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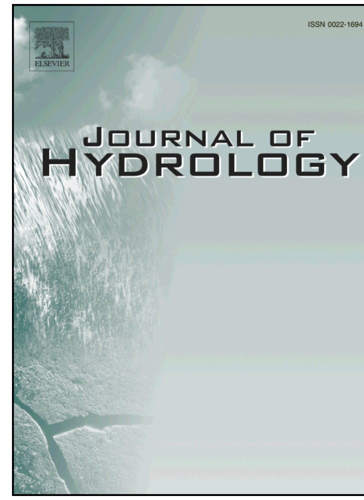

Research papers

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Stable isotopic composition of atmospheric precipitation on the Crimean Peninsula and its controlling factors

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Abstract. A first systematic study of the isotopic composition of precipitation on the Crimean Peninsula was carried over the period of 58 months at two stations located on the Crimean Piedmont (Simferopol, 290 m a.s.l.) and on the northern slope of the Main Range of the Crimean Mountains (Chatyr-Dag, 980 m a.s.l.). Oxygen and hydrogen isotope values of these stations yielded a Crimean Local Meteoric Water Line: $\delta^2H = 7.3\ \delta^{18}O + 4.8$; $r^2 = 0.97$. The isotopic composition of precipitation at the two stations is partly (25 % and 39 %, respectively) correlated with the local air temperature, but the degree of this correlation shows large temporal variability. No correlation between isotopic composition and precipitation amount was observed. Far-field controls, such as changing sources, supplying moisture for the Crimean precipitation, or varying strength of the North Atlantic Oscillation do not influence the isotopic composition of precipitation in Crimea on these short time scales.

1 Introduction

The stable isotopic composition of atmospheric precipitation represents important "baseline" information for numerous hydrogeological, climatological and ecological applications, ranging in scale from global (e.g., isotope-enabled general circulation models) to local (e.g., delineating catchment areas, municipal water use planning). Knowledge of the factors controlling the isotopic composition of precipitation is also indispensable for paleoclimatological studies using, for example, calcite of speleothems or cellulose of wood. For areas where no empirical data are available, this information is derived through extrapolation from observation stations (Bowen and Ravenaugh, 2003). At sites where the controlling factors are well understood (e.g., continental rain-out effect, latitude effect) the isotopic composition of precipitation can be predicted with high confidence. Sites located in more complex environments, e.g. near large water bodies, are controlled by additional factors and the isotopic composition of precipitation is less predictable in such areas. Quite commonly such sites defy interpolations (e.g., eastern Alaska, the Himalayas, and eastern and Saharan Africa; Bowen and Ravenaugh, 2003) and empirical data (i.e., long instrumental time series) are indispensable.

The Global Network of Isotopes in Precipitation (GNIP; IAEA/WMO, 2006) represents a milestone in collecting hydrogen and oxygen isotope data of modern precipitation on a worldwide basis. Many countries also maintain regional networks (e.g., Switzerland, Germany and Austria). In recent years a significant number of "local" time series of isotopes in precipitation have been acquired from settings ranging from continental (e.g., eastern Hungary and eastern Mongolia; Vodila et al., 2009; Yamanaka et al., 2006) to oceanic islands in the monsoon climate (Okinawa; Uemura et al., 2012). This emerging body of local time series shows that the commonly presumed primary controlling factors, temperature and precipitation amount, play a role at some sites, but other factors, such as moisture recycling, transient eddies and changing moisture sources exert the dominant control.

The Crimean Peninsula is surrounded by vast expanses of water, the Black Sea and the Sea of Azov, and has an extensive land mass in the north. The closest GNIP stations (Odessa, Ukraine; Rostov-na-Donu, Russia; Sinop and Rize, Turkey) are located 300 to 700 km away and are separated from Crimea by the sea. Although the meteorology and hydrogeology of the peninsula are reasonably well understood (Barabanov et al., 1970; Pershin, 1978; Lushchik et al., 1981; Vyed', 2000), no systematic stable isotope studies of precipitation have been performed so far. The only data were obtained in 1977–1979 (Seletsky et al., 1982) and comprise 34 oxygen isotope measurements from four rain gauges. These data should be used with caution, because the sampling was discontinuous, with warm-season precipitation being over-represented (23 vs. 9 measurements from the cold season).

The aims of this study were to: (1) acquire a representative dataset characterizing the isotopic composition of precipitation in Crimea and (2) to evaluate the controlling factors. To accomplish the first task, two precipitation sampling stations were installed on the northern slope of the Crimean Mountains and a 58 month-long data series was obtained between 2009 and 2016. The location of the stations was chosen to characterize the two main physiographic and climatic regions of Crimea which also play an important role in regional groundwater recharge. To assist the evaluation of the controlling factors, we undertook an assessment of the moisture sources of Crimean precipitation using the Lagrangian moisture source detection method.

2 Physiography and climate of Crimea

2.1 Physiography

Occupying an area of 27,000 km^2, the Crimean Peninsula comprises two main physiographic provinces, the Crimean Plains and the Crimean Mountains (Fig. 1). The plains occupy two thirds of the peninsula in the north, and their topography varies from fairly flat in the center to rolling plains and low hills on the Tarkhankut and Kerch peninsulas. The Crimean Mountains comprise (from north to south) the Outer, the Inner, and the Main Ranges. The Outer and the Inner Ranges are also collectively known as the Crimean Piedmont (Predgorje). They have the shape of a cuesta, i.e. showing a gentle slope on the northwestern side and steep cliffs on the southeastern side. The Outer Range gently rises from the Crimean plains to a maximum elevation of 340 m. To the southeast of the intermontane depression, the more prominent Inner Range rises further, reaching a maximum elevation of 560 m.

The Main Range has an asymmetrical structure with a much steeper slope on the south side and a series of plateaus known as yailas (from Turkic *yaylagh* for summer highland pasture). The yailas are subdivided into a western and an eastern group, separated by the Angarsky Pass. The western yailas (Baydarskaya, Ay-Petrinskaya, Yaltinskaya, Nikitskaya, Gurzufskaya, Babugan, and Chatyr-Dag) constitute the highest parts of the mountains, with elevations ranging between 700 m and 1,400 m. The eastern yailas (Demerdzhi, Dolgorukovskaya, and Karabi) are somewhat lower, with maximum elevations mostly between 700 m and 1,250 m. The yailas represent karst plateaus built up of Upper Jurassic and Cretaceous limestones resting on basement rocks and their surfaces feature rolling hills and karstic depressions.

2.2. Climate

Crimea can be subdivided into three broad regions characterized by different types of climate: (1) the plains with an arid climate, (2) the Crimean Mountains with a moderately warm and humid climate, and (3) the south coast with a Mediterranean-type climate (moderately warm with dry summers; Vyed', 1999). Based on relationships between temperature, relative humidity and wind characteristics, Crimea can also be subdivided into six mesoclimatic regions (Logvinova and Barabash, 1982): I – Coastal, II – Near-shore, III – Flat steppe, IV – Hilly flats, V – Southern Piedmont, and VI – Crimean Mountains (Fig. 1).

The main factors controlling the climate of Crimea are solar radiation, atmospheric circulation, topography and the surrounding seas. Being located between 44° and 46° N, Crimea experiences significant differences between summer and winter radiation, which results in a broad range of seasonal temperatures. Atmospheric circulation over Crimea is controlled by seasonal interactions between the Polar Jet Stream and the Siberian High (Cordova, 2015). Westerly winds drive mid-latitude cyclones from the Atlantic Ocean across continental Europe or across the Mediterranean Sea toward Crimea. According to Vyed', (2000), about 75 % of the air masses arriving at Crimea originate in the Atlantic Ocean, some 10 % are related to periodic invasions of cold fronts from northern latitudes, warm and moist air from the Mediterranean Sea contributes additional 8 %, and the remaining 7 % is represented by dry air originating in Asia. The atmospheric circulation patterns exhibit a pronounced seasonality. Winter circulation is controlled by the Asian anticyclone; cyclones arriving from south and southwest transport maritime subtropical air from the Mediterranean Sea. Early spring circulation is characterized by western cyclones, which in late spring give way to southern and southwestern cyclones, bringing warm air from the Mediterranean and the Black Sea. Summer circulation is commonly affected by a large high pressure system above the southern Ukraine. The pressure gradient diminishes in summer, leading to the development of local southwestern winds, northern night sea breezes and sporadic northeast storms, resulting from the interaction between the Azov Sea and the heated land surface on the peninsula. The autumn circulation is similar to the spring one, but evolves into an opposite sequence.

Local topography, particularly the high mountain chain in the south of the peninsula, affects the atmospheric circulation. The interplay between global atmospheric circulation and the relief results in a highly heterogeneous distribution of precipitation over Crimea. The latter varies between 250 mm in the northern, steppe parts of the peninsula and >1000 mm in the Crimean Mountains, increasing by ca. 60 mm per 100 m of altitude (Vyed', 2000; Fig. 2). Because most of the cyclones arriving at Crimea move from west to east or from southwest to northeast, the southwestern part of the peninsula receives most moisture. The combined effect of global circulation and local topography results in higher precipitation in the mountains in the west than in the east.

A cursory summary of air circulation patterns presented above (based on Vyed', 2000) indicates that the latter are highly variable, and that air masses bringing moisture to Crimea may follow very different paths. Air masses may travel for ca. 3000 km across the European continent; alternatively, they may cross the large water bodies of the Mediterranean, Black and Azov Seas. This means that different moisture sources, affected also by varying degrees by en-route transformations (rain-out and recycling by evaporation and evapotranspiration) are expected to contribute in a complex manner to the overall isotopic composition of precipitation on Crimea.

3. Isotopic composition of meteoric precipitation in Crimea

3.1. Sampling and analysis

Meteoric precipitation was sampled in the city of Simferopol (Nov 2009–Mar 2016) and on the lower plateau of Chatyr-Dag (Oct 2010–Jun 2014). Precipitation was sampled following GNIP recommendations (IAEA/GNIP, 2014). Isotopic analysis of water samples was performed at Innsbruck University. Details of sampling and analytical procedures can be found in Supplement. Data on air temperature and precipitation amounts were obtained from the two WMO weather stations located at the Simferopol airport and the Angarsky Pass (Table 1). The weather stations are located in close vicinity to and within the same mesoclimatic regions as the precipitation sampling sites (Fig. 1). Therefore, meteorological parameters measured at these stations (averaged on a monthly scale) provide robust approximations of the parameters at our precipitation sampling sites.

Table 1: Precipitation sampling and weather stations used in this study

Station	WMO(*) ID	Latitude	Longitude	Altitude (m a.s.l.)	Distance from isotope sampling station
Simferopol	n/a	N 44.98°	E 34.15°	290	n/a
Simferopol airport	33946	N 45.0522°	E 33.9753°	180	12 km WNW of Simferopol station
Chatyr-Dag	n/a	N 44.80°	E 34.29°	980	n/a
Angarsky Pass	33958	N 44.7556°	E 34.3411°	765	6 km SSE of Chatyr-Dag station

(*) WMO World Meteorological Organization; n/a not applicable.

3.2. Crimean Local Meteoric Water Line

In his pioneering work, Craig (1961) demonstrated that globally, the relationship between the hydrogen and oxygen isotopic composition of precipitation can be described by a linear function, referred to as the Global Meteoric Water Line (GMWL): $\delta^2H = 8 \cdot \delta^{18}O + 10$. Regional precipitation may deviate from this global relationship resulting in Local Meteoric Water Lines (LMWL). For example, the LMWL for the Mediterranean region is $\delta^2H = 8 \cdot \delta^{18}O + 22$ (Gat. 1980; 1982), i.e. this region is characterized by a significantly higher deuterium excess (*d-excess*), reflecting intense evaporation of the Mediterranean seawater.

LMWLs for Crimea were established for the first time based on the acquired time series (67 months for Simferopol and 44 months for Chatyr-Dag; Fig. 3). Both lines have very similar slopes and intercepts: $\delta^2H = 7.3\ \delta^{18}O + 5.1$ (Simferopol) and $\delta^2H = 7.3\ \delta^{18}O + 4.8$ (Chatyr-Dag). The composite Crimean LMWL is $\delta^2H = 7.3\ \delta^{18}O + 4.8$ ($r^2 = 0.97$).

3.3. Annual and seasonal isotopic effects in precipitation

3.3.1. Annual effects

Amount-weighted annual precipitation means were calculated for the years with no gaps in the record (Table 2). As expected, precipitation at the Chatyr-Dag station, located some 700 m higher than the Simferopol station, is depleted in both isotope values (0.7 to 1.7 ‰ $\delta^{18}O$ and 3.1 to 13.2 ‰ δ^2H). Annual means vary from year to year by up to 1 ‰ $\delta^{18}O$ and 10 ‰ δ^2H.

Table 2: Amount-weighted annual mean isotope composition of precipitation at Simferopol and Chatyr-Dag

Year	Precipitation (mm)	Weighted annual mean	
		$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Simferopol			
2011	391	-7.5	-52.0
2012	316	-8.5	-57.3
2013	533	-8.1	-55.8
Chatyr-Dag			
2011	1097	-8.2	-55.2
2012	733	-10.2	-70.5
2013	719	-9.1	-59.5
Difference Chatyr-Dag–Simferopol			
2011	706	-0.7	-3.1
2012	417	-1.7	-13.2
2013	186	-1.1	-3.7

3.3.2. Seasonal effects

In Crimea, the period November–March represents the cold season while April–October corresponds to the warm season (Vyed', 2000). The difference in isotopic composition of precipitation between the two seasons is highly variable from year to year

(Table 3).

Table 3: Precipitation amount, mean temperature and amount-weighted seasonal mean isotope composition of precipitation at Simferopol and Chatyr-Dag

Year	Precipitation amount (mm)/ T (°C)		$\delta^{18}O$ (‰)		Inter-seasonal difference $\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)		Inter-seasonal difference δD (‰)
	Cold	Warm	Cold	Warm		Cold	Warm	
Simferopol								
2011	163/4	285/17	-9.4	-7.3	-2.1	-59.9	-51.4	-8.5
2012	151/1	159/20	-10.4	-5.4	-5.0	-73.2	-34.5	-38.7
2013	176/4	306/18	-8.3	-8.1	-0.2	-55.6	-55.9	+0.3
2014	120/4	205/18	-8.5	-7.8	-0.7	-59.7	-54.7	-5.0
Chatyr-Dag								
2011	368/2	522/13	-8.4	-7.4	-1.0	-50.8	-49.7	-1.1
2012	357/-1	286/16	-13.3	-6.2	-7.1	-95.2	-40.4	-54.8
2013	134/3	218/14	-9.1	-9.6	+0.5	-58.6	-62.3	+3.7
2014	184/3		-9.1			-64.8		

Note: Cold season = November-March, warm season = April-October; the cold season of 2011 started in November 2010.

The inter-seasonal difference in the stable isotope composition seems to be inversely correlated with the difference between mean seasonal temperatures (statistical significance of this correlation cannot be ascertained due to low number of observations). The difference was the highest in 2012 when the cold-season $\delta^{2}H$ values were 39 ‰ and 55 ‰ more negative (for Simferopol and Chatyr-Dag, respectively) than those of the warm-season precipitation. The mean cold season temperature for this year was 18 and 17°C lower than that of the warm season (for Simferopol and Chatyr-Dag, respectively). In contrast, there was only a very small difference (and even an inversion at the Chatyr-Dag station) between cold- and the warm-season precipitation in 2013. The respective seasonal differences in temperature were 14 and 11°C, respectively.

3.4. Lapse rate

Considering the difference in altitude between the sampling sites (690 m), it is possible to assess the $\delta^{18}O$ and $\delta^{2}H$ lapse rate at the northern slope of the Crimean Mountains. In 2011-2013, the lapse rate ranged between -0.10 and -0.25 ‰/100 m (average -0.17±0.07 ‰/100 m; 1σ) for $\delta^{18}O$ and between -0.46 and -1.92 ‰/100 m (average -1.0±0.8 ‰/100 m) for $\delta^{2}H$. The $\delta^{18}O$ lapse rate is just slightly smaller than the average for Europe (-0.21 ‰/100 m; Poage and Chamberlain, 2001) and the global average (-0.2 ‰/100 m; Bowen and Wilkinson, 2002). An earlier study by Seletsky et al., (1982) reported $\delta^{18}O$ lapse rates for the southern and the northern slopes of the Main Range of the Crimean Mountains of -0.26 ‰/100 m and -0.14 ‰/100 m, respectively. For the three stations used in that study (at 300, 660 and 1100 m a.s.l.) the isotopic data, however, did not cover the entire year and the accuracy of the reported lapse rates is therefore compromised.

3.5. Time series

In this section we present a brief evaluation of the data. More detailed statistical data analysis is presented in Dublyansky et al., (2018). In the subsequent text the *significance* of correlation is assessed by comparing the calculated values of the Pearson's moment-product correlation coefficients *r* with critical values, corresponding to a certain significance level (α). To make the verbal description uniform, *strength* of correlation is classified as *very strong* if $r > 0.8$, *strong* if $r = 0.6$ to 0.8, *moderate* if $r = 0.4$ to 0.6, and *weak and very weak* if $r = < 0.4$ (Evans, 1996).

3.5.1. Air temperature

The monthly temperature pattern at Simferopol and Chatyr-Dag shows a strong seasonality, with mean 2010-2014 temperatures of the three warmest months (June-August) of 22.9±1.7°C (Simferopol) and 19.0±1.8°C (Chatyr-Dag; 1σ) and those of the three coldest months (December-February) of 1.5±2.9°C (Simferopol) and 0.4±2.6°C (Chatyr-Dag). The temperature range is 31.5°C (Simferopol) and 27.0°C (Chatyr-Dag). Temperatures measured in Simferopol and Chatyr-Dag show a very strong correlation (r = 0.99) over the 58-month observation period. Correlation is also very strong on short time scales (Fig. 4). On average, the temperature on Chatyr-Dag was 2.4 °C lower than in Simferopol. The difference is larger for the warmest months (3.9°C) and smaller for coldest ones (1.1°C).

3.5.2. Precipitation amount

Within the observation period (2010-2014) the precipitation amount recorded at both stations does not show any seasonality. The weather station Angarsky Pass, located in the Crimean Mountains mesoclimatic region (Fig. 1), receives on an annual basis 41-56 % more precipitation than Simferopol (the Hilly Flats mesoclimatic region). Although overall monthly precipitation amount at the two stations exhibits a significant and strong correlation ($r = 0.68$), this correlation varies dramatically on shorter time scales (Fig. 4). For 2010-2012 the degree of correlation between the precipitation amount at the two stations was significant in summer and deteriorated to insignificant levels in autumn and winter. In 2012-2013 this trend reversed and, except for a very short period at the beginning of 2014, precipitation amounts at the two stations were very poorly correlated.

3.5.3. Isotopic composition of precipitation

Overall, the time series of $\delta^{18}O$ and $\delta^{2}H$ shows a seasonal pattern, with minima associated with cold periods and maxima with warm periods. This seasonal pattern, however, is not stable. For the observational period (45 month) the isotopic composition of precipitation at the two precipitation sampling sites shows a strong and statistically significant correlation (r = 0.72 for $\delta^{18}O$ and r = 0.68 for $\delta^{2}H$). On shorter time scales, however, this correlation is more variable, often falling below significant levels for several months (Fig. 5).

3.5.4. Deuterium excess

Deuterium excess (*d-excess* = $\delta^{2}H - 8\delta^{18}O$; Dansgaard, 1964) varies between -0.5 and 20.4 ‰ and shows some seasonality, tending to be larger during cold months (December-February): 11.5±3.6 ‰ and 13.5±4.0 ‰ in Simferopol and Chatyr-Dag, respectively and smaller in warm months (June-August): 5.1±3.5 ‰ and 7.9±3.1 ‰ (uncertainty is 1σ). The long-term (45 months) average value of *d-excess* is slightly smaller in Simferopol than in Chatyr-Dag (9.2 vs. 11.1 ‰, respectively). The parameter shows a strong, statistically significant correlation between the sites (r = 0.70). As with other parameters, this correlation is variable on shorter time scales. It was strong and significant in 2011 and insignificant for most of 2012 and 2013 (Fig. 6).

4. Lagrangian moisture source detection

The origin of moisture on the Crimean peninsula was evaluated using a Lagrangian moisture diagnostics method implemented in the LAGRANTO code (Wernli and Davies, 1997), further developed by Sodemann et al., (2008) to allow demarcation of evaporative moisture sources. The model calculates backward trajectories of air parcels and weighs the moisture change (evaporation or precipitation) along the trajectories by their contribution to the local precipitation in the target area. Details of the method are described in the Supplement. Modelling was based on the global atmospheric reanalysis ERA-Interim dataset (spatial resolution 0.75°, temporal resolution of 6 hours) of the European Centre for Medium-Range Weather Forecasts. This moisture source detection technique allows identification of 51 % of the moisture responsible for the precipitation in the target region. The origin of moisture incorporated at the trajectory starting position (5 %) and derived from above the planetary boundary layer (44 %) remains indeterminate.

In our model trajectories start at the nodes of a 0.75° regular grid, located between 44.25° and 45.75°N and 33.75°–34.50°E, at equally spaced levels (Δp = 49.9 hPa) from the surface to 500 h Pa above ground level. A starting grid, thus, defined 66 trajectories per time step. The 15-day backward trajectories were calculated with 6 hour time steps. Humidity content and relative humidity were monitored along the trajectories and areas of moisture uptake or loss (precipitation) were identified. The subset of trajectories that resulted in precipitation over Crimea was used for post-processing.

The results of moisture tracking for the period 1979–2017 (Fig. 7) allow for several observations to be made. The overall shape of the moisture supplying region is elongated toward west, attesting for some degree of long-range westerly moisture transport. A closer look, however, reveals that the intensity of moisture supply from areas immediately surrounding Crimea is significantly higher than that of remote sources (e.g., Northern

Atlantic). Importantly, moisture of the Crimean precipitation is derived not only from sea surfaces, but also from the surrounding land (Anatolia, Balkans, southern Ukraine, and Caucasus).

In order to quantify contribution from different sources, the whole area from which the Crimean moisture is derived was subdivided into eight source areas: Black Sea, Sea of Azov, Mediterranean Sea, Caspian Sea, Baltic Sea, Northern Atlantic Ocean, land (the surrounding land surfaces, where moisture supply is due to moisture recycling by evaporation and evapotranspiration), and other sources (sum of areas of moisture supply outside the listed areas). The share of each source in the moisture supply to Crimea was determined by integrating the evaporative contribution (in mm/months) over the respective source areas. Calculations for 2010-2015 were made on a monthly basis, in order to match the discretization of meteorological and stable isotope data.

Overall, four sources contribute about 92% of the (detectable by the Lagrangian tracking) moisture to Crimea: the surrounding land (49%), the Mediterranean Sea (15%), Black Sea (14%) and the Atlantic Ocean (14%). Contributions of each of the three remaining sources (Sea of Azov, Caspian Sea and Baltic Sea) do not exceed 3%.

Supply of moisture from the major sources exhibits a pronounced seasonality (Fig. 8). During the warmest months of the year (June-August) 71±12% of the moisture in Crimean precipitation originate from the surrounding land (as a result of evaporative and evapotranspirative moisture recycling). Contribution of the land source reaches a minimum but remains substantial (ca. 24±5%) during winter (December-February). In winter, most of the moisture (55±10%) is supplied by the combined input of Atlantic Ocean and the Mediterranean Sea, whereas during summer contribution of these sources drops to ca. 5% or less. The only major source that does not show a statistically significant seasonality is the Black Sea; its pattern of moisture supply is noisy, but the contribution tends to be somewhat smaller and more uniform during the first half of the year (January-June) and greater and more variable during the second half (July-December).

5. Discussion: Controls on the isotopic composition of precipitation in Crimea

Two parameters, air temperature and precipitation amount, are known to be most important controls of the isotopic composition of precipitation worldwide (Gat et al., 2001). In particular, variations in the local temperature (or the closely related parameter of the precipitable water content) are the dominant parameter (Yurtsever, 1975; Fricke, O'Neil, 1999). At stations situated in mid-continental settings the isotopic composition of precipitation typically follows the seasonal air temperature cycle (Gat et al., 2001). In tropical regions, on the other hand, the isotopic composition scales negatively with the amount of precipitation (Dansgaard, 1964; Gat et al., 2001). Given Crimea´s setting as a peninsula adjacent to the Black Sea, both seasonal temperature and precipitation amount should exert a control on the isotopic composition of precipitation. On another hand, we found that sources supplying the moisture in the Crimean precipitation change seasonally between predominantly continental in summer to predominantly maritime (Mediterranean Sea and Atlantic) in winter. This change may also be, at least partly, responsible for the seasonal change of stable isotope properties in Crimean precipitation.

5.1. Evaluation of variables

Two variables for which we will try to identify controls (dependent variables) are the $\delta^{18}O$ and *d*-excess. It is noteworthy that there is statistically significant, moderate correlation between them (r = -0.55 and -0.52 for Simferopol and Chatyr-Dag, respectively), i.e., about 27-30% of the variability of one parameter can be explained by the variability of the other.

To assess the possible controls of the meteorological parameters (air temperature T and precipitation amount ppt) and the moisture sources on the dependent variables we calculated Pearson's coefficients of correlation for the 45 month-long time series. Results are summarized in Table 4. For the purpose of the regression analysis T, ppt, and contributions from different moisture sources will be treated as independent variables (predictors).

Table 4. Pearson's moment-product correlation coefficients *r* for the isotopic parameters of precipitation, meteorological parameters and moisture sources in Simferopol and at Chatyr-Dag (monthly means; Oct 2010 – Jun 2014)

	$\delta^{18}O$	*d-exess*	*T*	*ppt*
Simferopol				
$\delta^{18}O$	1			
d-exess	-0.548	1		
T	**0.495**	-0.468	1	
ppt	-0.143	-0.059	0.039	1
Land	0.458	**-0.545**	0.789	0.158
Med+Atl	-0.445	0.457	-0.849	-0.060
Black Sea	-0.008	0.136	0.151	-0.214
Med. Sea	-0.259	0.362	-0.595	0.051
Atlantic	-0.394	0.297	-0.639	-0.150
Chatyr-Dag				
$\delta^{18}O$	1			
d-exess	-0.522	1		
T	**0.628**	-0.383	1	
ppt	-0.158	0.191	-0.121	1
Land	0.505	**-0.534**	0.783	-0.023
Med+Atl	-0.529	0.424	-0.852	0.138
Black Sea	0.064	0.237	0.163	-0.223
Med. Sea	-0.299	0.386	-0.572	0.152
Atlantic	-0.478	0.220	-0.669	0.043

Notes: Values below significance level (α=0.05; r_{crit} = 0.296) are shaded. Highest values of *r* for each dependent variable are in bold.

It can be seen from Table 4 that the correlation between *T* and *ppt* is very weak and statistically insignificant (*r* = -0.04 and -0.12). These two parameters can therefore be considered independent. In contrast, the time series of sources of moisture contributions are not entirely independent. Sources land and Mediterranean Sea + Atlantic exhibit a strong anti-phase seasonal cyclicity (Fig. 8). Together they contribute 75±11% of the total moisture, which results in very strong negative correlation between them (*r* = -0.88; Table 5).

Table 5. Pearson's moment-product correlation coefficients *r* for contributions of different moisture sources to precipitation in Simferopol and at Chatyr-Dag (monthly means; Oct 2010 – Jun 2014)

	Land	Med+Atl	BlackSea	Med.Sea	Atlantic
Land	1				
Med+Atl	-0.884	1			
Black Sea	-0.245	-0.224	1		
Med. Sea	-0.667	0.761	-0.152	1	
Atlantic	-0.612	0.686	-0.175	0.050	1

Notes: Values below significance level (α=0.05; r_{crit} = 0.296) are shaded. Med+Atl is the sum of contributions of the Mediterranean Sea and the Atlantic.

Similar, albeit weaker effects are observed if the two sources, Mediterranean Sea and Atlantic, are considered separately. Being mutually uncorrelated (*r* = 0.05), each shows a strong negative correlation with the land source (*r* = -0.67 and *r* = -0.61, respectively). The land and the Mediterranean+Atlantic sources, therefore, are complementary; only one of them will be used in analysis.

A strong correlation also exists between the land and the Mediterranean+ Atlantic sources and the temperature at Simferopol and Chatyr-Dag (*r* = 0.79 and 0.78, and *r* = -0.84 and -0.85, respectively). These variables also cannot be considered entirely independent. Both are related to seasonality, which represents the complex nonlinear response of the physical climate system to annual solar forcing. Despite the fact that in case of air temperature this forcing operates more locally and directly (solar radiant exposure in Crimea ranges from 4.7-5.2 $\cdot 10^8$ J/m^2 in June to 4.0-6.0 $\cdot 10^7$ J/m^2 in December; Vyed', 2000), while in case of the seasonally changing moisture sources it operates globally, by affecting atmospheric circulation, the effects seem to be linked. The common forcing expresses itself as multicollinearity when constructing the multiple regression models. Out of the four major sources of humidity only the Black Sea is entirely independent of all other sources.

5.2. Oxygen isotope

The $\delta^{18}O$ value of precipitation exhibits no statistically significant correlation with precipitation amount (r = -0.14 and -0.16). In contrast, the correlation with air temperature is significant (r = 0.50 and 0.63), indicating that between 25% and 39% of the $\delta^{18}O$ variability can be explained by variations in T. Interestingly, the correlation for Simferopol is substantially worse than for Chatyr-Dag.

As was discussed above, the temperature and variables describing the moisture sources land and Mediterranean + Atlantic exhibit multicollinearity. The two remaining independent variables, precipitation amount and the Black Sea source, exert a statistically insignificant control on $\delta^{18}O$ of Crimean precipitation. Therefore, the multiple regression equations can be reduced to linear regressions: $\delta^{18}O = 0.16\,T - 9.07$ (‰) for Simferopol and $\delta^{18}O = 0.25\,T - 10.49$ (‰) for Chatyr-Dag. These empirical equations differ substantially from the relation for North Atlantic and European GNIP stations reported by Yurtsever (1975): $\delta^{18}O = (0.521 \pm 0.014)\,T - (14.96 \pm 0.21)$. Coefficients of determination r^2 = 0.25 and r^2 = 0.39 (Simferopol and Chatyr-Dag, respectively) indicate that only 25% and 39 % of variability in $\delta^{18}O$, respectively, can be explained by variations in T.

5.3. Deuterium excess

Deuterium excess is sensitive to moisture source conditions (specifically, the relative humidity at the ocean surface during evaporation; Merlivat and Jouzel, 1979; Johnsen et al., 1989; Pfahl and Wernli, 2008; Pfahl and Sodemann, 2014) and, therefore, is suitable for assessing the origin of water vapour. High *d-excess* values reflect fast evaporation (low RH) and stronger kinetic isotope effects during evaporation; low *d-excess* reflects slow evaporation in conditions of high RH (Clark and Fritz, 1997). For example, European precipitation originating in the Mediterranean Sea has higher values of *d-excess* = +22‰ (Gat and Carmi, 1970), while precipitation of Atlantic provenance has lower *d-excess* = +10‰ (Craig, 1961). The *d-excess* of precipitation can also reflect processes of terrestrial moisture recycling: evaporation from the ground (bare soil, surface water bodies) leads to the increase in *d-excess* (Salati et al., 1979; Gat and Matsui, 1991) while evapotranspiration and condensation have no effect (Gat, 2005).

It is becoming increasingly apparent, however, that the concept delineated above might be too simplistic. For example, Rank and Papesch (2005), Froehlich et al. (2008) and Hager and Foelsche (2015) reported that the seasonal pattern of *d-excess* in Austria is different for stations located in valleys and on the mountains, even if the horizontal distance between them is only a few kilometers. These authors also found no significant difference in *d-excess* at stations located on the northern and the southern side of the Alps (i.e., affected by different moisture sources). They suggested that these aberrations reflect secondary fractionation processes which occur when moist air masses ascend slopes of mountains so that the altitude effect and the effect of sub-cloud evaporation mask and distort the initial isotopic moisture source signal.

Over the entire period of observation in Crimea (45 months) *d-excess* shows a statistically significant, moderately negative correlation with the contribution from the land moisture source (r = -0.55 and r = -0.53 for Simferopol and Chatyr-Dag, respectively). Attempts of correlating the measured *d-excess* with the precipitation source land at shorter time scales was unsuccessful (Fig. 9). A statistically significant correlation is present in 13% and 25% of the time (Simferopol and Chatyr-Dag, respectively; at α = 0.05). The pattern is not stable on a year to year basis. Correlations are higher for warm months of 2011 and 2012, when the contribution of the land source was highest. In 2013, however, the highest contributions from land showed statistically insignificant correlation with *d-excess*.

The absolute values of *d-excess* of the land source are variable, ranging between -0.6 and 19.1 ‰. For warm months, when the contribution from this source is highest, mean *d-excess* values range between 7.0-7.6±4.6‰ for Simferopol and 7.8-8.7±3.6‰ for Chatyr-Dag (1σ). These values represent the best approximation of the *d-excess* "fingerprint" of the land moisture source. Evaluating the fingerprint for other major moisture sources is not possible, because the share of individual sources in Crimean precipitation is almost always less than 50%.

On average, *d-excess* is ca. 1.8 ‰ greater in Chatyr-Dag compared to Simferopol (45 months of observations). Considering the difference in altitude between the two stations, the altitude effect for *d-excess* is 0.26 ‰/100 m, which is smaller than the value 0.43 ‰/100 m reported by Rank and Papesch (2005) for the Alps.

One parameter that can be used to quantify the setting of a precipitation site is the ratio of the spread in *d-excess* values relative to the range in $\delta^{18}O$ (Gat et al., 2001). Over the European continent, this value varies from 1.8 to 2.8 at coastal stations (such as Reykjavik, Valentia in Ireland, and Faro in Portugal) to 0.35 to 0.7 at continental stations (e.g., Berlin, Krakow, and Vienna). For Simferopol and Chatyr-Dag this parameter is 1.3 and 1.4, respectively, placing the study area's setting in between the typical coastal and the typical continental ones.

Data in Table 4 show that the contribution of moisture from the land source is the independent variable, which shows the highest correlation with *d-excess*. Similarly to $\delta^{18}O$, potential predictor variables *T* and *Mediterranean + Atlantic* source can be discarded because of the multicollinearity issue, whereas the remaining variables (amount of precipitation and the moisture contribution from the Black Sea) were found to exert statistically insignificant controls on *d-excess*. The regression equations are: *d-excess* = -0.11·land + 14.45 for Simferopol and *d-excess* = -0.11· land + 16.12 for Chatyr-Dag. Coefficients of determination r^2 = 0.30 and 0.29 indicate that only 30% and 29 % of variability in *d-excess* are explained by variations in the moisture contribution from the land source at Simferopol and Chatyr-Dag, respectively.

5.4. NAO index

The North Atlantic Oscillation (NAO) is known to profoundly influence the isotopic composition of precipitation via its control on air temperature and the trajectories of the westerly winds that carry moisture onto Europe during winter (Comas-Bru et al., 2016). In central Europe, winter (October through March) precipitation δ^2H and $\delta^{18}O$ values are known to correlate with the winter NAO index (Hurrell, 1995; Deininger et al., 2016).

The NAO indices (Jones et al., 1997) were compared with the stable isotope time series. For the period of observation (45 month) the isotopic composition of precipitation ($\delta^{18}O$) at the two sampling sites show a very weak correlation only (*r* = -0.19 for Simferopol and *r* = -0.42 for Chatyr-Dag). Only 3 to 17% of variations in $\delta^{18}O$ of precipitation can therefore be attributed to the strength of the NAO. The correlation does not improve substantially if only the winter months, October-March, are included (*r* = -0.08 for Simferopol and *r* = -0.45 for Chatyr-Dag). These low numbers are not surprising given our finding that the Atlantic source contribution in October-March does not exceed, on average, 20% (sect. 4).

5.5. Local and far-field controls on the isotopic composition of precipitation in Crimea

For the entire period of observation (45 months) out of the two "local" factors, temperature and precipitation amount, only the former shows a statistically significant correlation with the isotopic composition of precipitation. The correlation between *T* and $\delta^{18}O$ is moderate (r = 0.50) for Simferopol and strong (r = 0.63) for Chatyr-Dag precipitation, indicating that some 25% of variability in $\delta^{18}O$ in Simferopol and 39% on Chatyr-Dag can be explained by the temperature regime at these sites. On shorter time scales (6 months running correlation), the picture is more nuanced (Fig. 10). The parameters remain strongly correlated for periods of several months, but then the correlation breaks down. Several observations can be made. The correlation between *T* and isotopic composition of precipitation is more pronounced in the mountain site Chatyr-Dag and stronger during cold months. The correlation time series for the two sites exhibit mutually consistent temporal patterns for some periods of the time (e.g., 2012-2013) but dissimilar ones for others (e.g., 2011). These observations suggest that the isotopic composition of precipitation in Crimea is affected by factors other than temperature, and that the influence of these other factors varies not only in time but also spatially (i.e., affecting the two sites to a different extent).

The considered far-field factors comprise evaporative sources of moisture, reconstructed by means of Lagrangian moisture tracking. Contributions of the main sources of moisture also show a significant correlation with the isotopic composition of precipitation. This correlation, however, may reflect the fact that contributions from different precipitation sources exhibit a strong seasonality. The roles of seasonally changing air temperature and (possibly) seasonally varying isotopic composition of the moisture derived from different sources cannot be disentangled, however.

Another far-field parameter known to exert a strong control on the isotopic composition of precipitation in Europe, the NAO index, shows no statistically significant correlation with Crimean precipitation.

5.6. Isotopic composition of cold- and warm-season precipitation

One of the findings of this study, which is relevant for isotope hydrogeology research in the area, is that for a number of years (three out of four for Simferopol and two out of three at Chatyr-Dag) there is little or no difference between the isotopic composition of precipitation in cold and warm seasons (sect. 3.3.2). This observation is partly in conflict with the concept that the low isotope values of some karst springs in Crimea reflect predominant winter recharge (Selecky et al., 1982; Dublyansky et al., 2012). We note that the distinction between cold and warm seasons, accepted by meteorologists, may not be entirely suitable when discussing the conditions of recharge on the karst plateaus of the Crimean Mountains.

6. Conclusions

Systematic sampling of precipitation was carried out over a period of 58 months at two stations in Crimea, located in the Crimean Piedmont (Simferopol, 290 m a.s.l.) and on the northern slope of the Main Range of the Crimean Mountains (Chatyr-Dag, 980 m a.s.l.). Oxygen and hydrogen isotopes in precipitation at both stations plot along tightly constrained lines with very similar slopes and intercepts. The Local Crimean Meteoric Water Line was constructed from the combined data set: $\delta^2H = 7.3\ \delta^{18}O + 4.8$ ($r^2 = 0.97$). Precipitation at the Simferopol and the Chatyr-Dag stations is not consistently controlled by the local air temperature nor the precipitation amount. Remote controls, such as moisture sources and the NAO, do not exert a major control on the isotopic composition of precipitation in Crimea either. To summarize, the isotopic composition of precipitation in Crimea seems to be controlled by a combination of local and far-field factors. Contributions of these parameters vary on different time scales as well as spatially. No simple controlling relationship was identified in the currently available dataset.

Data availability

Data are available at http://dx.doi.org/10.17632/jmtgcdcmm2.1.

Conflict of interests

The authors declare that they have no conflict of interest.

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Captions

Stable isotopic composition of atmospheric precipitation on the Crimean Peninsula and its controlling factors

(by Yuri V. Dublyansky, Alexander B. Klimchouk, Sergey V. Tokarev, Gennady N. Amelichev, Lukas Langhamer, and Christoph Spötl)

Figure 1: Physiography and climate regions of Crimea. Mesoclimatic regions: I – Coastal; II – Near-Shore; III – Flat-Steppe; IV – Hilly Flats; V – Southern Piedmont; VI – Crimean Mountains (by Logvinova and Barabash, 1982). Karst plateaus (yaylas): 1 – Baydarskaya; 2 – Ay-Petrinskaya; 3 – Yaltinskaya; 4 – Nikitskaya; 5 – Gurzufskaya; 6 – Babugan; 7 – Chatyr-Dag; 8 – Demerdzhi; 9 – Dolgorukovskaya; 10 – Karabi.

Figure 2: Seasonal distribution of precipitation (mm) and temperature (°C) in Crimea (by Vyed', 2000): (a, d) cold period (Nov-Mar), (b, e) warm period (Apr-Oct), (c, f) annual.

Figure 3: Relation between monthly mean $\delta^{18}O$ and $\delta^{2}H$ values defining the Local Meteoric Water Lines for Simferopol and Chatyr-Dag.

Figure 4: Running correlation (6 month window) for temperature (upper panel) and precipitation amount (lower panel) at the Simferopol airport and the Angarsky Pass weather stations for 2010–2014. Cold seasons are highlighted by shaded vertical bars. Horizontal dashed lines mark critical values of Pearson's correlation coefficient at different α values.

Figure 5: Time series and running correlation (6 month window) for $\delta^{18}O$ of precipitation at the Simferopol and the Chatyr-Dag sampling sites in 2011–2013. Cold seasons are highlighted by shaded vertical bars (horizontal dashed lines as in Figure 4).

Figure 6: Time series and running correlation (6 month window) for *d-excess* at the Simferopol and the Chatyr-Dag sampling sites in 2011–2013. Cold seasons are highlighted by shaded vertical bars (horizontal dashed lines as in Figure 4).

Figure 7: Mean moisture supply to the Crimean Peninsula in 1979-2017. Only areas supplying more than 0.002 mm/month are shown. Note that the color scale ends at 0.02 mm/month, whereas the maximum evaporative contribution is 0.264 mm/month.

Figure 8: Seasonality of major moisture sources for Crimea. Upper panel – contributions of Mediterranean Sea, North Atlantic and their sum; lower panel – contributions of all four major sources.

Figure 9: Running correlation for *d-excess* and moisture contribution from land sources in Simferopol and on Chatyr-Dag (6 month sliding window) and the time series for moisture contribution from land sources. Horizontal dashed lines as in Figure 4.

Figure 10: Running correlation for $\delta^{18}O$ and air T in Simferopol and on Chatyr-Dag (6 month sliding window). Horizontal dashed lines as in Fig. 4.

Highlights

- First systematic study of the isotopic composition of precipitation in Crimea.
- Monitoring over 58 months at two stations located at 290 and 980 m a.s.l.
- Cold-season precipitation is isotopically similar to the warm-season one.
- Moderate control by temperature, no control by precipitation amount.
- No links to far-field control e.g., sources of moisture or NAO.

CRediT author statement

Yuri Dublyansky: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Data curation, Supervision, Writing – Original draft preparation, Writing – Review & Editing, Project Administration, Funding Acquisition. **Alexander Klimchouk:** Conceptualization, Methodology, Investigation, Writing – Review & Editing, Supervision, Project Administration. **Sergey Tokarev:** Methodology, Investigation, Data curation, Writing – Review & Editing, Visualization. **Gennady Amelichev:** Methodology, Investigation, Data curation, Writing – Review & Editing. **Lukas Langhamer:** Methodology, Software, Formal Analysis, Investigation, Visualization. **Christoph Spötl:** Conceptualization, Methodology, Resources, Writing – Review & Editing.