WATER STABLE ISOTOPES AS DRINKING WATER QUALITY INDICATOR IN DUG WELLS OF EASTERN LATVIA

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Abstract
Stable isotope ratios of water (δ^2H and $\delta^{18}O$) are important indicators which describe hydrological processes in the environment. These parameters allow to analyse structure, status, migration of pollutants and processes of the groundwater system. Groundwater from dug wells is widely used as a drinking water source highlighting the importance of investigation of water quality and its possible flows and sources. Despite available centralized water systems, there are still wide territories where dug wells are the main source of drinking water supply. Dug wells are recharged from shallow groundwaters which makes them more vulnerable to anthropogenic contamination. Therefore, quality monitoring and estimation of anthropogenic influences are of importance. Quality requirements of drinking water do not provide measurements of stable isotope ratios in drinking water, but the combination of those elements can be valuable for the characterization of impacts on groundwater quality. The aim of this study was to survey 64 dug wells in Eastern Latvia and analyse water quality together with measurements of stable isotope ratios. Measurements were performed twice, i.e., autumn and spring to track water sources in wells and describe the extent of possible impacts. This approach can indicate the magnitude of local factor impacts on drinking water quality. Surveyed wells provide high differences in analysed parameters, for example, nitrate concentrations in autumn varies from 0.44 to 108.26 mg L^{-1}. Also, other detected parameters are variable; therefore, tracking water flow with stable isotope values gives better insight into the water quality of the studied region.
Key words: stable isotope ratio, drinking water, quality, dug wells.

Introduction

A significant source of drinking water is water supply from wells, especially in the countryside where centralized water supply possibilities are economically and technologically not feasible (Swistock *et al*., 2013; Adelakan *et al*., 2010; Fontenot, 2013). For water supply dug wells (excavated large diameter well, relatively shallow) as well as drilled wells (boreholes) can be used. The depth of drinking water wells depends on the geological structure of the well installation site and the distance to water-saturated layers, usually in Baltic countries it is not more than 20 m and thus water quality in such wells can easily be affected by anthropogenic contamination as well as other factors affecting groundwater level and quality, including climate change. Water from wells is used as a drinking water source worldwide (Klavins *et al*., 2016; Swistock *et al*., 2013; Adelakan *et al*., 2010). However, water quality control of these individual water supply facilities is not as intensive as it is for centralised water supply systems. On the other hand, water quality in wells can be used as a tool to characterise groundwater quality, groundwater flow patterns, intensity of anthropogenic pollution and other processes directly affecting groundwater quality. Several surveys have demonstrated high vulnerability of groundwater quality in wells, and elevated concentrations of contaminants (Han *et al*., 2016; Kitterød *et al*., 2022; Jadeja *et al*., 2022). Commonly high concentrations of nutrients like nitrogen compounds, phosphates, and pesticides have been found coming from agricultural applications of agrochemicals in agricultural areas, but microbiological contamination has been found from multiple human or animal faecal sources influenced by on-site specific factors (Khatri et al., 2015; O'Dwyer *et al*., 2018). Another major group of substances are of natural origin, such as inorganic substances, but also trace elements, such as heavy metals or arsenic seems to be a general problem affecting water quality in dug wells as well as boreholes (Wongsasuluk *et al*., 2014; Bai *et al*., 2022). Considering the vulnerability of water quality in wells, it is important to continue the search for new water quality characterisation tools to better understand drinking water contamination sources and processes affecting water quality.

A versatile tool for groundwater characterisation stable hydrogen (δ^2H) and oxygen ($\delta^{18}O$) isotope ratio analysis can be considered, which is a tool widely used for the characterisation of groundwaters (Hunt *et al*., 2005; Bowen *et al*., 2007; West *et al*., 2014). Stable isotope ratios are conservative at low temperature of groundwater, but they change (isotopical fractionation) in groundwaters due to inflows of atmospheric precipitation or surface waters. Thus, $^{18}O/^{16}O$ and $^2H/^1H$ ratios can be used to identify the source and residence time of groundwater flow (Al-Kubaisi *et al*., 2022; Massmann *et al*., 2008; Darling *et al*., 2003) as well as to identify possible contamination sources.

The aim of this study was to investigate water quality in wells used as drinking water source in Eastern Latvia and analyse water composition together with measurements of light stable isotope ratios.

Materials and Methods

The studied area is located in Eastern Latvia (Figure 1), it is of glaciogenic origin and mostly consists of till sediments in the highlands. In lowlands without glaciolimnic sediments also peat sediments can be found. Differences in sediment origin and their composition with site-specific factors, including location, amount of precipitation and infiltration speed are the main factors responsible for the natural composition of shallow groundwaters. The average annual temperature is 4-6 °C with max average temperature in July (~17.5 °C) and minimal in February (~ -5.5 °C). Long-term precipitation rates vary from 550 to 650 mm per year; however, in the study period 535 mm in 2020 and 526 mm in 2021 were recorded. With respect to water recharge rates, an important aspect is the actual precipitation rates in seasons of interest, respectively in autumn 2020 from September to the end of the year there was 162 mm of precipitation, but in 2021 from January to April 61 mm. In 2021, predominant snow accumulation (14 cm) was recorded until the 21st of February when rapid melting happened, and all snow was thawed by the 26th of February.

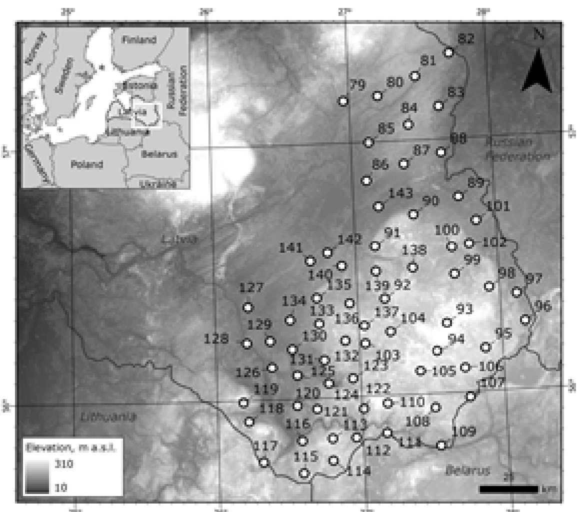

Figure 1. Location of sampling points in Eastern Latvia.

Water analysis

Water samples from wells were collected in two 1 L plastic bottles for water and stable isotope analysis and were placed at 4 °C. For the detection of phosphate ions ascorbic acid method was used, chlorine content was determined using titration, sulphate contents were determined using the turbidity method, and other nutrients were determined by spectrophotometric methods using Hach DR3800 Spectrophotometer and Hach-Lange reagents. For the turbidity HANNA HI88703 Turbidity Meter was used, and for pH and conductivity HANNA HI 2210 pH meter and HANNA HI 9932 Microprocessor Conductivity Meters were used, respectively. Macro components and trace elements were measured using an inductively coupled plasma spectrometer − ThermoScientific ICP spectrometer iCAP 7000 series.

Stable isotope ratio measurements

Stable isotope ratios of hydrogen and oxygen in water were analyzed in the Laboratory of Environmental Dating at the University of Latvia (Faculty of Geography and Earth Sciences). Isotope ratios are expressed in standard δ-notation relative to the Vienna Standard Mean Ocean Water (Craig, 1961). Both isotope ratios of hydrogen and oxygen were measured using the cavity ring-down laser spectroscopy method (Brand *et al*., 2009) with a Picarro L2120-i Isotopic Water Analyzer. The reproducibility of stable isotope measurements was less than ± 0.1‰ for $\delta^{18}O$ and ± 1‰ for $\delta^{2}H$. To assure the quality of water sampling and processing in the laboratory, internationally accepted procedures elaborated by the IAEA (Aggarwal *et al*., 2007) were followed. The laboratory has successfully participated in worldwide open proficiency tests on the determination of stable isotopes in water organised by the IAEA in 2016 and 2020 (Wassenaar *et al*., 2018).

Data analysis

Multivariate correlation, Principal Component analysis (PCA) and cluster analysis (Ward's minimum clustering method) were done using SAS JMP ® data discovery software version 17.0.

Results and Discussion

Dug wells are fed by precipitation and their infiltrate into groundwaters. Temperate climate groundwater recharge is biased towards late winter/early spring (Nygren *et al*., 2020). In the precipitation isotope ratios data are available at the IAEA/GNIP (Global Network of Isotopes in Precipitation) database. The three closest stations to the study area are Riga, Tartu and Minsk (IAEA, WMO, 2022). Considering that more recent precipitation samples are collected in station Riga, it was further chosen to represent precipitation input values.

The notion of d-excess (deuterium excess) is a convenient way to illustrate the deviation of water isotope observation from the GMWL, calculated as d-excess = $\delta^2H - 8*\delta^{18}O$ (Craig, 1961) (Figures 2; 3), indicating the deviation of the δ^2H ‰ and $\delta^{18}O$ ‰. The weighted d-excess for local precipitation at the Riga station was 11.2‰ (Babre *et al*., 2016). The least squares fit (LSF) regression lines between two isotope ratios for the period: 2016−2022 are 9.84 $\delta^{18}O$‰ -69.8 δ^2H‰ (VSMOW).

The background isoscape for $\delta^{18}O$ in groundwater was interpolated from direct observations by Raidla et al. (2016). It varies from − 10.8 to − 11.5‰. The average of 10 direct $\delta^{18}O$ groundwater observations (Babre *et al*., 2016; Raidla *et al*., 2016) in the study area is –11.34‰ ± 0.19‰ standard deviations (SD). Direct observations are consistent with interpolated values of the isoscape. The interpolated groundwater isoscape is spatially continuous; therefore, in this study, it is used as a reference instead of individual direct observation. The mean of 7 direct δ^2H groundwater observations (Babre *et al*., 2016; Raidla *et al*., 2016) is − 78.9% ± 2.2% SD. The linear regression line between observed $\delta^{18}O$ and δ^2H has a slope of 12 ± 3 SD and an intercept of 55 ± 36 SD; note the high uncertainty. Moreover, the modelled global precipitation map (Terzer *et al*., 2013) shows that the modelled precipitation's $\delta^{18}O$ in the BAB is only slightly depleted (less than 0.5‰) with respect to the isotopic composition of shallow groundwater in the region. At the same time, our results show a difference of up to 2‰. The isotopic composition of shallow groundwater in the BAB area is depleted with respect to mean weighted annual values of local precipitation (Babre *et al*., 2016; Raidla *et al*., 2016).

The results of collected 64 samples repeated during two sampling campaigns are compiled in Table 1. Average values for all analysed samples are -10.41 $\delta^{18}O$‰ (SD 0.93) and -73.52 δ^2H‰ (SD 7.19) respectively. There are differences in the mean values for the sampling season. As expected, the mean values in the samples collected in the autumn were slightly enriched due to the more enriched isotopic input signal from the precipitation. Therefore, mean values of autumn sampling are -10.07 $\delta^{18}O$‰ (SD 0.75) and -70.78 δ^2H‰ (SD 5.88) and slightly lower spring values, i.e., -10.75 $\delta^{18}O$‰ (SD 0.97) and -76.27 (SD 7.37) δ^2H‰. Deuterium excess is less distinct and reflects the direct recharge of precipitation with the expectance of individual samples that show more pronounced evaporation during a particular season.

The stable isotope ratio range of all samples and both sampling campaigns are 5.40 ‰ for $\delta^{18}O$ and 43.52‰ for δ^2H. The difference is lower if compared to a single sampling site. Wells with a higher error between sampling timing reflect less mixed annual signal, therefore, have more seasonal recharge. This difference is noticeable in sampling sites No. 83, 87, 97, 101, 108, 128 and 133 where exceed 3‰ $\delta^{18}O$ indicating less mixed annual signal as well as higher vulnerability to contamination and groundwater droughts.

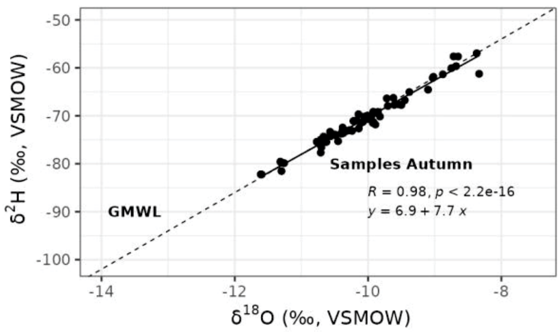

Figure 2. Water stable isotopes and regression line (filled) for samples collected in the autumn campaign with the Global Meteoric Water Line by a dashed line (Craig, 1961).

Dug well No. 101 has higher d-excess values indicating evaporation during the recharge in its origin source before autumn sampling, meanwhile, in well No. 103 has a more evaporative signal during the spring sampling. Regarding more stable isotopic signal, wells No. 82, 86, 91, 94, 95, 96, 105, 106, 111, 115, 117, 124, 126, 131 and 138−140 have almost undetectable differences in the isotopic signal between sampling campaigns, regarding both analyzed stable isotopes. These wells are considered to have more retained groundwater recharge, better mixing, longer residence times and less pronounced annual groundwater level fluctuations. However, long-term monitoring is necessary to unmistakably deduce groundwater seasonal and annual recharge for particular sites.

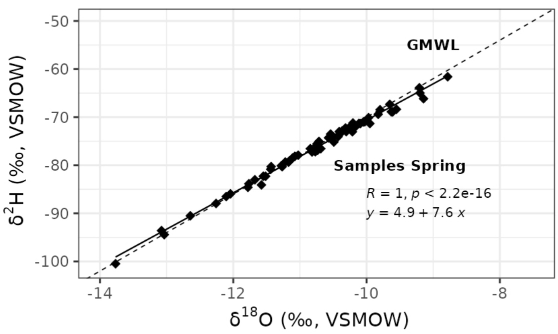

Figure 3. Water stable isotopes and regression line (filled) for samples collected during the spring campaign with the Global Meteoric Water Line by a dashed line (Craig, 1961).

The depth of studied water wells (groundwater table) in Eastern Latvia varies from 0 m to 6.5 m while the average depth is only 2.5 m. Water wells are installed mainly for water supply; however, other human activities are present in this area which can affect overall water quality. Anthropogenic activities with agricultural applications are mainly responsible for elevated amount of nutrients in groundwaters and in studied area in some wells nitrate ions exceed even 100 mg L^{-1}. In 9 over 64 wells, phosphate concentration was detected in significant amount reaching more than 1 mg L^{-1}. Despite high concentrations in the autumn season, in spring some of those parameters showed even higher values. Overall, the hardness of water in the wells of this area can be characterized as hard and very hard with only a few exceptions with soft water. Other parameters show that in Eastern Latvia wells with high water quality, that are safe for use, can be found; however, in around 15% of the studied wells some of the parameters show elevated values, for example, ammonia, nitrites, nitrates, phosphates, iron, colour, and turbidity. In 2 wells elevated sodium and chlorine content was detected which can be the result of human activities and is not coming from natural sources and their natural fluctuation in Latvia (Retike *et al*., 2016).

Table 1

Variability of analysed parameters in dug wells in Eastern Latvia

Parameters		Autumn 2020	Spring 2021
Hydrochemical parameters	NO_2-, mg L^{-1}	0.01–0.68	0.01–0.37
	NO_3-, mg L^{-1}	0.44–108.26	1.77–222.24
	PO_4^{-3}, mg L^{-1}	0.03–2.72	0.06–3.93
	NH_4^+, mg L^{-1}	0.11–2.72	0.06–0.73
	Si, mg L^{-1}	2.61–21.23	4.76–18.39
	SO_4^{-2}, mg L^{-1}	1.00–42.00	1.00–37.00
	Colour, Pt Co scale	1.00–115.00	1.00–92.00
	Conductivity, µS cm^{-1}	96.10–2127.00	6.32–1974.00
	pH	6.98–8.42	6.77–8.11
	Turbidity, NTU	0.07–5.71	0.10–12.70
	COD, mg L^{-1}	7.27–69.20	N/A
	Cl^-, mg L^{-1}	3.55–254.86	2.84–180.10
	HCO_{3-}, mg L^{-1}	40.26–1022.36	42.70–1008.94
	Total hardness, mg eq L^{-1}	1.43–11.17	1.74–16.23
Isotopes	δ^{18}O‰, VSMOW	-11.31– -8.37	-13.77– -8.78
	δ^{2}H‰, VSMOW	-82.23– -56.96	-100.48– -61.60
	Deuterium excess, ‰ VSMOW	6.86–12.11	7.00–11.17
Macro-components	Ca, mg L^{-1}	7.53–159.58	7.53–159.57
	Fe, mg L^{-1}	0.007–0.52	0.007–0.50
	Mg, mg L^{-1}	2.00–107.03	2.00–90.66
	Zn, mg L^{-1}	0.005–0.62	0.005–0.61

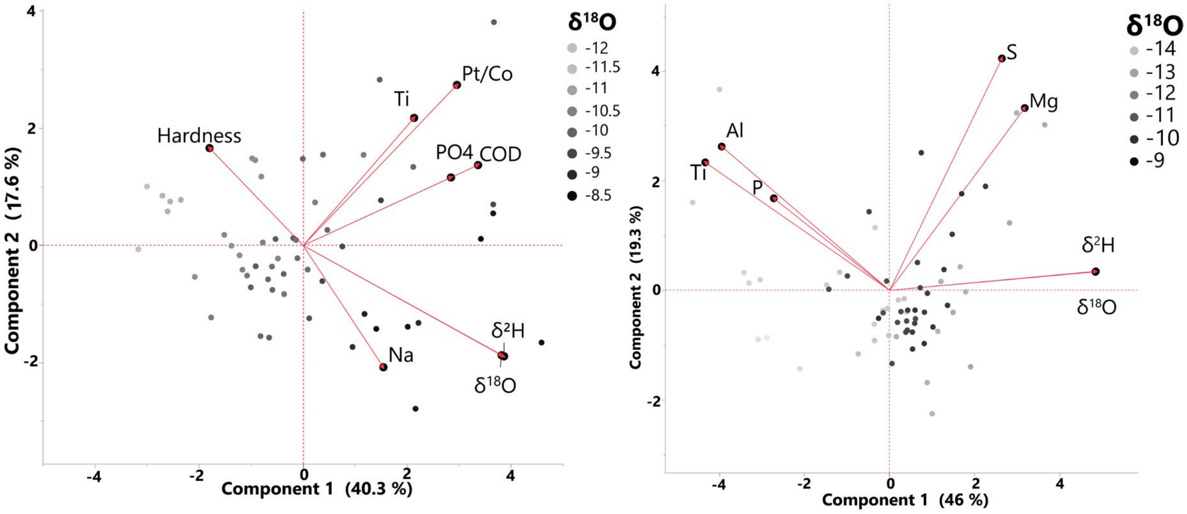

Figure 4. Principal component analysis of isotopes and hydrochemical parameters in autumn 2020 (left) and spring 2021 (right).

To track potential correlations between studied hydrochemical parameters and stable isotopes, principal component analysis (PCA) were performed.

The principal component analysis (Figure 4) matrix was not indicating a significant correlation of isotopes with analyzed hydrochemical parameters. The strongest relationship was recorded in autumn with such parameters as chemical oxygen demand (COD), phosphates, total hardness, Na, Ti and colour. Those parameters indicate major differences between relief forms with noticeable higher values for lowland, therefore, corresponding to actual differences also in isotope data.

Samples collected in spring also did not show any correlation with the measured parameters. High variability and dispersion of data was recorded which is due to the presence of snow melting water, and high variability of individual parameters between studied wells (Table 1). Only phosphorus had a detectable correlation as indicated by the PCA results from spring 2021 (Figure 4). These results can be affected by anthropogenic activities while other parameters can be influenced by both natural and anthropogenic factors and particularly in the spring when visible impact from snow thawing and soil infiltrate in groundwaters can be seen, which very well corresponds with trace elements and their concentration in snow (Pilecka *et al*., 2017) and soil media in other studies (Vincevica-Gaile *et al*., 2013).

Due to the fact that individual correlations between other studied parameters could be found, the data was analyzed using cluster analysis in order to characterize potential patterns of water quality with isotope measurements.

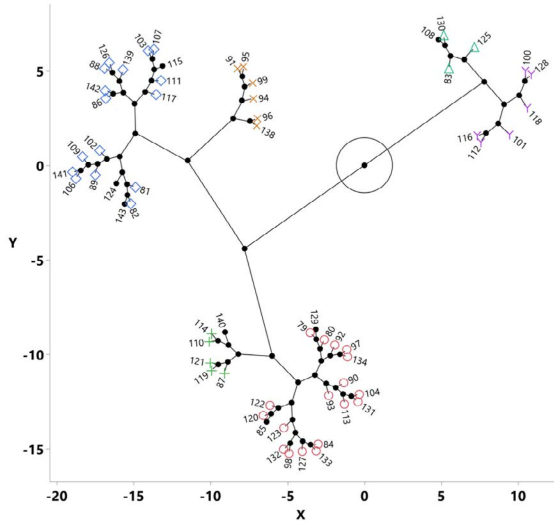

Figure 5. Constellation plot of the measured $\delta^{18}O$ and $\delta^{2}H$ in the autumn season of 2020 showing clustering of the sampled wells (No. 79−143) according to Ward's method. X and Y represent the distance overcome at each cluster joint from the origin (0;0).

Cluster analysis (Figures 5; 6) in both seasons grouped water wells into three major groups although the wells are only partially grouped between sampling seasons. In comparison to PCA analysis which showed a correlation with several parameters in water, found clusters correspond to major findings with isotope measurements in the autumn season. For example, wells No. 82, 86, 91, 94, 95, 96, 105, 106, 111, 115, 117, 124, 126, 131 and 138-140 have almost undetectable differences in the isotopic signal between sampling campaigns in the autumn season. However, these wells are grouped in one particular cluster although in spring those wells are distributed within 2 clusters. This group of wells have a similar pattern with their location in the highland, with a tendency for average water turbidity and relatively high hardness.

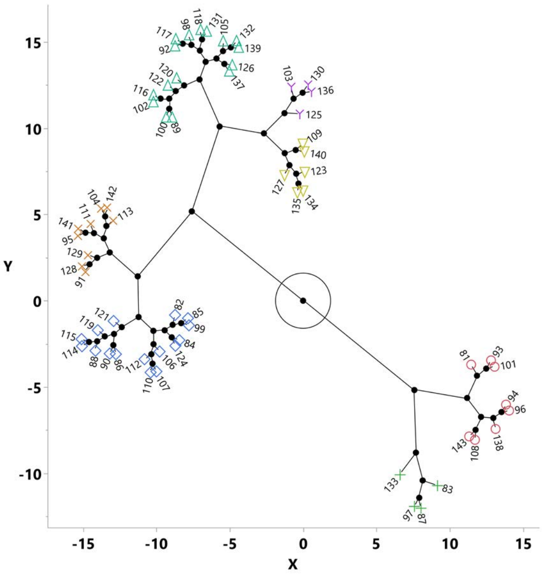

Figure 6. Constellation plot of the measured δ^{18}O and δ^{2}H in the spring season of 2021 showing clustering of the sampled wells (No. 79−143) according to Ward's method. X and Y represent the distance overcome at each cluster joint from the origin (0;0).

Other group of wells (83, 87, 97, 101, 108, 128 and 133) which due to their higher seasonal water recharge can be concluded as more vulnerable to potential contamination of groundwater made detectable distribution in cluster analysis (Figures 5; 6). Respectively in the autumn season, those wells are located in two other clusters while in the spring season, they dominantly made one cluster. In the spring season, the other two clusters grouped all other studied wells, thus indicating differences between wells and their potential vulnerability. These grouped wells by isotope data and cluster analysis detected as vulnerable ones, have similar patterns to other hydrochemical parameters in the autumn season showing a noticeable amount of phosphates, relatively high colour and COD. This group of wells are located in lower terrain with a high groundwater table and wells also contain microbiological pollution.

Wells with higher water recharge rate in spring have some differences from autumn indicating that values of colour and phosphates are comparable in both seasons, but in spring noticeably increases turbidity and has significantly smaller total hardness and amount of hydrocarbonates due to intense recharge of snow melting water. These results correspond to findings in other studies (Kalvans *et al*., 2020) and changes in tested parameters without infiltration indicate also potentially direct surface water flow in water wells during intense precipitation or snow melting. In such areas, water wells with proper isolation against surface water infiltration should be equipped. Although in highland individual differences between water wells are noticeable, isotope data and depth of groundwater level demonstrate more stable water recharge rates.

Local conditions with location in relief and groundwater recharge patterns may play an important role in overall water quality and therefore indicate potential risks to meeting criteria for water quality standards. This phenomenon demonstrates correspondence with findings in PCA analysis and a strong correlation with individual ions from such sources as snow and soil. Moreover, the influence of intense water recharge in these wells also impact their water quality from anthropogenic activities can play an important role, because these sampling sites dominantly are in urban areas, near farms or agricultural areas.

Conclusions

Studied dug wells have high individual variability on analyzed parameters, thus making it difficult to apply statistical analysis and find convincing patterns. Nevertheless, there are visible differences between water quality parameters in wells located in different terrain as more vulnerable to anthropogenic contamination indicating wells in lowlands. PCA analysis indicates several parameters which correspond to isotope values and their seasonal fluctuations, but do not prove the potential of isotope values as the main tool for characterizing shallow groundwater quality. A significantly better overview described cluster analysis by grouping wells by their major differences, thus indicating areas with higher potential risk for water contamination and the usefulness of including stable isotope analysis for characterization of water quality aspects.

Acknowledgements

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