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The $\delta^{18}O$ and δD isoscapes of recent groundwater in Poland

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Abstract

Considering the country's development and quality of life, recognition of the water cycle mechanism is of great importance. A significant contribution to this comes from the isotopic composition of particular elements of the water cycle. However, a weak point is that in Poland only one element of the water cycle, precipitation, is sampled and measured over more than 312 thousands km^2 at a single station. It is therefore necessary to seek extension of or alternatives for these rare data. Such an alternative is the sampling of groundwater containing tritium in the national monitoring network of groundwater bodies that is maintained by the Polish Geological Institute. Based on such data we have constructed $\delta^{18}O$ and δD isoscapes (i.e., maps of $\delta^{18}O$ and δD values) of recent groundwater. These data provide spatial distribution of $\delta^{18}O$ and δD values which can be used as input to hydrogeological models.

Key words: stable isotopes of water, groundwater, tritium, precipitation, isoscapes

1. Introduction

It has been recognized long ago that changes in the water cycle are of immense importance for industrial development, recognition of climate change and quality of life. In the past, changes in water cycle intensity occurred as natural phenomena, but they are becoming more tightly linked with human activity. Therefore, quantitative knowledge of elements of the water cycle and its behavior is worth gaining. The goal of the present study is to understand under which conditions the distribution of groundwater isotopic values ($\delta^{18}O$ and δD) mimics those of weighted average precipitation across the territory of Poland. Surface waters belonging to atmospheric circulation have highly linearly correlated $\delta^{18}O$ and δD values, with slopes of 8 (Craig, 1961) and 8.13 (Różański et al., 1993), respectively. Direct isotope $\delta^{18}O$ and δD data of precipitation are not always available, although a worldwide network of $\delta^{18}O$ and δD data acquisition is available in the Global Network of Isotopes in Precipitation – GNIP (IAEA, 2018). This network provides isotopic data as yearly weighted average. This is particularly useful in cases that require spatiotemporal reconstruction of the isotopic composition of average precipitation and as input to hydrological, ecological, archaeological, forensic and other models (Kendall & Coplen, 2001; Longinelli et al., 2006; Bowen et al., 2007; Aggarwal et al., 2010; Liu et al., 2010; Bowen et al., 2011; Stumpp et al., 2014, West et al., 2014; Harms et al., 2016; Regan et al., 2017). In view of the lack of precipitation data as geographical input of $\delta^{18}O$ (δD) values, groundwater isoscape (isotopic landscape) could replace the missing isotopic average values of precipitation. The $\delta^{18}O$ and δD values of relatively shallow groundwater as equivalent to $\delta^{18}O$ and δD values of recent precipitation can be used as a proxy for long-term average $\delta^{18}O$ and δD values of precipitation, thus reducing the need for true, long-term precipitation isotope ratio monitoring data. Therefore, it provides researchers with isotope data for all territory of Poland. Stable isotope compositions of precipitation ($\delta^{18}O$ and δD) register environmental changes that are associated with distance from the ocean (continental effect), latitude effect, field temperature, intensity of precipitation (mass), seasonal effect and elevation; all of these are averaged in groundwater. In order to document these causatives in a particular area better, the construction of a stable isotope precipitation map (precipitation isoscape) is helpful (Longinelli & Selmo, 2003; Longinelli et al., 2006; Stumpp et al., 2014; Raidla et al., 2016; Regan et al., 2017). However, groundwater movement integrates all of the above causatives to such an extent that separation of even a seasonal effect is often made impossible. In Poland there is only one station which has provided isotopic data of precipitation (Kraków, Wola Justowska) since 1973 (Duliński et al., 2001). The monthly data obtained, the amount of precipitation, $\delta^{18}O$ and δD and temperature values are available at GNIP (Vienna) with a two year delay. If there is a need to use precipitation deltas on a regional or local scale far from Kraków, this will introduce considerable uncertainty.

The circulation regime of the atmosphere over Europe has remained constant over the past 35,000 years (Różański, 1985; Różański et al., 1997; Darling et al., 2003), which allows us to use the groundwater isoscape as a proxy for the precipitation isoscape. The groundwater isoscape for Poland was pioneered by d'Obyrn et al. (1997). Their Holocene groundwater was sampled from about 1,000 wells across Poland (Table 1).

Our data are based on the national groundwater observation network that is representative of groundwater bodies in EU terminology. The idealized sampling strategy is provided in a flowchart (Fig. 1). Wells are kept in an excellent technical state and their profile descriptions are exhaustive, including a long record (15 years) of variations in quantity and quality of groundwater. The sample set was chosen from the System of Hydrogeological Observation (SOH) and Monitoring Database

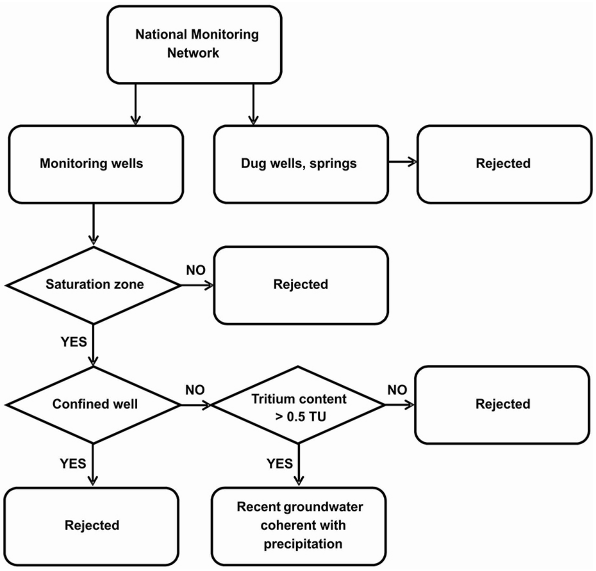

Fig. 1. Idealised flowchart for selection of groundwater samples from the SOH and MONBADA data bases

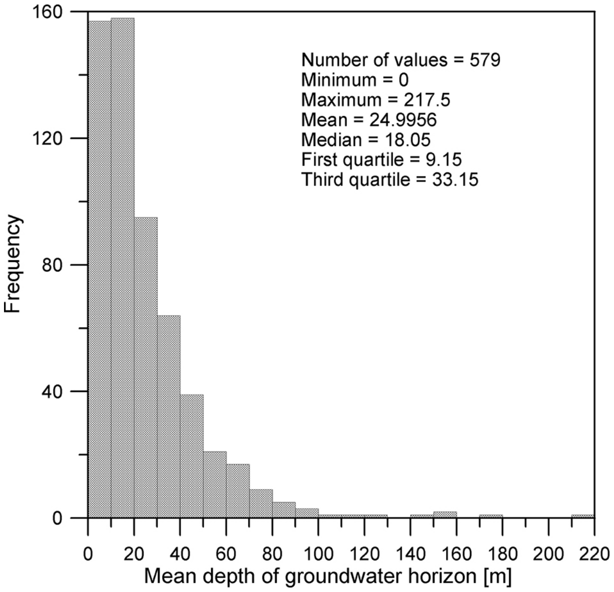

Fig. 2. Frequency of sampling depths of groundwater, $n = 579$

Table 1. Comparison of data input to groundwater isoscapes.

	This work	d'Obyrn et al. (1997)
Number of samples	$n = 579$	$n = 989$
Tritium content	Groundwater samples, TU > 0.5	Including samples TU > 0, TU = 0, and unknown, $n = 432$
Defined "age"	Recent groundwater	Holocene groundwater
Aquifer specifications	Unconfined, saturated zone	Non specified features
Sampled objects	National network, without springs and dug wells	Non specified but springs and dug wells involved

(MONBADA) in groundwater bodies mostly from a depth range of 4 to 50 meters BGL, with a mean of 25 and a median of 18.1 meters BGL (Fig. 2). Springs draining a usually undefined aquifer and dug wells, as exposed to clear surface evaporation, were not considered for sampling (Fig. 1). Essentially, reliable groundwater to provide δ^{18}O proxy values of precipitation should be derived from unconfined aquifers, although this criterion is not always met (Fig. 1). However, regardless of other criteria, a rigid condition accepted for sampling was that only groundwater with a tritium content in excess of 0.5 TU (Fig. 1; Table 1) was used (n = 579). This provides samples from a population of clearly defined "ages" or transit time of recent groundwater.

2. Methods

The isotopic composition of abstracted groundwater has been measured by laser spectroscopy using the LGR (Los Gatos Research, Inc., San Jose, USA) DT100 instrument at the Polish Geological Institute-National Research Institute. Samples were taken in 50 ml bottles in the period between March and November from 2012 to 2017 and were processed in the laboratory. The isotopic values δ^{18}O and δD are defined as:

$$\delta‰ = 10^3(R_{sample} - R_{st})/R_{st} \tag{1}$$

where R_{sample} and R_{st} stand for sample and standard isotope ratios ^{18}O/^{16}O and D/H, respectively. The two-point calibration procedure was applied and results were recalculated by LIMS (Coplen & Wassenaar, 2015) against international standards, VSMOW (δ^{18}O and δD = 0‰) and SLAP (δ^{18}O = −55.5‰, δD = −428‰) with uncertainties of ±0.1 and ±0.5, respectively. The results were processed by ESRI ARC-GIS 10.3 software; the maps obtained display isolines of δ^{18}O and δD values. Analyses of tritium, upon which our selection of groundwater was based, were performed at the Academy of Mining and Metallurgy in Kraków between 2012 and 2017.

3. Results and discussion

Essentially, groundwater from confined, deep, isolated aquifer without tritium (mostly Holocene and older groundwater) is not a reliable candidate for substitution of isotope precipitation data. The excellent isotope data gathered from the monitoring wells mentioned above, including tritium concentration, enable a distinction to be made between tritium-containing groundwater and that devoid of tritium. In the pre-nuclear bomb era (before 1952) the natural production of tritium oscillated around 5 TU or less. For this reason we have arbitrarily assumed that tritium-containing groundwater should be consistent with δ^{18}O and δD values of weighted average precipitation. The groundwater δ^{18}O and δD values (−13 to −5‰; see Fig. 3; −95 to −45‰; see Fig. 4, respectively) within the plot of meteoric waters (Craig, 1961; Różański et al., 1993) confirm the predominance of the continental isotope effect on groundwater. Surprisingly, two samples exhibit extremely negative delta values that are difficult to explain. In contrast, three samples reveal an evap-

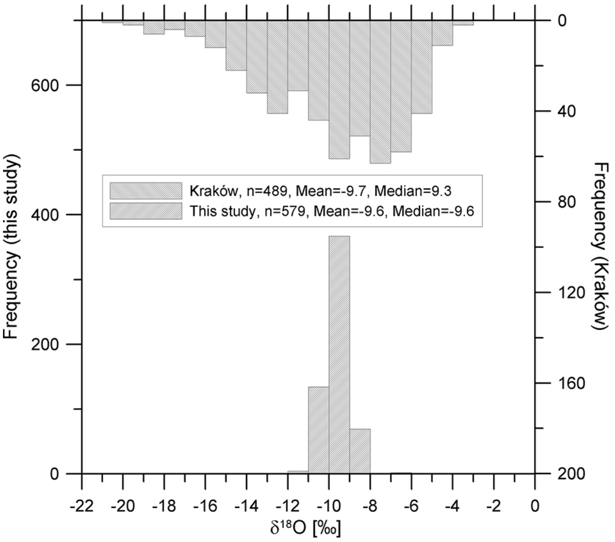

Fig. 3. Frequency of δ^{18}O values in groundwater and Kraków precipitation, n = 579

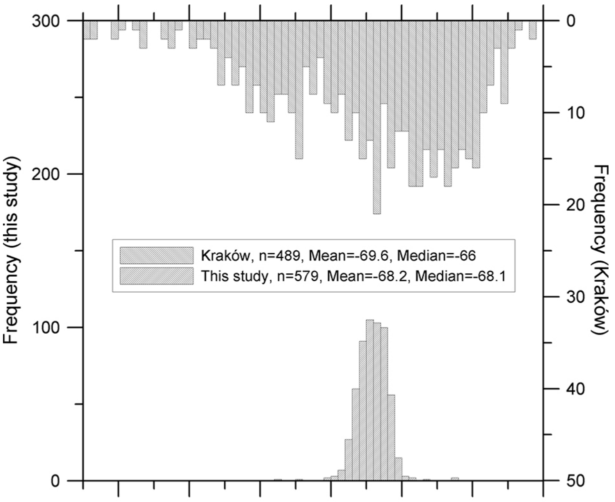

Fig. 4. Frequency of δD values in groundwater and Kraków precipitation, n = 579

orative behavior. In view of the fact that groundwater analyzed in the present study percolates the unconfined zone (Fig. 2), with a negligible delta isotope seasonal effect, its residence time (transit time) should not exceed 40–60 years, depending on the flow-model (Nowicki et al., 2016; Duliński et al., 2017). This is referred to as recent groundwater (Table 1). The essential question is to what extent the groundwater set of isotopic values ($\delta^{18}O$, δD) sampled will mimic the precipitation isoscape in a consistent way.

In comparison to monthly precipitation data at 28 stations in Germany (Stumpp et al., 2014), with −24 to 2‰ in $\delta^{18}O$ values, and −170 to +18‰ in δD values, groundwater in Poland naturally reveals a smaller range of delta values from −12 to −5‰ for $\delta^{18}O$, and from −80 to −50‰ for δD, respectively. Precipitations across Germany display a long-term (36 years) relation:

$$\delta D = (7.72 \pm 0.13)\delta^{18}O + (4.90 \pm 0.01),\ n = 8007,\ R^2 = 0.97 \tag{2}$$

and 41 years (1975–2016) of monthly record of Kraków precipitation derived from GNIP-IAEA database amount to:

$$\delta D = (7.807 \pm 0.037)\delta^{18}O + (6.53 \pm 0.38),\ n = 489,\ R^2 = 0.990. \tag{3}$$

In comparison to the above-mentioned isotope projections, recent groundwater in Poland can be described by the following equation (Fig. 5):

$$\delta D = (6.71 \pm 0.08)\delta^{18}O + (3.87 \pm 0.71),\ n = 579,\ R^2 = 0.94. \tag{4}$$

In the tritium-containing groundwater of the present study the $\delta D/\delta^{18}O$ slope resembles the evaporative slope, which may be due to partial evaporation of precipitation that leaks through the subsoil towards the groundwater. In the unsaturated zone the maximum isotope effect of evaporation is shown to persist at a depth of 25 meters (Barnes & Allison, 1988). The slope of the evaporation line may be as low as 2; it depends clearly on the size of sand grains; the lower the size, the lower the slope (Sonntag et al., 1985). However, the $\delta D/\delta^{18}O$ slope obtained for Polish groundwater, equal to 6.71, must be studied in more detail and explained better. In their study, d'Obyrn et al. (1997) also recognized evaporitic influence exerted on their set of groundwater and suggested that, in many cases, groundwater isotopic composition must have been influenced by lakes (hence a $\delta D/\delta^{18}O$ slope lower than 8) during the early Holocene. However, this explanation does not apply to our tritium-containing groundwater.

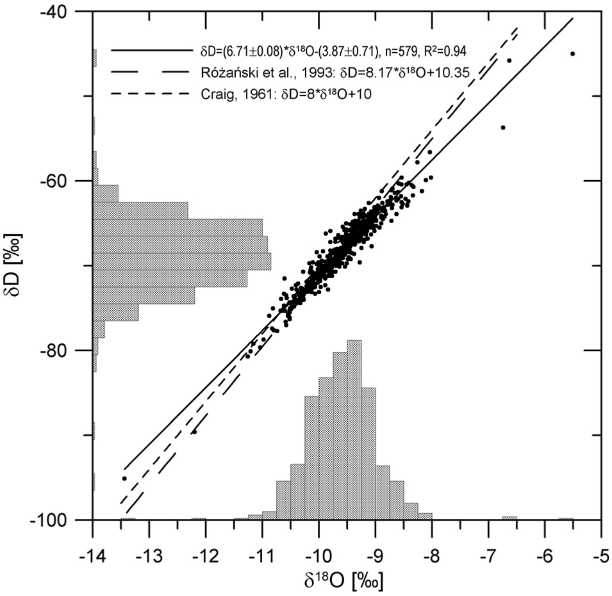

Fig. 5. Craig (1961) and Różański et al. (1993) precipitation line and recent groundwater of Poland with tritium TU > 0.5TU, *n* = 579. Histograms of groundwater delta values are also shown

The groundwater isotopic $\delta^{18}O$ and δD compositions are devoid of seasonal influence, a fact that has also been documented in other studies across Europe (e.g., Darling et al., 2003) and also covers areas of higher elevation in southern and eastern Poland.

The $\delta^{18}O$ and δD isoscape determinations of d'Obyrn et al. (1997) were based on groundwater that was mostly of Holocene age (0 to −11,700 years). Our selection of samples (containing tritium) is more homogeneous and limited to recent groundwater (age to *c.* −60 years). However, two isoscapes demonstrated in the present study and those of d'Obyrn et al. (1997) present similar distributions of isotopes (higher $\delta^{18}O$ and δD values in the west and lower ones in the east; see Figs 6, 7). They display similar $\delta^{18}O$ and δD longitude gradients of around −1.5 ‰ and −12 ‰, respectively. It is clear that such groundwater longitudinal gradients in $\delta^{18}O$ and δD values repeat continental isotope gradients of precipitation as revealed by Różański (1985). Correlations of $\delta^{18}O$ and δD values in groundwater and precipitation differ only in the respective values and not in their slope and intercept (Figs 3, 4). It has become clear that the groundwater isoscape can imitate (Figs 6, 7) the precipitation isoscape, which enables us to extend future studies to a larger set of $\delta^{18}O$ and δD data obtained in groundwater monitoring networks.

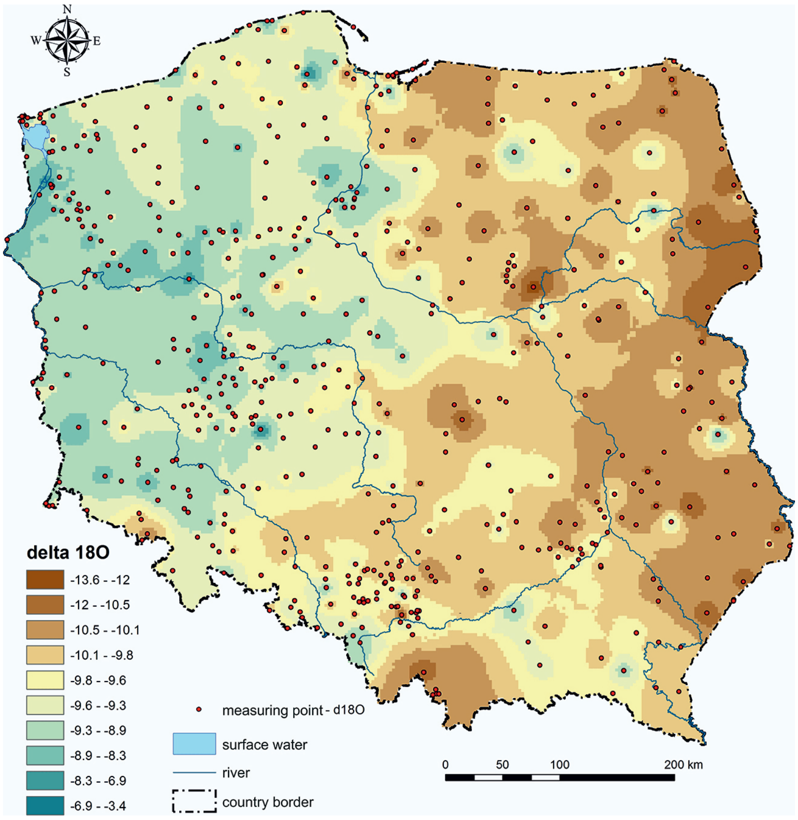

Fig. 6. Interpolated groundwater isoscape of $\delta^{18}O$ values in ‰, n = 579. Points are groundwater sampling points with measured tritium content (TU > 0.5TU)

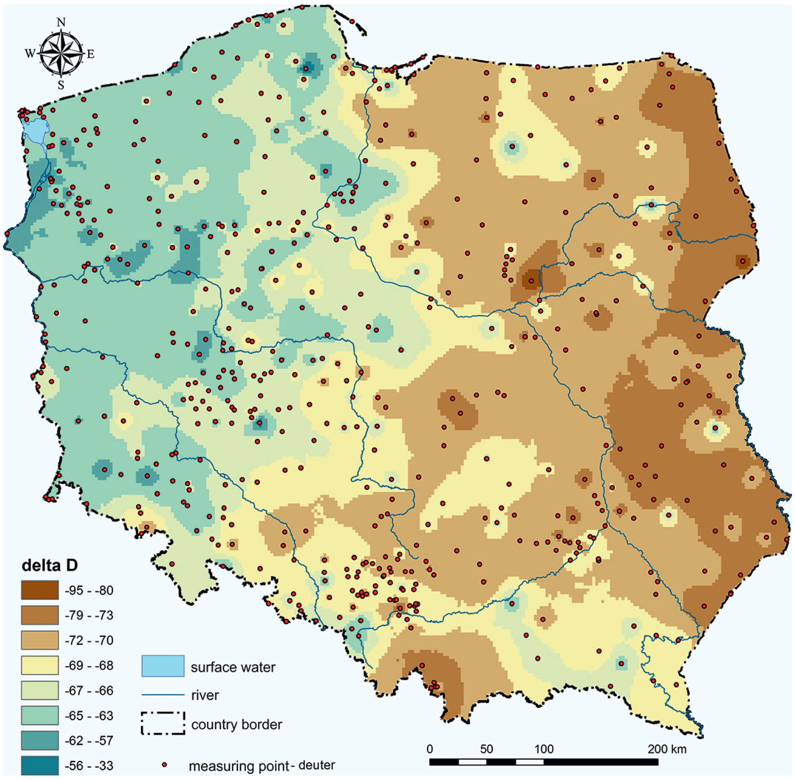

Fig. 7. Interpolated groundwater isoscape of δD values in ‰, n = 579. Points are groundwater sampling points with measured tritium content (TU > 0.5TU)

4. Conclusions

A new groundwater isoscape ($\delta^{18}O$ and δD) for Poland, based on tritium-containing groundwater, is presented. It is the integrated result of stable isotope measurements between 2012 and 2017, within the scope of activities at the Polish Hydrogeological Survey. There is an apparent evaporitic effect that influences groundwater $\delta^{18}O$ and δD. At this level of generality, the averaged groundwater $\delta^{18}O$ and δD isoscape satisfactorily reproduces the precipitation isoscape within $\delta^{18}O$ and δD values across the territory of Poland by displaying a clear continental gradient of isotopic values ($\delta^{18}O$ and δD). However, there is a mediocre coherence with groundwater isoscapes in the northeast of Poland (Raidla et al., 2016) and precipitation data in the west (Stumpp et al., 2014). The accumulated groundwater isotope data suggest that an effort to construct a European-wide groundwater isoscape so as to resolve most inconsistencies should be undertaken. It is also suggested that isotope groundwater monitoring should be included routinely in the monitoring of EU groundwater bodies.

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