

## GROUNDWATER QUALITY FROM WATER WELLS OF THE KOPRIVNICA-KRIZEVSCI COUNTY, NORTHWESTERN CROATIA

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### ABSTRACT

The aim of this study was to investigate during two-years monitoring campaign the physicochemical and microbiological quality of groundwater from water wells of the Koprivnica-Križevci County in Northwestern part of Croatia. Tested groundwaters are used as the sources of drinking water for local population i.e. over 115.000 people, and they are originated from few aquifers with different geological structure and terrain morphology, which has a significant impact on the groundwater quality.

A groundwater samples were taken from five water wells (Ivanščak, Trstenik, Vratno, Đurđevac and Delovi) were analyzed on seven microbiological parameters (total coliforms, *Escherichia coli*, colony count at 22°C and 37°C, enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringens*) and forty seven physical and chemical parameters. Since recent studies shown frequent appearance of heightened nitrate concentrations in natural waters in Koprivnica-Križevci County, due to relatively high degree of agriculture activity, among analyzed parameters, special focus of interest was nitrate concentration in sampled water wells.

Comparing the concentrations of dominant anions and cations at sampled groundwaters, the water-bearing zones are determined. The results shown that groundwater samples taken from water well Delovi continuously were non-compliance due to regulation because of elevated values of turbidity and total iron concentration. All other groundwaters sampled during this two-years study was in compliance with Croatian regulations and European Directive.

**Keywords:** groundwater quality, water wells, water-bearing zones, Koprivnica-Križevci County, Croatia

### 1. Introduction

Koprivnica-Križevci County is placed in northwest part of the Republic of Croatia. This County, with over 115.000 inhabitants and total area of 1748 km<sup>2</sup>, borders from the northeast side with the Republic of Hungary and with five other Croatian Counties.

The groundwater is the main source of drinking water for the population of Koprivnica-Križevci County and the most of groundwaters are obtained from five largest water-wells.

Previous researches (Nemčić-Jurec *et al.* 2007; Nemčić-Jurec *et al.* 2013) emphasized the problem of heightened nitrate concentrations in the groundwaters at the area of Koprivnica-Križevci County due to a relatively high degree of agricultural activity.

The previous hydrogeological researches implied the existence of few aquifers with different geological structure and terrain morphology, which can also have a significant impact on the groundwater quality (Nemčić-Jurec *et al.* 2007; Nemčić-Jurec *et al.* 2013).

The aim of this study was to investigate the quality of groundwater sampled from five main water-wells in the area of Koprivnica-Križevci County and to determined water-bearing zones. The quality of groundwater were determined during this two-years study via seven microbiological parameters (total coliforms, *Escherichia coli*, colony count at 22°C and 37°C,

enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringens*) and over forty physical and chemical parameters, while the water-bearing zones were determined comparing the concentrations of dominant anions and cations at sampled groundwaters.

## 2. Methods and materials

### 2.1. Sampling area

As it was already mentioned, Koprivnica-Križevci County is placed on northwest of Croatia and northwest part of Pannonian basin (Fig 1). This area is characterized by agricultural activity and significant number of oil and gas drillholes. The lowland part of this area is makes Drava river valley while mountain part makes Kalnik hills and Bilogora (<http://kckzz.hr/en/>).



**Figure 1:** Map of the Koprivnica-Križevci County and location of four examined wells.

### 2.2. Sampling, analysis and regulations

Groundwater samples from five tested water-wells (Trstenik, Vratno, Ivanščak, Đurđevac and Delovi) were collected quarterly during two-year study (2011-2012).

All samples were taken into polyethylene bottles and maintained at 4°C until laboratory analysis. Following microbiological analysis of collected groundwater samples were conducted: total coliforms, *Escherichia coli*, colony count at 22 °C and 37°, enterococci, *Clostridium perfringens* and *Pseudomonas aeruginosa*.

Within this two-years study, following physicochemical parameters was regularly determined: temperature, color, turbidity, odor, taste, pH, conductivity, total solids dried at 105°C, total suspended solids, chemical oxygen demand (COD), hardness, hydrogen sulfide, ammonium, nitrite, nitrate, hydrogencarbonate, fluoride, calcium, potassium, sodium, magnesium, phosphate, chloride, sulfate, cyanide, silicate, lead, cadmium, arsenic, zinc, iron, nickel, chromium, manganese, copper, mercury, selenium, aluminum, and cobalt. The total organic carbon (TOC) and organic compounds: phenols, mineral oils, organochloride pesticides, delta-HCH, endosulfan and PAH were also determined.

All above mentioned microbiological and physicochemical water quality parameters were determined using accredited HRN EN ISO analytical methods. Used analytical methods and results interpretation were due to provisions of Croatian Regulations of parameters compliance and analysis methods of water for human consumption (MZHR, NN 125/2013) which has been written in accordance with European Community Directive guidelines (98/83/EC) and quotes maximum permissible level (MPL) for each water quality parameter.

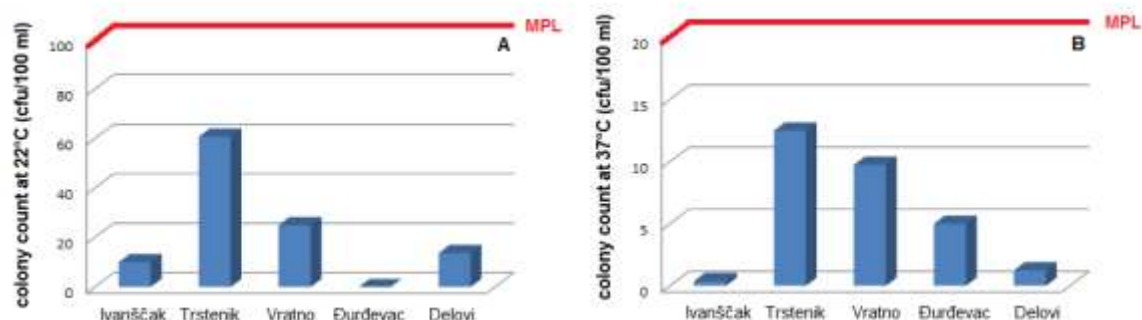
### 3. Results

Five main groundwater-wells (Ivanščak, Trstenik, Vratno, Đurđevac and Delovi), used as sources of drinking water for the population of Koprivnica-Križevci County, have been quarterly sampled during two-years and analyzed on seven microbiological and forty seven physical and chemical parameters.

#### 3.1. Microbiological parameters

A total of 80 groundwater samples were analyzed for total coliforms, *Escherichia coli*, colony count at 22°C and 37°C, enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringens* using accredited methods due to Croatian Regulations of parameters compliance and analysis methods of water for human consumption (MZHR, NN 125/2013). Total coliforms, *Escherichia coli*, enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringens* were not detected in any of analyzed groundwater sample. The positive results of microbiological analysis were obtained when groundwater samples were tested for colony count at 22°C and 37°C. Colony count is microbiological parameter that indicates the presence of the general population of heterotrophic bacteria in water whose natural habitat is the water environment or they originated from soil or vegetation (EA UK, 2002). The average values of colony count at 22°C and 37°C obtained via microbiological analysis of groundwater from five water-wells are presented at Figure 2. As it can be observed from Figure 2A, those results were in compliance with Regulations, although one sample, taken from water-well Trstenik during the second sampling in 2011, had value of colony count at 22°C of 300 cfu/100 ml. In all other tested groundwater samples during this two-years study, obtained values of colony count at 22°C were below maximum permissible level of 100 cfu/100 ml due to Croatian and European Regulation.

The above mentioned groundwater sample taken from water-well Trstenik, also had the highest noted value of colony count at 37°C (60 cfu/100 ml) which was also over maximum permissible level of 20 cfu/100 ml. All other analyzed groundwater sample from Trstenik and the rest of four water-wells had values of colony count at 37°C below MPL.

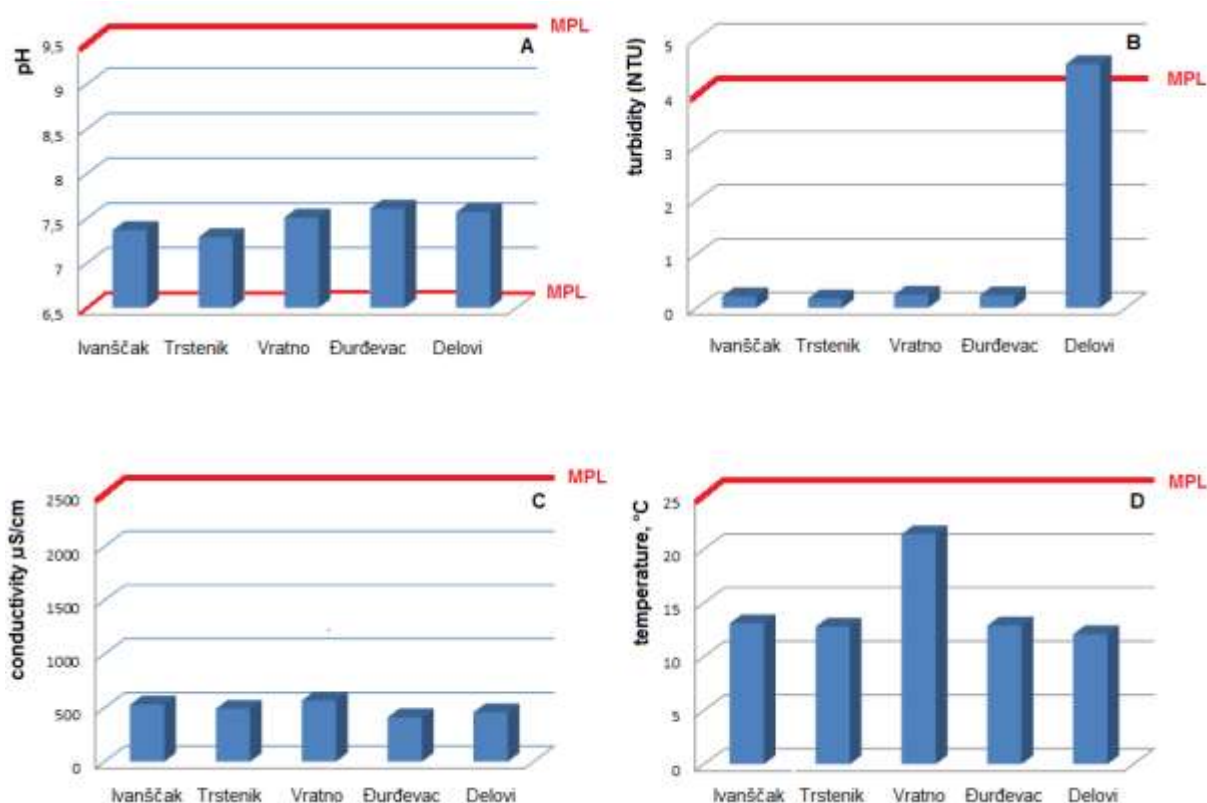


**Figure 2:** Average values of colony count at 22°C and 37°C of groundwaters sampled from five water-wells at the Koprivnica-Križevci County.

#### 3.2. Physicochemical parameters

Within this study forty seven following physicochemical parameters was determined quarterly during two-years period (2011-2012): temperature, color, turbidity, odor, taste, pH, conductivity, total solids dried at 105°C, total suspended solids, chemical oxygen demand (COD), hardness and hydrogen sulfide, ammonium, nitrite, nitrate, hydrogencarbonate, fluoride, calcium,

potassium, sodium, magnesium, phosphate, chloride, sulfate, cyanide, silicate, lead, cadmium, arsenic, zinc, iron, nickel, chromium, manganese, copper, mercury, selenium, aluminum, cobalt, total organic carbon, phenols, mineral oils, anionic detergents, organochloride pesticides, delta-HCH, endosulfan and PAH. All mentioned parameters were determined using accredited analytical methods and compared with MCL values regulated with Croatian Regulations of parameters compliance and analysis methods of water for human consumption (MZHR, NN 125/2013).

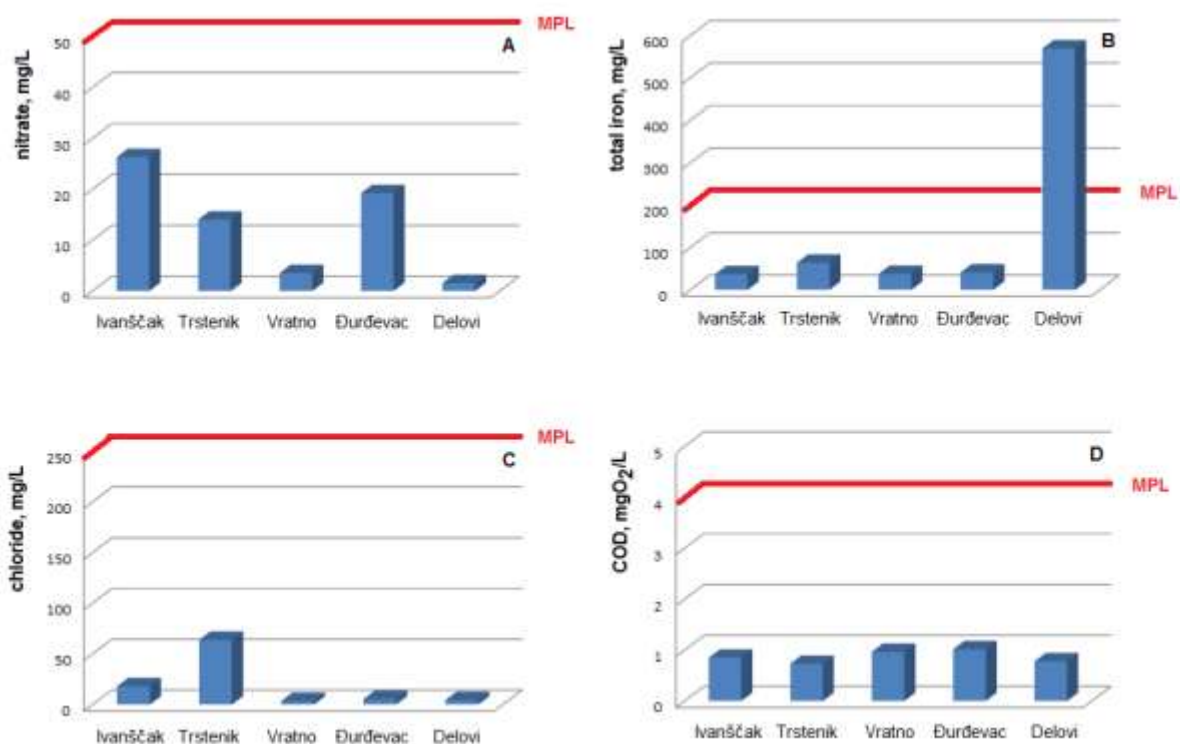


**Figure 3:** Average values of pH, turbidity, conductivity and temperature of groundwaters sampled from five water-wells at the Koprivnica-Križevci County.

Figure 3 and 4 shows average values of pH, turbidity, conductivity, temperature, nitrates, total iron, chlorides and COD of groundwaters sampled from five water-wells at the Koprivnica-Križevci County. As it can be observed, all parameters at all tested groundwaters, except groundwater from water-well Delovi, were less than MCL. Study shown (Fig 3B) that groundwater from Delovi had average value of turbidity 5.2 NTU (min. 0.3 NTU; max. 60 NTU) which was higher than MPL of 4 NTU. From the Figure 3D it also can be observed that heightened temperatures of groundwater were measured in groundwater samples from water-well Vratno (min. 20.7 $^{\circ}\text{C}$ ; max. 22.4 $^{\circ}\text{C}$ ) but measured temperatures were still less than MPL of 25 $^{\circ}\text{C}$ .

From Figure 4B it can be observed that the groundwater from the same water well Delovi, also had average total iron concentration (min. 55.4 mg/L; max 1620 mg/L) higher than MPL of 200 mg/L.

Although previous studies reported occurrence of heightened nitrate concentration in some groundwater at examined area (Nemčić *et al.* 2007; Nemčić-Jurec *et al.* 2013), during our study nitrate concentration at all groundwater samples taken from five water wells were than MPL. The higher concentrations were detected at groundwater sampled form water well Ivanščak (min. 20 mg/L; max. 29.9 mg/L).



**Figure 4:** Average values of nitrates, total iron, chlorides and COD of groundwaters sampled from five water-wells at the Koprivnica-Križevci County.

All other measured physicochemical parameters had average values less than MPL determined via Croatian Regulation and European Directive (total solids dried at 105°C - max. 480 mg/L (Ivanščak) – MPL <1000 mg/L; total suspended solids – max. 8 mg/L (Delovi) – MPL 10 mg/L; chemical oxygen demand (COD) – max. 3.0 mgO<sub>2</sub>/L (Vratno) – MPL 5.0 mgO<sub>2</sub>/L; hardness max. 316 mg CaCO<sub>3</sub>/L (Vratno); hydrogen sulfide - <0.002 mg/L (all analyzed groundwater samples) – MPL without; ammonium – <0.3 mg/L (all analyzed groundwater samples) - MPL 0.5 mg/L; nitrite – <0.1 mg/L - (all analyzed groundwater samples) – MPL 0.5 mg/L; hydrogencarbonate – max. 150 mg/L (Ivanščak); fluoride – max. 0.281 mg/L (Ivanščak) – MPL 1.5 mg/L; calcium – max. 94 mg/L (Vratno); potassium – max. 1.05 mg/L (Ivanščak) – MPL 12 mg/L; sodium – max. 18 mg/L (Ivanščak) – MPL 200 mg/L; magnesium – max. 30 mg/L (Ivanščak), phosphate - max. 0.098 mg/L (Delovi) – MPL 0.3 mg/L; chloride - max. 25.7 mg/L (Ivanščak) – MPL 250 mg/L; sulfate - max. 40 mg/L (Vratno) – MPL 250 mg/L; cyanide - <0.01 mg/L (all analyzed groundwater samples) – MPL 0.05 mg/L; silicate - max. 19.5 mg/L (Trstenik) – MPL 300 mg/L; lead - max. 0.5 µg/L (Ivanščak) – MPL 1 µg/L; cadmium - < 0.1 µg /L (all analyzed groundwater samples) – MPL 0.5 µg/L, arsenic – 6.9 µg /L (Delovi) – MPL 10 µg/L; zinc – 40.9 µg /L (Ivanščak) – MPL 3000 µg/L; nickel – 17 µg /L (Ivanščak) – MPL 20 µg/L; chromium – 9.8 µg /L (Vratno) – MPL 50 µg/L; manganese – 36.2 µg /L (Trstenik) – MPL 50 µg/L; copper – 11 µg /L (Trstenik) – MPL 2000 µg/L; mercury – 0.7 µg /L (Delovi) – MPL 1 µg/L; selenium – 1.4 µg /L (Ivanščak) – MPL 10 µg/L; aluminum – <0.1 µg/L (all analyzed groundwater samples) – MPL 0.2 µg/L; total organic carbon - max. 2.1 mg/L (Ivanščak); phenols - max. 0.01 µg/L (Delovi); mineral oils -17.5 µg/L (Delovi) – MPL 20 µg/L; organochloride pesticides - <0.01 µg/L (all analyzed groundwater samples) – MPL 0.5 µg/L; delta-HCH -- <0.01 µg/L (all analyzed groundwater samples); endosulfan - <0.01 µg/L (all analyzed groundwater samples); PAH - <0.01 µg/L (all analyzed groundwater samples) – MPL 0.1 µg/L).

### 3.3. Determination of water-bearing zones

Determination of water-bearing zones helps to define origin of groundwater i.e. replay to the question does the groundwater cached from different water-wells belongs to same aquifer.

**Table 1:** Percentages in differences among average concentrations of dominant anions and cations in tested groundwaters.

| <b>hydrogencarbonate</b> |          |          |        |          |        |
|--------------------------|----------|----------|--------|----------|--------|
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 9.5      | 16.5   | 8.7      | 16.6   |
| Trstenik                 | 9.5      | -        | 24.5   | 0.9      | 24.5   |
| Vratno                   | 16.5     | 24.5     | -      | 23.8     | 0      |
| Đurđevac                 | 8.7      | 0.9      | 23.8   | -        | 23.8   |
| Delovi                   | 16.6     | 24.5     | 0      | 23.8     | -      |
| <b>chloride</b>          |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 6.5      | 78.7   | 66       | 71.3   |
| Trstenik                 | 6.5      | -        | 80.0   | 68.1     | 25.6   |
| Vratno                   | 78.7     | 80.0     | -      | 37.3     | 73.1   |
| Đurđevac                 | 66       | 68.1     | 37.3   | -        | 15.7   |
| Delovi                   | 71.3     | 73.1     | 25.6   | 15.7     | -      |
| <b>nitrate</b>           |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 48       | 88.8   | 20.0     | 93.2   |
| Trstenik                 | 48       | -        | 78.5   | 35.0     | 86.9   |
| Vratno                   | 88.8     | 78.5     | -      | 86.0     | 39.3   |
| Đurđevac                 | 20.0     | 35.0     | 86.0   | -        | 91.5   |
| Delovi                   | 93.2     | 86.9     | 39.3   | 91.5     | -      |
| <b>sulfate</b>           |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 7.4      | 32.4   | 56       | 75.2   |
| Trstenik                 | 7.4      | -        | 27     | 59.3     | 77.0   |
| Vratno                   | 32.4     | 27       | -      | 70.3     | 83.2   |
| Đurđevac                 | 56       | 59.3     | 70.3   | -        | 43.6   |
| Delovi                   | 75.2     | 77.0     | 83.2   | 43.6     | -      |
| <b>sodium</b>            |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 7.7      | 76.2   | 54.6     | 43.9   |
| Trstenik                 | 7.7      | -        | 74.2   | 50.8     | 39.2   |
| Vratno                   | 76.2     | 74.2     | -      | 47.5     | 57.5   |
| Đurđevac                 | 54.6     | 50.8     | 47.5   | -        | 19.2   |
| Delovi                   | 43.9     | 39.2     | 57.5   | 19.2     | -      |
| <b>potassium</b>         |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 50.0     | 27.3   | 11.3     | 0      |
| Trstenik                 | 50.0     | -        | 90.9   | 43.7     | 50.0   |
| Vratno                   | 27.3     | 90.9     | -      | 35.5     | 27.3   |
| Đurđevac                 | 11.3     | 43.7     | 35.5   | -        | 11.2   |
| Delovi                   | 0        | 50.0     | 27.3   | 11.2     | -      |
| <b>magnesium</b>         |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 28       | 24     | 32       | 20     |
| Trstenik                 | 28       | -        | 5.3    | 5.6      | 10     |
| Vratno                   | 24       | 5.3      | -      | 10.5     | 5.0    |
| Đurđevac                 | 32       | 5.6      | 10.5   | -        | 15     |
| Delovi                   | 20       | 10       | 5.0    | 15       | -      |
| <b>calcium</b>           |          |          |        |          |        |
|                          | Ivanščak | Trstenik | Vratno | Đurđevac | Delovi |
| Ivanščak                 | -        | 26.3     | 16.5   | 5.26     | 11.8   |
| Trstenik                 | 26.3     | -        | 38.5   | 22.2     | 16.4   |
| Vratno                   | 16.5     | 38.5     | -      | 20.9     | 26.4   |
| Đurđevac                 | 5.26     | 22.2     | 20.9   | -        | 6.9    |
| Delovi                   | 11.8     | 16.4     | 26.4   | 6.9      | -      |

Determination is made based on the difference between average concentration of dominant anions and cations. If the difference among concentrations is larger than 15%, then it can be estimated that groundwaters cached from different wells belongs to different aquifers. Calculated percentages in difference among average concentrations of dominant anions (hydrogencarbonate, chloride, nitrate, sulfate) and cations (sodium, potassium) in tested groundwaters are presented in Table 1 where it can be observed that percentages in difference between concentrations of dominant anions and cations is, in most of cases, larger than 15% which suggest that tested groundwaters from five water wells belongs to five different water-bearing zone i.e. aquifer.

#### 4. Conclusions

This study investigated quality of groundwater from five largest water wells of the Koprivnica-Križevci County in Northwestern part of Croatia (Ivanščak, Trstenik, Vratno, Đurđevac and Delovi). A groundwaters were sampled during this two-years study (2011-2012) and analyzed on seven microbiological parameters (total coliforms, *Escherichia coli*, colony count at 22°C and 37°C, enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringers*) and forty seven physicochemical parameters.

The total coliforms, *Escherichia coli*, enterococci, *Pseudomonas aeruginosa* and *Clostridium perfringers* were not detected in any sampled groundwater while elevated values of heterotrophic bacteria expressed as number of colony count at 22 °C and 37 °C were only detected in sample taken from water well Trstenik during 2011.

All forty seven physicochemical parameters analyzed during this study had values less than MPL set by Croatian Regulation and European Directive, except groundwater sampled from water well Delovi which were usually non-compliance due to regulation because of elevated values of turbidity and total iron concentration. Groundwaters from water-wells Ivanščak, Trstenik, Vratno and Đurđevac can be proclaim as high-quality.

Comparing the concentrations of dominant anions and cations at sampled groundwaters, it was concluded that tested groundwaters from five water wells belongs to five different water-bearing zones.

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