Pb. PC4 is related mainly to Bi. The last factor is associated mainly with Cr. The proposed conditional names of these PCs were also shown in Table 10.

The projection of the main components scores (PC1 to PC2 and PC1 to PC3) was also plotted (Fig. 4). It represents the relations between all the analyzed samples. When two data points on the plot are closer together, they are more similar to each other. The differences are larger when the distance increases [24]. PCA score plot helped in deducing the degree of water mineralization.

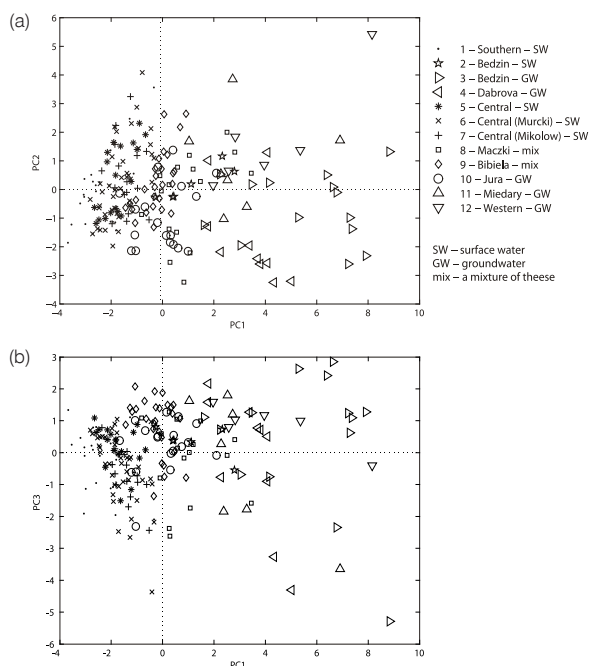
To make the score plot (Fig. 4) more transparent and easier to interpret, all objects from each group are presented using a different symbol. Samples of surface water with lower conductivity and hardness appear to the left of the figure (negative values of PC1). Highly mineralized waters appear on the right side of the figure (positive values of PC1). Mixture of surface and deep in the middle is followed by a cloud of data. The exception is the Bedzin SW group (sub-region 2), in which the samples have a slightly greater degree of



**Figure 3.** Loading plots - parameters on the plane spanned by: (a) PC 1 and PC 2, (b) PC 1 and PC 3.

**Table 10.** Factor loadings (values below 0.20 were omitted).

	PC1	PC2	PC3	PC4	PC5
'Cond'	0.39				
'pH'	0.33	0.26		-0.35	
'Alk'	0.44				
'Hard'	0.43				
'As'		0.59			
'Bi'	-0.21			0.53	
'Cd'		-0.25	-0.56		
'Co'				0.37	0.21
'Cr'					0.62
'Mo'	0.31				
'Ni'				0.28	
'Pb'	-0.20		-0.59		
'Rb'				0.36	
'Sb'			-0.41		-0.46
'Se'			-0.26		
'Te'		0.66			
'TI'	0.23				-0.33
'V'				0.33	0.40
<b>conditional name</b>	<i>water mineralization</i>	As+Te	Cd+Pb	Bi	Cr
<b>explained variance</b>	36.1%	14.2%	10.5%	7.9%	5.8%

**Figure 4.** PCA score-plots: (a) all samples on the plane spanned by PC 1 and PC 2, (b) all samples on the plane spanned by PC 1 and PC 3.

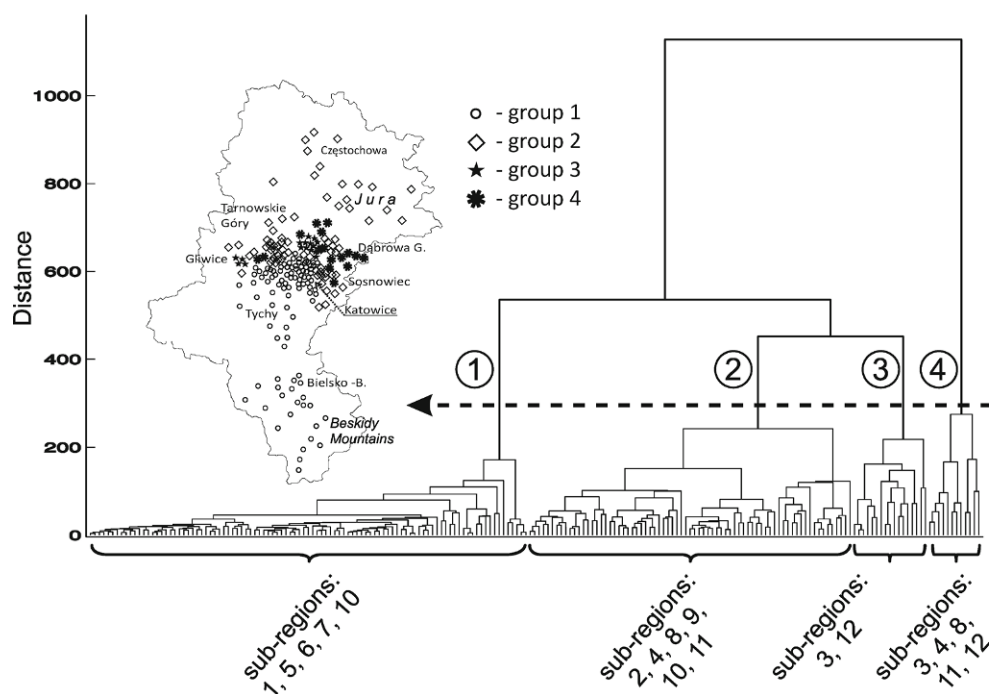
mineralization, as well as water from Jura region (sub-region 10), where mineralization is lower. It was also observed that samples of surface water (SW) and mixed water (SW+GW) are clustered in one group, while the

groundwater (GW) of the Bedzin, Czeladz, Zabrze and Gliwice samples are scattered.

Also, Cluster Analysis with the Ward's linkage method was applied to the data set. The results for each sub-region were shown in the dendrogram on Fig. 5. The selected level of similarity was about 30% of the maximal similarity distance. Together with the dendrogram, map of the Silesian District with all samples was attached.

This dendrogram shows the similarity of water samples based on their chemical composition. Four main groups are visible. Group 1 is represented mainly by surface water samples, with low degree of mineralization. These samples come from the southern part of the district. Group 2 contains middle mineralized surface and groundwaters (mainly – the northern part of the district). Groups 3 and 4 are represented by groundwaters with higher degree of mineralization (some cities in central part of the province: e.g. Gliwice, Dabrova Gornicza, Bedzin). The results of sub-regions clustering are quite similar to the results obtained from the variance correlation test and Spearman's test (Table 9).

This dendrogram also showed the differences within the sub-region (e.g. 8 - Jaworzno and eastern part of Sosnowiec). This could be caused by different amounts of surface and groundwater in the mixture in each city. In Jaworzno, surface water from Maczki Water Plant is mixed with more amount of groundwater.



**Figure 5.** The dendrogram and the map showing the clustering of all samples from the Silesian District.

In conclusion, these chemometric methods showed that the correlation between the studied parameters can be easily determined. The degree of mineralization of water also could be easily specified. Those methods were perfect for the study of water samples from unknown sources - the origin of the water (surface sources or underground intakes) could be easily determined from resulting plots.

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## Abbreviations

WHO	- World Health Organization
UE	- European Union
ICP-MS	- Inductively Coupled Plasma Mass Spectrometry
SW	- Water from surface reservoirs
GW	- Groundwater
mix	- a mixture of surface water and groundwater
PCA	- Principal Component Analysis
CA	- Cluster Analysis
SVG	- Singular Value Decomposition
s-r	- sub-region
cond	- Conductivity of water
alk	- Alkalinity
hard	- Total hardness

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