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Characterizing hydrological processes within kettle holes using stable water isotopes in the Uckermark of northern Brandenburg, Germany

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Abstract

Understanding the hydrologic connectivity between kettle holes and shallow groundwater, particularly in reaction to the highly variable local meteorological conditions, is of paramount importance for tracing water in a hydro(geo)logically complex landscape and thus for integrated water resource management. This article is aimed at identifying the dominant hydrological processes affecting the kettle holes' water balance and their interactions with the shallow groundwater domain in the Uckermark region, located in the north-east of Germany. For this reason, based on the stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$), an isotopic mass balance model was employed to compute the evaporative loss of water from the kettle holes from February to August 2017. Results demonstrated that shallow groundwater inflow may play the pivotal role in the processes taking part in the hydrology of the kettle holes in the Uckermark region. Based on the calculated evaporation/inflow (E/I) ratios, most of the kettle holes (86.7%) were ascertained to have a partially open, flow-through-dominated system. Moreover, we identified an inverse correlation between E/I ratios and the altitudes of the kettle holes. The same holds for electrical conductivity (EC) and the altitudes of the kettle holes. In accordance with the findings obtained from this study, a conceptual model explaining the interaction between the shallow groundwater and the kettle holes of Uckermark was developed. The model exhibited that across the highest altitudes, the recharge kettle holes are dominant, where a lower ratio of E/I and a lower EC was detected. By contrast, the lowest topographical depressions represent the discharge kettle holes, where a higher ratio of E/I and EC could be identified. The kettle holes existing in between were categorized as flow-through kettle holes through which the recharge takes place from one side and discharge from the other side.

KEYWORDS

evaporation, groundwater inflow, kettle hole, stable water isotope, surface–groundwater interactions

1 | INTRODUCTION

The Pleistocene landscapes of northern Europe, Asia, and America are composed of a multiplicity of interwoven freshwater ecosystems including wetlands, riparian zones, and lake systems (Brock, Yi, Clogg-Wright, Edwards, & Wolfe, 2009; Patzig, Kalettka, Glemnitz, & Berger, 2012). Prolific and widely distributed within these regions are the so-called kettle hole or pothole ponds. Kettle holes are generally small (<1 ha), shallow depressional wetlands of postglacial origin, and have a density in north-eastern Germany of up to 40 per km^2. Small water bodies such as kettle holes have been shown to play a significant role in maintaining biodiversity in otherwise harsh, monoculture agrarian landscapes (Joniak, Kuczynska-Kippen, & Nagengast, 2007; Lischeid & Kalettka, 2012; Patzig et al., 2012; Platen, Kalettka, & Ulrichs, 2016). These ponds provide permanent habitats for numerous threatened and endangered Red List species as well as presenting important migratory habitats to waterfowl (Hildrew, Townsend, & Francis, 1984; Platen et al., 2016; Prowse & Conly, 2000). Due to their location within often agriculturally intensive regions, kettle holes are regularly subjected to large anthropogenic forcing including pollution by agrochemicals, the removal of habitats, and buffer zones with farm machinery as well as unsustainable wetland drainage practices (Kalettka & Rudat, 2006; Lischeid, Kalettka, Merz, & Steidl, 2016). Though kettle holes are of small size, it has been shown that depressional wetlands and small water bodies <0.001 km^2 give rise to disproportionately greater atmospheric carbon emissions when compared with other, often larger surface water bodies (Holgerson & Raymond, 2016; Lischeid et al., 2018). Moreover, recent studies on similar small water bodies and lakes in Canadian freshwater ecosystems have shown prominent declines in water levels resulting from climate change (Brock et al., 2009; Emmerton, Lesack, & Marsh, 2007).

Studies of kettle holes within central European postglacial landscapes have until recently, focused predominantly on biological interactions between macrophyte plant species and zooplankton with internal water quality parameters and internal biogeochemical cycling at the local scale (Joniak et al., 2007; Joniak, Kuczynska-Kippen, & Gabka, 2017; Joniak, Nagengast, & Kuczynska-Kippen, 2009; Kuczynska-Kippen & Joniak, 2016; Patzig et al., 2012). Though the degree of biological interaction among kettle holes is an important current prominent research topic, a detailed hydrological investigation of central European depressional wetlands is presently lacking. A consideration for the hydrological conditions within and between kettle holes is essential considering the importance for understanding the impacts that climate change may have on these unique wetland regions as well the development of hydrologically controlled agricultural pollutant pathways (EC., 2006).

Many previous studies on central European kettle holes have considered them frequently as hydrologically isolated, individual water bodies located above regional groundwater. The filling dynamics were implied to be dominated chiefly by winter run-off from snowmelt and rain on frozen soil and drying by significant summer evaporation producing pronounced wet–dry cycles without significant groundwater interaction (Kalettka & Rudat, 2006; Nitzsche et al., 2017).

Hydrogeological investigations however from similar age Pleistocene kettle holes within the prairie region of north America and Canada have propounded that a more significant interrelation between groundwater and kettle holes can exist (Dempster, Ellis, Wright, Stone, & Price, 2006; Hayashi, van der Kamp, & Rudolph, 1998; Winter & LaBaugh, 2003). Within the prairie region, kettle holes have been identified to form topographically dependent, shallow groundwater connected networks, allowing the delimitation and classification of kettle holes into recharge, flow-through, and discharge hydraulic types (Hayashi et al., 1998; van der Kamp & Hayashi, 2009).

In order to address the question of kettle hole hydrology and groundwater dependence, several tools are available including the installation of hydrometric devices for water level derivation coupled with modelling approaches. Although these methods are locally highly useful, they suffer from high costs and limited spatial coverage often to a few specific sites. This is particularly restricting within regions of high spatial hydrologic variability and numerous water bodies such as within Pleistocene landscapes (Yi, Brock, Falcone, Wolfe, & Edwards, 2008). Despite the fact that the skills of mechanistic hydrological models are often oversold, there is a broad agreement on their capabilities in plausible simulation and prediction (Beven, 1989; Woolhiser, 1996).

However, the validity of physics-based hydrological models for process simulation poses formidable challenge mainly due to their computational burden/overparameterization resulted from the watershed heterogeneity and challenges with model identifiability. For the given reasons, their applicability to large scales has been restricted for practical decision support role (Ratto, Castelletti, & Pagano, 2012).

To overcome the limitations posed by traditional hydrological techniques in these environments, tracer approaches can be of high value. Stable isotopes of water (18O/16O, 2H/1H) are considered as ideal tracers of hydrological processes due to their presence within all parts of the hydrosphere and the simplicity and rapidity of sample collection and analysis (Bajjali, Clark, & Fritz, 1997; Bhat & Jeelani, 2018; Clark & Fritz, 1997; Hao et al., 2019; Yi et al., 2008). The ability of stable water isotopes, resulted from a temperature-based fractionation, to quantify evaporation has been asserted in several studies as effective hydrological tracers (Longinelli & Selmo, 2003; Euliss, Ned, & Mushet, 2004; Price, Swart, & Willoughby, 2008; Vreča, Bronić, Horvatinčić, & Barešić, 2006).

Globally, the stable isotopic composition of terrestrial waters is typified by the global meteoric water line (GMWL) of Craig, Gordon, and Horibe (1963): $\delta^2 H = 8 \times \delta^{18}O + 10$. On a local level, however, meteoric waters often possess a variable composition producing a local meteoric water line (LMWL; Brock et al., 2009; Craig et al., 1963). Typically during progressive evaporation of a water body such as a kettle hole, isotopic fractionation leads to enrichment of heavy stable isotopes of ^2H and ^{18}O within the residual water whilst the lighter isotopes of ^1H and ^{16}O are removed to a vapour phase. The result is the systematic evolution of kettle hole isotopic composition in δ-space along a local evaporation line (LEL) whose gradient is typically smaller than both the GMWL and LMWL. The relative position and movement of the isotopic composition of a water body along the

LEL have been shown to relate intimately to the water balance of that specific water body, which may be quantified using isotope mass balance models (Brock et al., 2009; Gat & Gonfiantini, 1981; Gibson & Edwards, 2002). The outputs from these isotope mass balance models have been proposed to represent an effective method by which to classify water bodies into groups based on the degree of hydrologic connectivity or isolation from streams and/or groundwater (Brock et al., 2009). So far, no attempts have been made to classify central European kettle holes on this basis.

Kettle holes have a high informative value functioning as a suitable indicator for changes of regionally connected hydrological system. The unsolved challenge of kettle holes arise from their complexity, high abundance, and a stunning degree of heterogeneity to a wide range of scales and parameters including media properties (e.g., hydraulic conductivity), fluxes (e.g., run-off), or state variables (e.g., soil moisture) that necessitate advancing our understanding of their elaborate hydrological system (Brock et al., 2009; Skrzypek et al., 2015). The challenge becomes even more formidable for the characterization and quantification of complex and sporadic interaction between seemingly isolated kettle holes and their adjacent shallow groundwater as a result of high dynamics of the effective transmission zone where the flux exchange takes place between the two domains (e.g., groundwater and kettle hole; Brannen, Spence, & Ireson, 2015). This quantification is important not only for water resource management but also for maintaining the biodiversity of kettle holes in order to resolve conflicts related to water use and for restoring water ecosystems.

Several studies have sought to characterize and distinguish the water balance components that possibly contribute to kettle holes located across central North America (Haque, Ali, & Badiou, 2018; Hayashi, van der Kamp, & Rosenberry, 2016; Hayashi et al., 1998; Hayashi, van der Kamp, & Schmidt, 2003; Lissey, 1971; Neff & Rosenberry, 2018; Upadhyay, Pruski, Kaleita, & Soupir, 2019; van der Kamp & Hayashi, 2009) that encompass three southern Canadian provinces and five upper Midwest states, that is, the prairie pothole region. Nevertheless, by contrast, the importance of kettle hole–groundwater interactions in the Uckermark region has remained as one of the most important questions underlying the investigations into the hydrology of these small water bodies. To that respect, the initial studies conducted in the Uckermark region suggested that kettle holes are disconnected from groundwater domain and they should be treated as isolated water standings (Kalettka, Rudat, & Quast, 2001). Recent studies have suggested that the isolated kettle holes can be variably connected to each other as well as to the shallow groundwater and may show seasonally variable interactions (Gerke, Koszinski, Kalettka, & Sommer, 2010; Kalettka & Rudat, 2006; Lischeid et al., 2017; Nitzsche et al., 2017). This connection could potentially be related to the topographical position of a kettle hole with respect to the shallow groundwater system (Lischeid et al., 2018).

With respect to the major water suppliers of potholes, pond's permanence of the prairie pothole region is highly dependent on the direct rainfall on the potholes and upland run-off generated form snow drift, snowmelt run-off, and occasional summer run-off during heavy rains (Brooks et al., 2018; Hayashi et al., 2016). By contrast, the pond's permanence of the kettle holes in the north-east of Germany is heavily reliant upon the shallow groundwater inflows (Lischeid et al., 2017; Lischeid et al., 2018; Nitzsche et al., 2017) and is partially supplied with the direct rainfall on ponds and diffuse run-off produced as a result of rainfall occurrence on the frozen soils (Gerke et al., 2010). Therefore, as there are a few studies in the north-east of Germany (where the kettle holes are highly scatted) that have attempted to gain insights into the water storage suppliers of these kettle holes, the results of this study can be compared with an intensive and progressive research undertaken so far in the North of America. Consequently, we can enhance our understanding of the effects of geological setting, meteorological condition, and dominant hydrological processes that sustain the pond permanence (hydroperiod) in each of these distinguishable systems.

In this study, first, we aim to identify the main factors controlling the observed patterns of enrichment and dilution phases in kettle holes by investigating the isotopic composition of samples taken from rainfall, 50 kettle holes across the Uckermark region of north-east Brandenburg, and observation wells installed in their nearby. Second, we explore the possible connectivity of kettle holes to shallow groundwater based on the calculation of evaporative losses across the region via evaporation/inflow (E/I) ratios obtained from the isotopic mass balance model "Hydrocalculator." Third, we investigate the topographical-driven connectivity among the kettle holes by analysing the relationships between E/I ratios and electrical conductivity of kettle holes with their respective landscape elevations. Based upon these results, a hypothetical landscape model for the Uckermark region portraying hydrologic connectivity among the kettle holes and in relation to their adjacent shallow groundwater domain will be proposed.

Addressing the research questions set for this study provides profound insights into tracing and quantifying the waters through the hydrologic cycle, which has not been taken into consideration for the kettle holes located in the north-east of Germany in relation to whose adjacent shallow groundwater system. We anticipate that our findings will be of use in future water management decisions to protect these wetlands, particularly as farmers expand crop production in this region.

2 | METHODOLOGY

2.1 | Site description

The Quillow catchment located in the Uckermark region covers an area of approximately 138 km^2 (N 53.317°, E 13.863°) within the northernmost region of Brandenburg county in north-eastern Germany (Figure 1; Nitzsche et al., 2017). Meteorologically, the Uckermark region displays a semiarid climate with a mean annual temperature of 8.6°C, determined from continuous meteorological monitoring at the climate station from the Leibniz Centre for Agricultural Landscape Research (ZALF) in Dedelow from 1992 until 2015

FIGURE 1 Overview of the geographical location of the Uckermark region in relation to Germany, as well as the location of all kettle holes included in the 2017 study. Red triangles correspond to individual kettle holes sampled during the 2017 sampling campaign
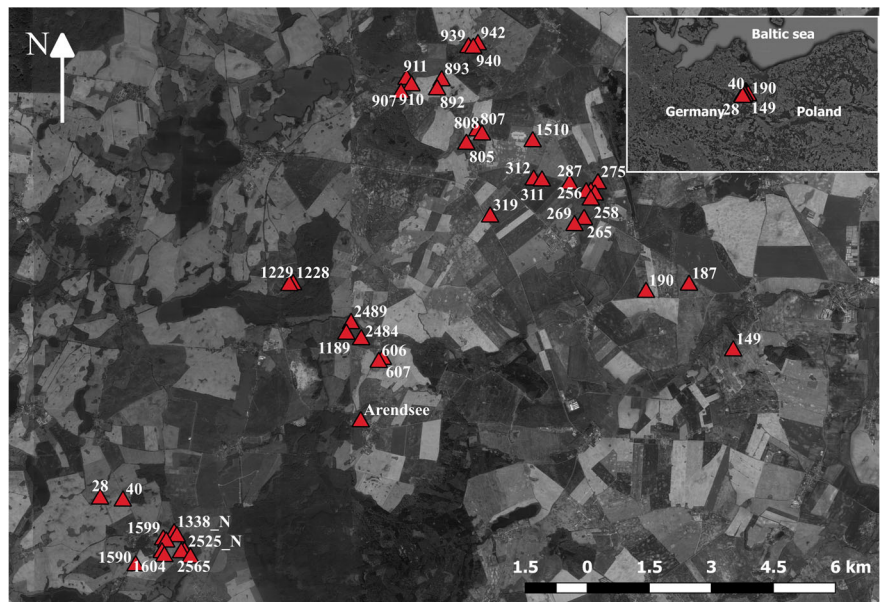
FIGURE 2 Meteorological variables recorded at Dedelow meteorological station over the period of January 2015 to August 2017
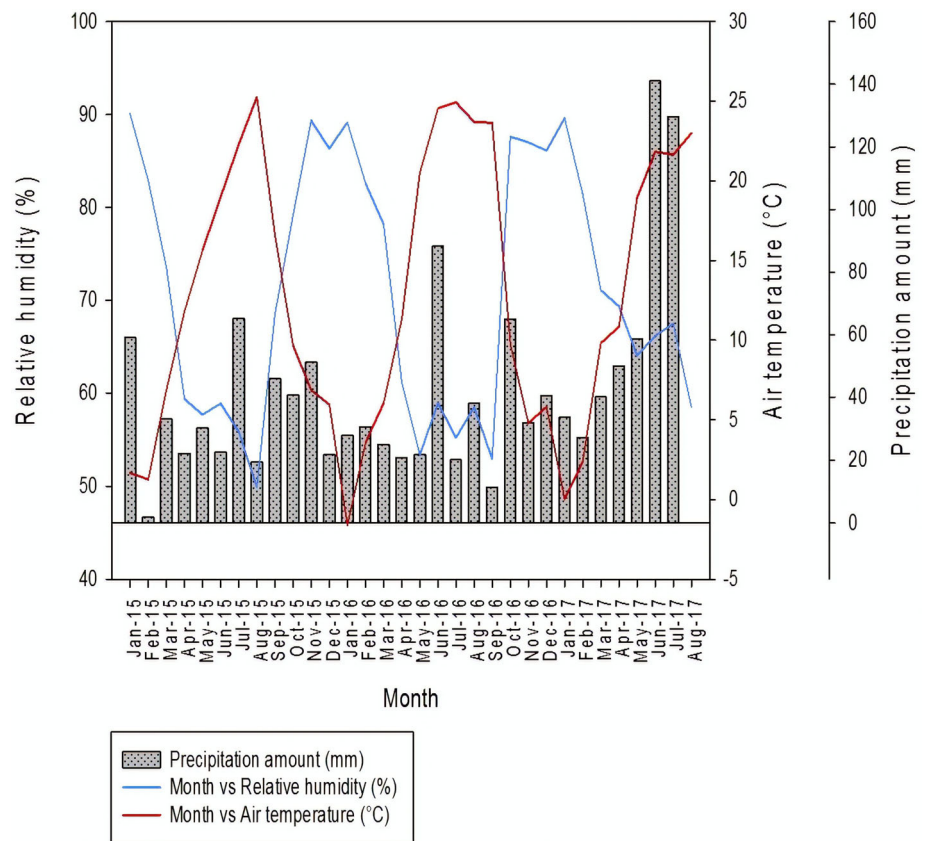
(Nitzsche, et al., 2017). The calculated annual averages of temperature in 2015 to 2017 are 11.9°C and 13.7°C, respectively. Relative humidity changes from 70.99% to 69.51% in 2015 and 2016, respectively. The variations of relative humidity, temperature, and precipitation for the studied period are illustrated by Figure 2. Based on the meteorological data obtained from the Dedelow Research Station in the northern part of the catchment, the average of precipitation varies from 490 to 640 mm/year, indicating a temperate to continental climate

(Merz & Steidl, 2015). Potential evapotranspiration, calculated as reference grass evapotranspiration, according to Allan et al. (1998) ranges from 570 to 635 mm/year. Annual groundwater recharge, on average, is rather low and changes from 70 to 90 mm/year (Lahmer & Pfützner, 2003). Long-term mean discharge 1972–1990 of the Quillow stream after confluence with the stream from the adjacent catchment amounted to 143 mm/year (Lischeid et al., 2017). Despite that fact that the region is characterized by an abundance of

groundwater resources, wetlands, and in particular kettle holes, major fraction of the precipitation evaporates, and surface run-off is negligibly small (Nutzmann & Mey, 2007), generating mostly from agricultural land (Schindler, Müller, Thiere, & Steidl, 2004).

The region demonstrates a moderately undulating topography between 40 and 112 m above sea level (MASL), typical of hummocky ground moraine landscapes with abundant kettle holes and wetlands occurring between hummocks. The number of classified kettle holes in the Uckermark region has been estimated to be greater than 1,550 based on extensive fieldwork over the past decades (Kalettka & Rudat, 2006; Nitzsche et al., 2017). Geologically, the region itself consists of Pleistocene glacial sediments derived from three large glaciations of the Elsterian, Saalian, and Weichselian. The present landscape of the Uckermark region was particularly strongly shaped during the Weichselian glaciation (Ehlers, Gibbard, & Hughes, 2011). The regional groundwater structure of Brandenburg is closely related to the Pleistocene glacial landscape, with different regional groundwater systems being delineated on the basis of large geomorphological structures including end moraines, glacial valleys, and till upland regions. Sediment types deposited over the study area consist of a range of clastic sediments of glacial fluvial origin and till. Typically, permeable and porous sands form aquifer bodies, and more impermeable and lower conductivity till beds consisting of clay, silt, and calcium-containing sands forming predominantly aquitards (Ehlers, Grube, Stephan, & Wansa, 2011; Merz & Pekdeger, 2011; Merz, Steidl, & Dannowski, 2009).

Altitude decreases from 80 MASL in the western part of the catchment to 30 MASL in the south-east (Glacial Valley of the Ucker). Correspondingly, regional groundwater flow is directed to the east/south-east; the River Quillow is the main drainage recipient of the region. Hydraulically, these regions are characterized by regional transient and local recharge dynamics of the groundwater. Local, unconfined, and only temporarily saturated aquifers of Weichselian age are deposited above the till layers. Groundwater is suggested to be recharged in these upland areas and discharged into lowland wetlands, lakes, kettle holes, and river systems. Hydraulically, these local shallow aquifers are connected relatively quickly to the smaller surface water system; thus, a height dependence on recharge and discharge dynamics has been suggested (Merz & Pekdeger, 2011).

2.2 | Stable isotope analysis

2.2.1 | Selection of kettle holes

Fifty kettle holes were selected for this study on the basis of predetermined biogeochemical and ecology importance in the Uckermark region (Tables 1 and 2; Figure 1). The selection was based on previous work by Kalettka and Rudat (2006) who presented a classification of kettle hole. Hydrogeomorphic types delineated from various physical and biogeochemical parameters. The selected kettle holes were chosen to cover a variety of Hydrogeomorphic types (Table 1), vegetational succession stages, and landscape elevations (Table 2). In order to increase spatial coverage and sample size, seven more kettle holes

were later included into the study from all vegetation succession stage types.

2.2.2 | Sampling strategy and data detection

Sampling of the kettle holes took place at the end of the winter season in February 2017 and in monthly time steps until August 2017 (February–August period). This time range was selected on the assumption of kettle hole filling dynamics and the subsequent start of the evaporative year during February and March and culminating towards the end of August (Hayashi et al., 1998). In addition, the isotopic compositions of two edge-type kettle holes (259 and 807) as available for the period of 2015–2016, provided by Nitzsche et al. (2017), was utilized.

During sample periods, sampling was carried out monthly with a column bucket sampler in order to minimize the disturbance of the water column. It is lowered into each kettle hole body to a depth of 10 cm below the water surface near the kettle hole centre region following literature suggested sampling practices (Brock et al., 2009; Yi et al., 2008). However, this approach was not always possible due to high water depths and soft, unpassable sediments during the early sampling months, as well as vegetation growth and obstruction later within the summer. Where the centre region was unreachable, a suitable alternative edge proximal location was selected and consistently sampled each month. In order to justify this approach, isotopic samples were taken from the edge and centre of two, well studied, edge-type kettle holes (259 and 807; Table 1) during the May sampling period and compared (Table 3).

Due to shallow system characteristic of the studied kettle holes, represented by a water depth less than 150 cm in nearly all of the kettle holes, and assuming a well-mixed setting, we did not measure the temperature profiling for the kettle holes, whereas we provided the isotopic composition profiling.

Water samples obtained for isotopic analysis were collected from each waterbody and were immediately transferred to high-density polyethylene sample bottles, filled, and sealed to minimize evaporative loss of water during further processing and transport.

In addition to surface water samples taken from the kettle holes, water samples for isotopic analysis were obtained from four groundwater wells surrounding both kettle holes 807 and 259 using a battery-operated groundwater pump. Prior to groundwater abstraction, each groundwater well was pumped until gone dry and allowed to recharge, thus ensuring that solely groundwater was sampled and that no prior in-well mixing with external sources had occurred.

Four shallow monitoring wells are installed in the close vicinity of kettle holes 807 and 259 to monitor groundwater levels at the shallow unconfined layer. The observation wells are inserted into a depth of 2 to 4 m, out of which 1 m at their bottom is covered by screen. Depth to the groundwater level in the vicinity of kettle holes 807 and 259 varies from 1 to 2 m, depending on the growing season and precipitation events.

TABLE 1 Kettle holes sampled during 2017 based on vegetational succession stage and hydro-geomorphology as defined by Kalettka and Rudat (2006) and landscape elevation classes

Kettle hole's ID	Longitude	Latitude	Vegetation successional stage type	Hydrogeomorph type	Water present	Height (m)
0	13.53	53.32	Puddle	Puddle	No	
28	13.53	53.32	Full reed	Big[a]-shallow[b] storage	Yes	102.22
40	13.54	53.32	Wood	Small[c]-shallow storage	Yes	98.69
133	13.73	53.37	Puddle	Puddle	No	
149	13.76	53.35	Wood	Big-shallow storage	Yes	63.32
183	13.75	53.37	Edge	Small-shallow storage	No	
187	13.74	53.36	Edge	Small-shallow storage	Yes	61.16
190	13.73	53.36	Edge	Small-shallow storage	Yes	73.46
256	13.71	53.38	Edge	Small-shallow overflow	Yes	74.67
258	13.71	53.38	Edge	Big-shallow overflow	Yes	73.67
259	13.71	53.38	Edge	Small-shallow overflow	Yes	74.62
260	13.71	53.38	Edge	Small-shallow overflow	Yes	74.53
265	13.70	53.38	Edge	Big-shallow overflow	Yes	71.79
269	13.70	53.38	Edge	Big-shallow storage	Yes	73.15
275	13.71	53.39	Edge	Big-shallow overflow	Yes	
287	13.70	53.39	Edge wood	Small-shallow storage	Yes	76.67
311	13.69	53.39	Edge wood	Small-shallow storage	Yes	81.38
312	13.69	53.39	Edge	Big-shallow overflow	Yes	81.69
319	13.67	53.38	Wood	Big-shallow storage	Yes	88.21
606	13.63	53.35	Full reed	Small-shallow overflow	Yes	85.40
607	13.63	53.35	Full reed	Big-shallow overflow	Yes	84.79
608	13.63	53.35	Puddle	Puddle	No	
805	13.66	53.39	Edge wood	Small-shallow overflow	Yes	89.35
807	13.67	53.40	Edge	Small-shallow storage	Yes	88.39
808	13.67	53.40	Edge wood	Big-shallow storage	Yes	87.51
892	13.65	53.41	Edge	Big-shallow overflow	Yes	91.41
893	13.65	53.41	Puddle	Puddle	Yes	91.10
907	13.64	53.41	Edge	Small-shallow overflow	Yes	95.93
908	13.64	53.41	Full reed	Small-shallow overflow	No	
910	13.64	53.41	Edge	Small-shallow wadeable	Yes	96.53
911	13.64	53.41	Edge wood	Small-shallow overflow	Yes	94.28
939	13.66	53.42	Full reed	Small-shallow storage	Yes	93.05
940	13.66	53.42	Full reed	Small-shallow storage	Yes	93.18
942	13.67	53.42	Edge	Small-shallow storage	Yes	92.16
1189	13.62	53.35	Edge	Small-shallow storage	Yes	88.50
1228	13.60	53.36	Edge wood	Small-shallow storage	Yes	106.45
1229	13.60	53.36	Wood	Small-shallow storage	Yes	106.76
1328	13.56	53.31	Edge	Small-shallow storage	Yes	90.89
1338	13.56	53.31	Puddle	Puddle	Yes	92.73
1510	13.69	53.40	Puddle	Puddle	Yes	80.89
1590	13.54	53.30	Wood	Big-shallow storage	Yes	96.72
1598	13.55	53.31	Full reed	Small-shallow overflow	Yes	94.06
1599	13.55	53.31	Full reed	Small-wadeable overflow	Yes	94.39
1604	13.55	53.31	Full reed	Small-wadeable overflow	Yes	89.11
2484	13.62	53.35	Edge	Big-shallow overflow	Yes	82.29

(Continues)

TABLE 1 (Continued)

Kettle hole's ID	Longitude	Latitude	Vegetation successional stage type	Hydrogeomorph type	Water present	Height (m)
2489	13.62	53.36	Edge	Small-shallow overflow	Yes	84.49
2565	13.56	53.31	Edge wood	Big-shallow storage	Yes	86.95
1338_N	13.56	53.31	Puddle	Puddle	Yes	92.41
1604_0	13.55	53.31	Puddle	Puddle	Yes	88.76
2525_N	13.56	53.31	Edge wood	Small-shallow storage	Yes	86.71
805_N	13.66	53.39	Edge wood	Small-shallow overflow	Yes	87.07
942_N	13.67	53.41	Edge	Small-shallow storage	Yes	92.58
Arendsee	13.62	53.33	Lake	Lake	Yes	80.66

Note: Some kettle holes were excluded from the DEM height classification due to a lack of water present at any time during the study period. According to a Hydrogeomorphic classification made for the kettle hole of the north east of Germany by Kalettka and Rudat (2006), puddle-type kettle holes are "very small and characterized by a nonpermanent shore due to periodic complete use as arable land, especially in dry periods."
[a]Kettle holes with catchment size ≥31.6 ha (Kalettka & Rudat, 2006).
[b]Kettle holes with depth ≤0.4 m (Kalettka & Rudat, 2006).
[c]Kettle holes with catchment size ≤10 ha (Kalettka & Rudat, 2006).

TABLE 2 Enumeration of type and height class of the kettle holes listed in Table 1

Type	Number	Height class	Number
Puddle	8	60–80	10
Full reed	9	80–90	17
Edge	21	90–100	16
Edge wood	9	>100	3
Wood	5		
Lake	1		

Stable isotope analysis of water samples was carried out using the Los Gatos Research (Johnson et al., 2011) liquid water isotope analyser. This analyser allowed the calculation of the oxygen and hydrogen isotopic composition of water samples δ^2H and $\delta^{18}O$ that were required for this study.

Additionally, deuterium excess was calculated on a basis of processed δ^2H and $\delta^{18}O$ isotopic data after the equation of Dansgaard (1964; Equation 1):

$$d - excess = \delta^2H - 8\delta^{18}O. \tag{1}$$

2.3 | Calculation of kettle hole E/I ratios

Based on the assumption of connectivity of kettle holes with shallow unconfined groundwater, E/I calculations of this study assumed a steady-state approach. This assumed that kettle holes were continually replenished by inflowing shallow groundwater water that compensated for evaporative loss and groundwater outflow (Skrzypek et al., 2015). In other words, the water level in the kettle holes are a subdued replica of that of the adjoining shallow groundwater (Lischeid et al., 2018). As a result, they fluctuate in unison.

Although due to the recharge flux resulted from precipitation, the groundwater level rises quicker rather than that of a kettle hole due to the porosity-driven effect of porous material, they will reach to an equilibrium ultimately. Assuming the groundwater allowed adequate replenishment of water losses to kettle holes, the E/I ratio was calculated using the Hydrocalculator programme for each individual kettle hole using a reformulated equation (Allison & Leaney, 1982; Mayr et al., 2007; Equation 2). The required input variables are listed in Table 4.

$$E/I = \left[\frac{\delta_L - \delta_P}{(\delta^* - \delta_L) \times m}\right], \tag{2}$$

where δ_P shows initial value of isotopic composition of kettle hole surface water and δ_L is the isotopic composition of kettle hole water at the subsequent sampling interval, δ^* states the limiting isotope enrichment factor (Equation 3), and m is the enrichment slope (Equation 4).

$$\delta^* = \frac{h \times \delta_A + \varepsilon}{h - \frac{\varepsilon}{1,000}}. \tag{3}$$

δ^* is normally computed by means of air humidity (h), the isotope composition of moisture in ambient air (δ_A), and a total enrichment factor (ε).

$$m = \frac{h - \frac{\varepsilon}{1,000}}{1 - h + \frac{\varepsilon_k}{1,000}}, \tag{4}$$

where ε states the total fractionation factor (Equation 5) that is a summation of the equilibrium isotope fractionation factor (ε^+; Equation 6) and the kinetic isotope fractionation factor ε_k (Equation 7; Gibson & Reid, 2010).

$$\varepsilon = \varepsilon^+ / \alpha^+ + \varepsilon_k, \tag{5}$$

TABLE 3 The percentage of difference calculated between the edge and centre of two edge-type kettle holes (807 and 259)

Kettle hole's ID	Sampling distance (m)	δ^2H	$\delta^{18}O$	Percentage of difference in δ^2H	Percentage of difference in $\delta^{18}O$	Mean percentage of difference
807 (edge)		−38.60	−4.22			
807 (centre)	17.40	−39.29	−4.22	1.78	0.16	0.97
259 (edge)		−39.10	−4.55			
259 (centre)	14.70	−40.83	−4.66	4.33	2.40	3.36
		−38.60	−4.22			2.17[a]

[a]The average of total percentage of difference.

$$\varepsilon^+ = (\alpha^+ - 1) \times 1{,}000, \tag{6}$$

$$\varepsilon_k = (1 - h) \times C_k, \tag{7}$$

where C_k represents the kinetic fractionation constant, which is 12.5‰ for δ^2H and 14.2‰ for $\delta^{18}O$ (Araguas-Araguas, Froehlich, & Rozanski, 2000; Gonfiantini, 1986).

Following Horita and Wesolowski (1994), α^+ is calculated for hydrogen and oxygen isotopic compositions using Equations (8) and (9), respectively.

$$10^3 \times \ln(\alpha^+) = 1158.8 \left(\frac{T^3}{10^9} \right) - 1620.1 \left(\frac{T^2}{10^6} \right) + 794.85 \left(\frac{T}{10^3} \right) - 161.04 + 2.9992 \left(\frac{10^9}{T^3} \right), \tag{8}$$

$$10^3 \ln(\alpha^+) = -7.685 + 6.7123 \left(\frac{10^3}{T} \right) - 1.6664 \left(\frac{10^6}{T^2} \right) + 0.35041 \left(\frac{10^9}{T^3} \right), \tag{9}$$

where temperature (T) is given in Kelvin degrees.

The initial value of input water (δ_P) was decided as the isotopic composition of kettle hole surface water during February when the evaporation is minimum and as a result of the precipitation events, the maximum dilution can occur, irrespective of their setting (flow-through or discharge). Therefore, in this period (dilution phase), the maximum water depths were also expected (Figures S1–S2). In cases where isotopic depletion occurred in kettle holes from February to March, filling was assumed to have been completed in March, and this value utilized for the input (δ_P). The outflow from each kettle hole (δ_L) was taken as the isotopic composition of kettle hole water at the subsequent sampling interval, with thus the final δ_L being obtained in August 2017. The isotopic composition of atmospheric moisture δ_A was difficult to measure in the field and was thus calculated using the isotopic composition of precipitation between sampling periods (δ_{Rain}), which was computed with respect to stable isotope composition of precipitation, equilibrium isotope fractionation factor, and the slope of LEL. The individual kettle hole specific LEL was derived from regression of all isotopic samples obtained at each analysed kettle hole in

TABLE 4 Relevant variables and parameters required for the Hydrocalculator isotopic mass balance (Skrzypek et al., 2015; further information is available in the Supporting Information)

Variable	Description	Remark
T	Temperature (PC), mean between sampling #1 and #2	Measured or assumed
h	Relative humidity (fraction), mean between sampling #1 and #2	
δ_{Rain}	Precipitation, mean between sampling #1 and #2 and 02 (for δ_A calc only)	
δ_P	Pool water initial value[a] or inflow[b] (‰), sampling #1	
δ_L	Pool water initial value[a] or inflow[b] (‰), sampling #2	
LEL	Slope of local evaporation line	
δ_A	Air ambient moisture (%), mean between sampling #1 and #2	
ε_k	Kinetic isotope fractionation factor (‰) (h dependent)	Calculated from the model
ε^+	Equilibrium isotope fractionation factor (‰) (T dependent)	
δ^*	Limiting isotope composition (‰)	
m	Calculation factor $(h - \varepsilon/1000)/1 - h + \varepsilon_k/1000$	
E/I	Result for steady-state model: Evaporation over inflow ratio	Results
f	Result for non-steady-state model: Evaporated fraction of the volume	

[a]Non-steady-state model, f calculation.
[b]Steady-state model, E/I calculation.

2017, which were then included in Hydrocalculator (Figure S4). δ_{Rain} was obtained from monthly regional measurements of the isotopic composition of precipitation at the Dedelow research station from 2014 to 2016 with standard deviations (given in per mil) 2.32 and 18.51 (per mil) for $\delta^{18}O$ and δ^2H, respectively. These isotopic compositions of the rainfall sampled during 2014–2016 were used to construct the LMWL (Figure 4). These isotopic values were then averaged for each monthly interval from each year to provide a value of δ_{Rain} for each month.

2.4 | Monthly regional LELs and regional evaporative loss calculation

In addition to the calculation of E/I ratios, it has been suggested that to estimate the water balance changes at a regional scale, differences in gradients of the regional LEL in monthly intervals may be used (Nitzsche et al., 2017). Regional monthly LELs were constructed from regression of all isotopic samples obtained in each sampling month (Figures S5–S7). This methodology implied firstly calculating the difference in LEL gradients between two monthly sampling intervals from the LMWL. Second, these normalized LELs were then differenced and expressed relative to the LEL of the first sampling interval of the period. Third, the final outcome was expressed as a percentage of water loss or gain. Monthly LELs used in this method are illustrated in Figures S5–S7.

2.5 | Calculating groundwater enrichment through kettle holes

Utilizing a two-component mixing model, adapted from Brock et al. (2009), could make it possible to estimate the percentage of isotopic enrichment endured by groundwater flowing through two kettle hole waterbodies (807 and 259) equipped with groundwater observation wells. This approach assumed the isotopic composition of each kettle hole as one end-member. In other words, the inflowing groundwater is mixed with kettle hole's water and is therefore affected by the dilution and enrichment processes, whereby these effects will be reflected in the isotopic compositions of the groundwater outflow. Using this, a simple equation was derived that permitted the calculation of percentage enrichment, following Brock et al., 2009; Equation 10):

$$\text{Groundwater enrichment}(\%) = \frac{\delta\,\text{GW Outflow} - \delta\,\text{GW Inflow}}{\delta\,\text{lakewater} - \delta\,\text{GW Inflow}} \times 100. \quad (10)$$

Groundwater enrichment was calculated at both kettle holes in each month between February and August 2017 and then averaged.

3 | RESULTS

3.1 | Temporal isotopic variations in kettle hole surface waters

An overview of changes in average isotopic compositions of all kettle holes sampled in 2017 can be seen in Table 5 and Figure 3a–d. Two edge-type kettle holes (259 and 807) possessed isotopic datasets additionally in 2015 and 2016. The puddle-type (1604_0) and wood type (040) only possessed data collected during the 2017 February–August period. Figure 3a–c displays temporal variations in δ^2H, $\delta^{18}O$, and deuterium excess at each of the four aforementioned kettle holes. Generally, a strong annual cycle may be observed, whereby the summer months in each year demonstrated enriched values of δ^2H and

$\delta^{18}O$ and contrasting antiphase deuterium excess values. In contrast, during the winter months, kettle hole surface waters were typically depleted showing strongly negative δ^2H and $\delta^{18}O$ values and positive peaks in deuterium excess. Generally, the most depleted isotopic values were reached between December and February with the enriched values occurring between June and August. This is however annually variable with the most enriched isotopic values in the summer of 2015 occurring at kettle hole 807 later in September (Figure 3a–d). The annual variations are non-linear and show, particularly in the winter months of 2015/2016, rapid, short-term fluctuations in the isotopic composition of surface water (Figure 3a–c).

3.2 | Isotopic framework for evaluating kettle hole water balances

3.2.1 | LELs, local meteoric water line, and regional water loss calculation

Utilizing stable isotopic data from precipitation data from 2014 to 2016, the LMWL for the Uckermark region was produced (Figure 4a). The LMWL possessed a gradient of 8.01 close to that of the GMWL, namely, 8.00. In addition, plotting the isotopic composition from all studied kettle holes from every sampling period in the Uckermark region in 2017 yielded a useful overview of the annual regional LEL (Figure 4a). From a regression of 341 kettle hole surface water isotopic samples analysed in 2017, the resulting February–August regional LEL-derived possessed a gradient of 4.98 and intercepted the LMWL at a $\delta^{18}O$ value of −8.10‰ and δ^2H of −57‰ (Figure 4a). Figure 4b shows the seasonal shifts in the isotopic composition of kettle hole surface waters along the LEL. Significantly, the most enriched isotopic values along the regional LEL were observed in June compared with the substantially more depleted values observed in February, which clustered closer to the LMWL on the LEL (Figure 4). In July and August 2017, the LEL enrichment was stunted and regressed to depleted isotopic values. In this case, the isotopic composition of several kettle holes in July and August lay close to the isotopic composition of summer precipitation at the LMWL Figure 4b.

Regional water loss calculated using monthly regional LELs from February to July 2017 was calculated as 27.8%. This water loss did not occur uniformly with the greatest loss reported from April to May (21.2%). Furthermore, two periods of water gain were observed. These gain phases were witnessed as a slight gain from February to March (2.3%) and a more significant gain of 15% from July to August.

3.2.2 | E/I ratios for February–August 2017 period

Generally, E/I ratios in the earliest months (February to March) of the February–August period clustered close to zero with a mean E/I ratio across all kettle holes during this period of 0.01 (1% evaporation of inflow; Figure 5b). The variance about the mean during this period

TABLE 5 Calculated monthly averages of isotopic and deuterium excess composition from all kettle holes sampled in 2017

Month	February		March		April		May		June		July		August	
	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD	Avg.	SD
δ^2H	−55.93	6.58	−54.38	4.77	−43.86	6.06	−39.57	6.49	−32.64	13.74	−35.00	8.83	−36.48	8.85
δ^{18}O	−7.69	2.52	−7.39	0.85	−5.53	1.20	−4.50	1.47	−3.36	2.96	−3.96	1.91	−4.25	1.92
d-excess	5.57	3.61	4.72	2.62	0.38	3.83	−3.61	5.61	−5.78	10.27	−3.32	6.94	−2.43	6.78
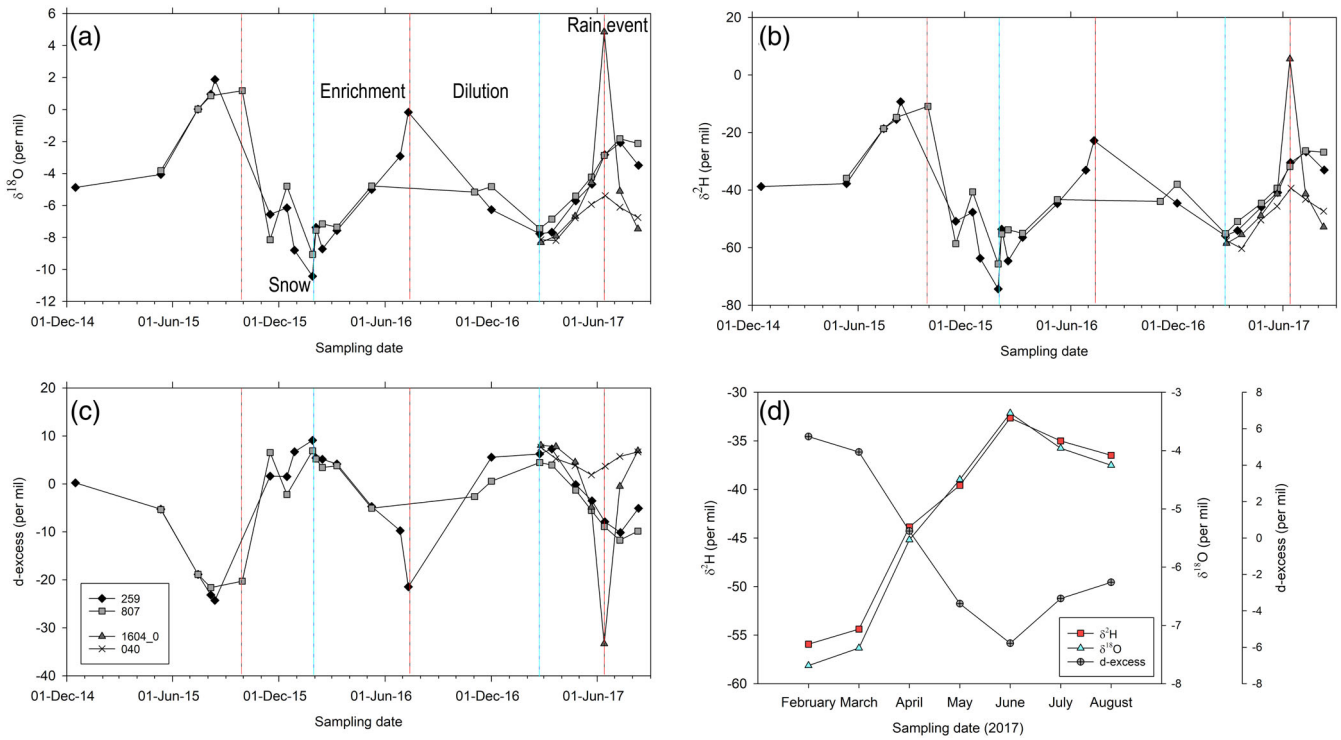
FIGURE 3   (a) Isotopic dilution and enrichment of δ^2H; (b) isotopic dilution and enrichment of δ^{18}O; (c) isotopic dilution and enrichment reflected by d-excess; (d) antiphase monthly relationship between d-excess and isotope systems calculated for all kettle holes. Note that blue lines represent the end of a dilution phase and start of enrichment trend. Red lines represent the end of enrichment phases and beginning of subsequent dilution phases. Minor and major ticks represent monthly intervals. Note that "Rain event" in (a) denotes an exceptionally extreme precipitation amounting to 141.1 mm in June 2017

was very low (0.0004). The wood-type kettle hole (040) demonstrated a negative E/I ratio in the initial sampling period from February to March associated with depletions in δ^2H and δ^{18}O isotope ratios, whereas the edge-type (259 and 807) and puddle-type (1604_0) kettle holes showed marginal positives (Figure 5). During the subsequent March to April period, E/I ratios in all kettle holes increased to strong positive values with a mean across all kettle hole waterbodies of 0.097 and increased variance of 0.007. This was synchronous with the largest increase in average δ^2H and δ^{18}O and decrease in d-excess for all kettle holes observed in Figure 3d.

Furthermore, overall E/I ratios calculated for each individual kettle hole in the Uckermark region during the 2017 February–August period are presented in Figure 6. Overall, a large range in E/I ratios was observed during the February–August period in 2017 ranging from a minimum of 0.08 (8%) at kettle hole 805_N to a maximum of 0.94 (94%) at the puddle-type kettle hole 1604_0. Averaging the calculated E/I ratios for each kettle hole over the course of the 2017

February–August period proposed a mean E/I ratio of 0.26 (26% evaporation of inflow).

Using a literature-derived classification, the E/I ratio of 86.7% of kettle holes sampled in 2017 was found to be below an E/I threshold of 0.4 (40%), suggesting that on average, more than 60% of the water volume present within kettle holes was retained during the February–August period; 13.3% of kettle holes in 2017 possessed E/I ratios that exceeded an E/I ratio of 0.4 but did not exceed one. This group included 80% of puddle-type kettle holes including 1604_0 (Figure 6). No kettle holes in the 2017 February–August period demonstrated ratios greater than 1 (>100% evaporation of inflow).

3.3 | Groundwater isotopes

Isotopic analysis of groundwater at kettle holes 807 and 259 from June to August 2017 showed distinct enrichment trends in the
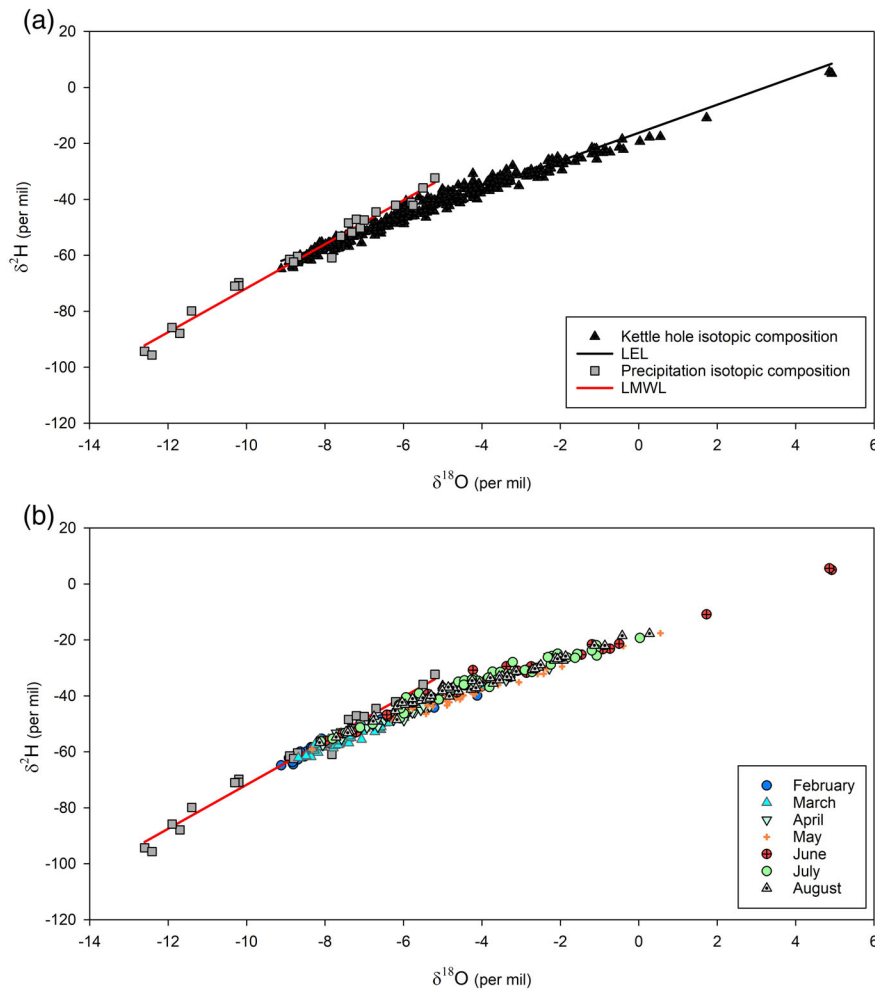
FIGURE 4 (a) The regional local evaporation line (LEL) as well as the local meteoric water line (LMWL) calculated for February–August 2017 and 2014–2016, respectively, and (b) axial shift of kettle hole isotopic composition along the LEL during February–August 2017
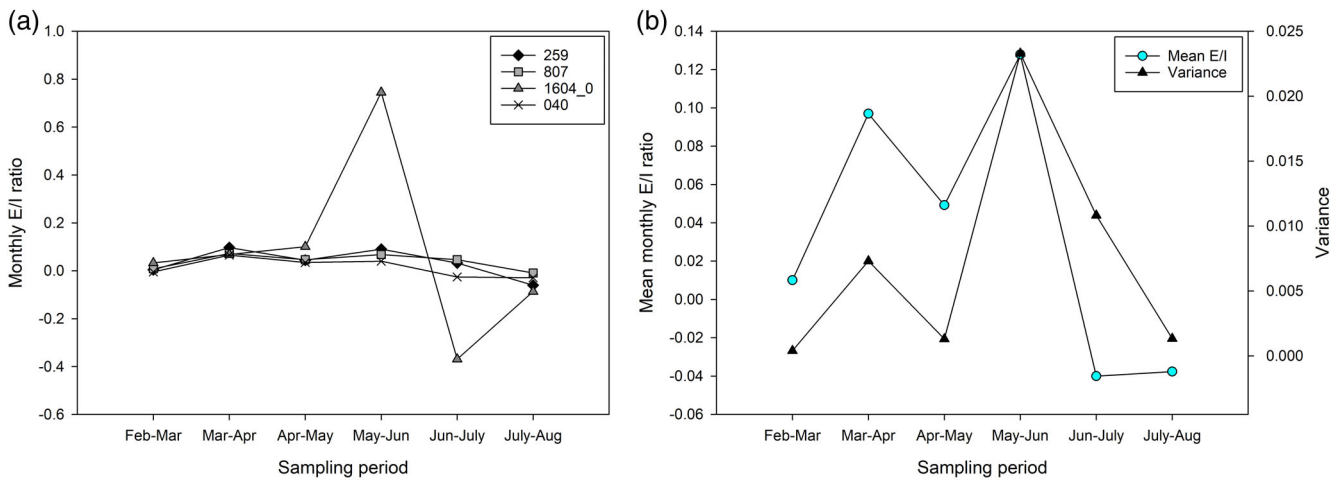

FIGURE 5 (a) Monthly E/I ratios calculated for four representative kettle holes and (b) mean monthly E/I ratios from all kettle holes sampled in 2017

isotopic composition of groundwater in comparison with that of the precipitation data that could be identified at both kettle holes (Figure 7a,b). This enrichment trend proved useful in the identification of groundwater flow directions without the usage of conventional techniques. Of particular interest was the clustering of

identified inflowing groundwater at kettle holes 807 and 259 at the LMWL with a mean δ^2H and $\delta^{18}O$ isotopic composition of −55.40‰ and −7.89‰ at 807 and −52.49‰ and −7.28‰ at 259, respectively. The mean isotopic composition of outflowing kettle hole groundwater obtained synchronously with inflowing kettle
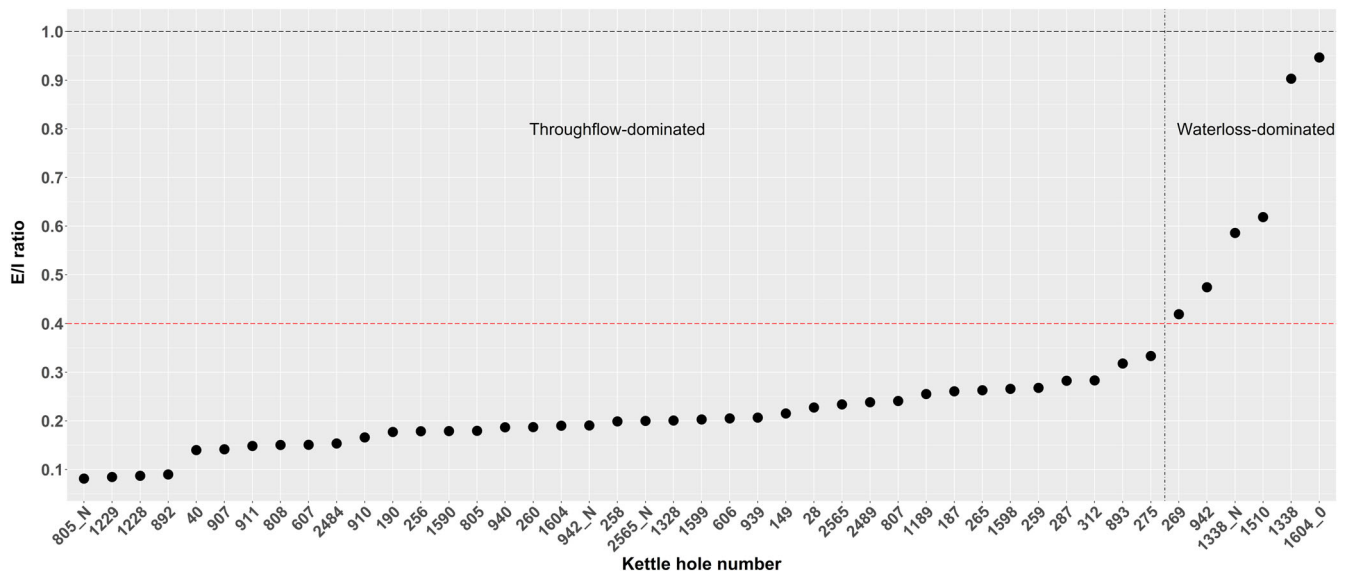
FIGURE 6 Evaporation-to-inflow (E/I) ratios calculated for each individual kettle hole of the Uckermark region sample group in 2017
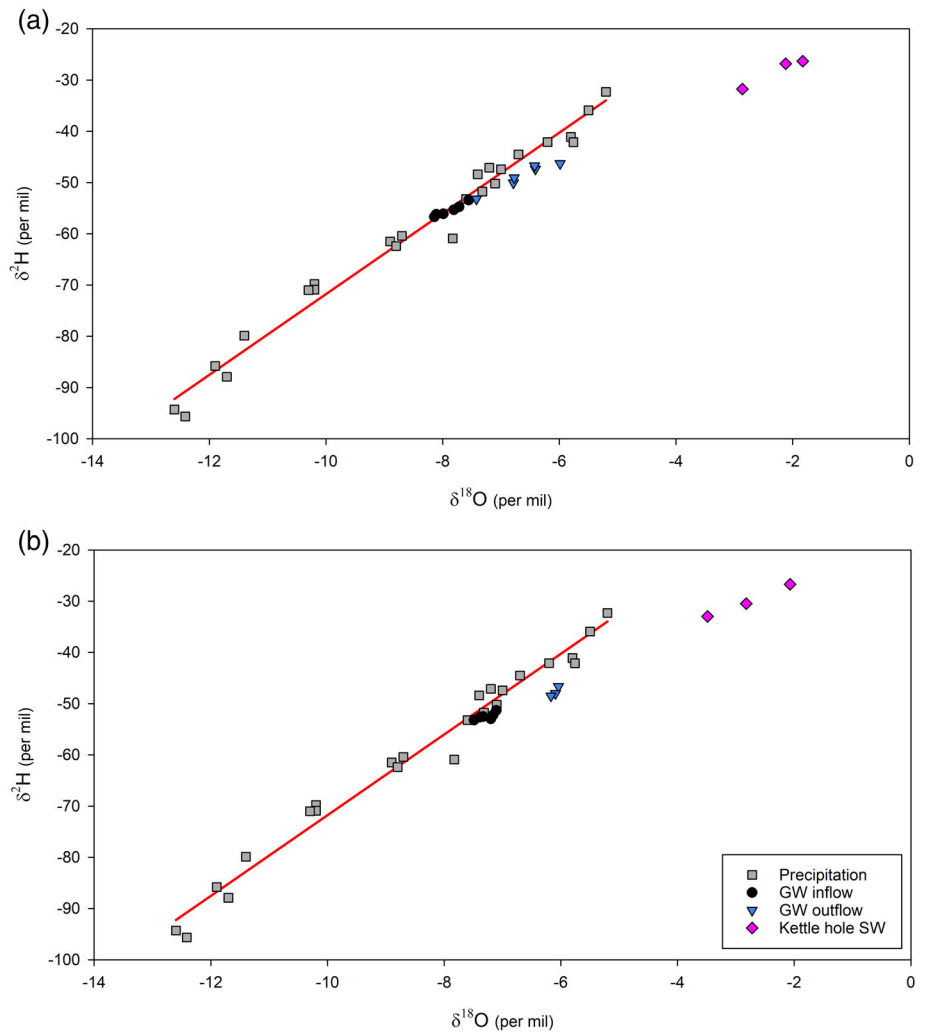
FIGURE 7 Isotopic composition of groundwater measured at four groundwater wells in 2017 at (a) kettle hole 807 and (b) 259. Inflowing groundwater could be seen to cluster close to the local meteoric water line in all months. Outflowing groundwater was always more enriched and lay on an enrichment line with the isotopic composition of kettle hole surface water

hole groundwater samples was counteracted from that of inflowing water and lay on an enrichment line towards kettle hole surface water during the sampling periods (Figure 7a,b). The average

isotopic composition of outflowing groundwater was −48.78‰ and −6.6 ‰ for kettle hole 807 and −47.72‰ and −6.10‰ for 259 for δ^2H and $\delta^{18}O$, respectively.

Using Equation (10), groundwater at kettle hole 259 demonstrated a calculated enrichment from inflowing to outflowing groundwater of 25.4%, whereas kettle hole 807 showed a slightly higher value of 30.70%. This yielded an average enrichment percentage of groundwater in 2017 of 28.10%.

3.4 | E/I ratios and landscape elevation

Simple regression of all kettle hole E/I ratios in 2017 with elevations suggested that puddle-type kettle holes such as 1604_0, 1510, 893, 1338, and 1,338_N showed a unique behaviour not explained by landscape elevation (Figure S8). Therefore, for the subsequent statistical analyses, all puddle-type kettle holes were removed. The result of a regression of all remaining kettle holes (N = 41) suggested the presence of a moderate correlation with landscape elevation, whereby kettle holes situated at lower landscape elevations typically possessed higher E/I ratios than their higher situated counterparts (Figure 8).

Statistical analyses of this relationship demonstrated a Pearson correlation coefficient value of −0.53 and Spearman's rank value of −0.50. These values confirmed the presence of a negative correlation between E/I ratios and landscape elevation.

3.5 | Correlation between altitudes of kettle holes and their electrical conductivity

Generally, results showed that an inverse correlation exists between the altitudes of the kettle holes and their corresponding electrical conductivities (Figure 9). For instance, the lowest mean value of electrical conductivity observed over the February–August period (218 µS/cm) was identified at the highest elevation of 106.80 m. Conversely, the kettle holes situated at lower minimum elevation across the study area of 61.20 m displayed higher values of electrical conductivity (Figure 9). Statistical analyses of the observed elevation-electrical conductivity correlation indicated a coefficient of determination of 0.46 with both Pearson and Spearman's rank correlation coefficients displaying values of −0.68 and −0.57, respectively.

4 | DISCUSSION

4.1 | Annual variability in enrichment phase length

A representative of the shallow puddle-type kettle holes (1604_0) suggested that a maximum enrichment was already reached in June; this was further observed within the forested, wood-type kettle hole of 040 (Figure 3a–d). The two selected edge-type kettle holes (259 and 807) however demonstrated continued enriched isotopic compositions into July. This was also observed within the monthly E/I ratios for these selected kettle holes observed in Figure 5 whereby all E/I ratios remained positive in the May–June period with a maximum in the E/I ratio of kettle hole 1604_0. The subsequent decrease in E/I
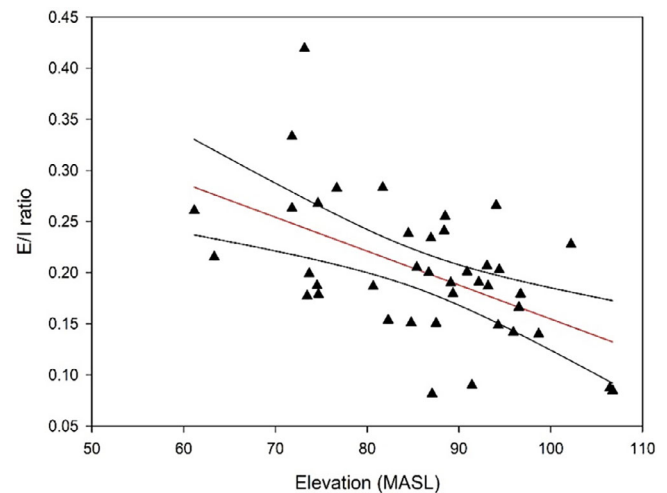
FIGURE 8 (a) Correlation between E/I ratios for all kettle holes excluding puddle-type kettle holes (N = 41) with their respective elevations in 2017
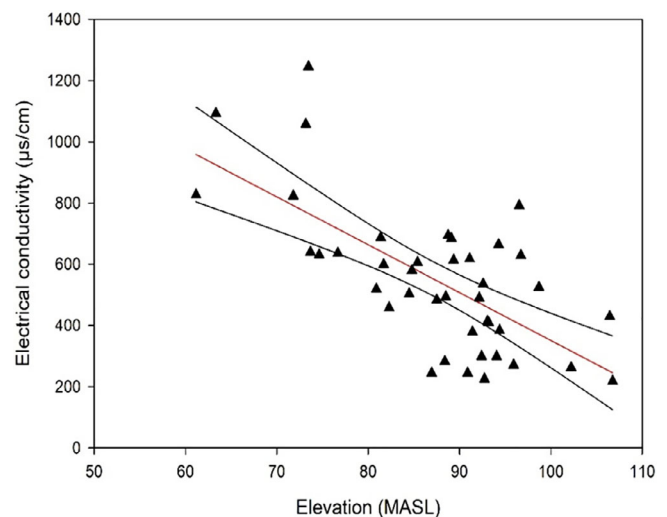
FIGURE 9 Correlation between electrical conductivity ratios for all kettle holes with their respective elevations in 2017

ratios to negative ratios for both 1604_0 and 040 in the June–July period and the slightly positive but diminished E/I ratios for 259 and 807 suggested the end of enrichment in June 2017 for kettle holes 1604_0 and 040, but a somewhat slightly longer enrichment phase at kettle holes 807 and 259. According to Equation (2), if isotopic composition of kettle hole water at the subsequent sampling interval (δ_L) is lower than that of starting/initial values for the kettle holes (δ_P), E/I values get negative. Thus, when evaporation occurs only as the determining factor over time, delta values are always increasing, leading to positive E/I values. However, if before the subsequent sampling, kettle holes receive a new source of water such as direct precipitation on them or generated run-off from uplands, the isotopic compositions of the kettle holes' water become diluted. As a result, the calculated E/I values get negative. As it was the case in the Uckermark region due to an exceptionally heavy rainfall in July 2017 (Figure 2) that led to a strong refilling of many of the kettle holes for this period and

accordingly resulted in negative E/I values (Figure 5). On appraisal of the regional LEL for June and July, it may be seen that the most enriched kettle hole isotopic values leading to the greatest axial shift along the LEL with regard to both δ^2H and δ^{18}O occurred during June 2017. It has been widely discussed that a lowering of the LEL gradient over the course of the summer enrichment phase is also indicative of isotopic enrichment due to local environmental and climatic conditions acting to reduce the LEL slope (Skrzypek et al., 2015). The lowest LEL gradient for 2017 (see Figures S5–S7) was observed for kettle holes during July 2017 (3.90; Figure S7a) after which a stark increase in gradient was observed in August (Figure S7b). Moreover, the calculated mean E/I ratios across all kettle holes reached its maximum from the May–June period before decreasing rapidly to negative E/I ratios in the June–July period (Figure 7b). To that respect, Nitzsche et al. (2017) implied an end to the enrichment phase in July during their sampling years (2013, 2014, and 2015). The high temporal resolution data from this work agree somewhat with the results obtained by Nitzsche et al. (2017). It is therefore proposed that the enrichment phase for the kettle holes typically ended in 2017 in the Uckermark region during the June to July period.

4.2 | Analysis of stable oxygen and hydrogen isotopes measured for observation wells

Groundwater observation wells installed at the edge-type kettle holes 259 and 807 (Figure S3) have shown a clear connection between kettle hole water and the groundwater surface at these two locations during the entire 2017 February–August period. Isotopic enrichment profiles through these two kettle holes in 2017 have demonstrated that groundwater flows through and is enriched during this movement (Figure 7a,b). Winter & LaBaugh (2003) referred to kettle holes of this type across the Canadian prairie region as flow-through or transition kettle holes. As illustrated in Figure 7, inflowing groundwater, shown by solid-black circles, is more negative (less enriched) as compared with the outflowing groundwater, indicated by blue triangles. Not surprisingly, the isotopic compositions of the kettle holes are higher enriched or more positive, represented by pink diamonds (Figure 7a,b), as it has been highly affected by the evaporation process. Therefore, by comparing the isotopic compositions of kettle holes and observation wells installed in the groundwater inflowing and outflowing sides of the kettle holes, the mixing effect of the isotopic composition has become evident. The isotopic composition of the outflowing water is a mixture between the surrounding groundwater and the kettle hole water and therefore more enriched than the inflowing groundwater but less enriched than the kettle hole water.

4.3 | E/I ratio-based classification of kettle hole groundwater connectivity

According to recommendations of Wolfe et al. (2007) and Turner, Wolfe, and Edwards (2010), we ascertained an E/I ratio of 0.40 as the threshold between flow-through and discharge /recharge types. Whereby, a similar classification scheme adopted in this study showed that two confirmed groundwater connected flow-through kettle holes (807 and 259) demonstrated E/I ratios below 0.40 in 2017 (807 = 0.24; 259 = 0.27). Thus, we classified them as kettle holes possessing E/I ratios below 0.40, and those possessing E/I ratios above 0.40 but below 1, including the puddle type 1604_0 (E/I = 0.95; Figure 6). No kettle holes demonstrated E/I ratio values exceeding 1. As such, kettle holes below the E/I threshold of 0.40 were classified as groundwater connected, partially open, flow-through-dominated kettle holes, demonstrating a dominance of inflow relative to water loss through evaporation and the passage of groundwater through the kettle hole body (Figure 6). Kettle holes above 0.40 were classified as partially closed, water loss-dominated based on the prevalence of evaporative loss relative to inflow (Figure 6). It is worth mentioning that discharge kettle holes are mainly characterized according to their topographical positions, relative to the nearby upland kettle holes (Rosenberry & Winter, 1997). From a hydrological point of view, they are indeed dominated-discharge kettle holes, as a subsurface hydrologic connectivity to the proximate river network exempt them from being treated as endoreic or terminal basin. In addition, depending on the local shallow groundwater head, a discharge kettle hole might convert to a recharge one. This takes place, in particular, when a sustained drought period lowers considerably the groundwater head. Accordingly, the hydrologic functions of these kettle holes, classified as recharge, flow-through, and discharge systems, are time dependent.

Applying this classification to all kettle holes in 2017, it was observed that partially open, flow-through-dominated kettle holes were the most abundant species of kettle hole (86.7%) in the western region of the Uckermark landscape. Kettle holes classified as water loss-dominated typically consisted of puddle-type kettle holes and were a minority over the landscape. These results are in agreement with isotopic and geochemical classification by Nitzsche et al. (2017) who confirmed that most kettle holes in the Uckermark region could be classified as partially closed to partially open systems based on evaporation and lateral groundwater flow. Studies on kettle hole groundwater dynamics based on mixed geochemical and water table height measurements surrounding kettle holes in the prairie regions have also shown a prevalence of flow-through-dominated behaviours with general lateral shallow groundwater flow (Hayashi et al., 1998; van der Kamp & Hayashi, 2009; Winter & LaBaugh, 2003).

In comparison with the previous studies conducted in the northeast of Germany (e.g., Kalettka et al., 2001) as reported that the topographically isolated kettle holes are not hydrologically connected, our findings provide sufficient evidence supporting the role of the hydrologic connectivity among the seemingly isolated kettle holes. Nevertheless, the term "isolated" has been criticized as a misnomer (Mushet et al., 2015), because physiographically isolated kettle holes can yet influence the watershed integrity. Groundwater connectivity is the only possible type of hydrologic connection between isolated kettle holes and downstream water bodies in areas that drain internally and have no surface water outlet, as was found to be the case in Uckermark.

4.4 | Interannual variability in E/I in response to meteorological conditions

The mean in kettle hole E/I ratio across Uckermark kettle holes increased from 2015 to 2016 by 0.08 (8%). Of interest was the increase of kettle hole 259 from a 2015 E/I ratio below the 0.4 threshold (0.36) to above this in 2016 (0.48) implying a change in hydraulic behaviour to water loss dominated. Subsequently, in the 2017 February–August period, these values became reduced, falling again to values below 0.4 (mean = 0.26). A possible cause of inter-annual variation in E/I ratios may be due to an increase in evapo-transpiration brought about by increased air temperature over the growth season (Figure 2). Furthermore, the similarity in relative humidity and precipitation amounts in both of these years may imply that the E/I ratio was influenced mainly by air temperature differences.

The mean air temperature from March to July in 2017 was 0.85°C lower than observed in 2016 but witnessed dominantly higher pre-cipitation amounts over the summer months than observed in either of the previous years. The combination of these factors may have led to a lower E/I ratio in 2017 due to a higher impact of growth season precipitation. A similar phenomenon was observed by Cui, Tian, Biggs, and Wen (2017) whereby seasonal variations in E/I ratios of Cona lake over a 3-year period were linked to interannual meteorological condi-tions. The authors suggested that a lower E/I ratio observed in 2011 was caused by a larger monsoon precipitation amount and hence groundwater inflow than was observed in successive years of higher E/I ratios (Cui et al., 2017).

A simple water balance for each sample period using lysimeter-derived evapotranspiration data and precipitation amounts showed that following a generally negative water balance from March to June 2017, within the subsequent June to August period, the water balance became almost balanced (Figure 10). It has been widely discussed that the Brandenburg region as a whole demonstrates a negative water balance throughout the summer months with high annual evapotrans-piration rates (Merz & Pekdeger, 2011). The meteorological data obtained for 2017 however shows that it is possible to have a reduc-tion in the negative water balance and even a positive summer water balance under exceptional rainfall conditions such as that witnessed in June and July 2017, which can lead to substantial refilling of kettle holes during these months. Having linked this to the isotopic composi-tions, a similarity can be drawn between the positive and negative water balance periods with the isotopic compositions during the enrichment and dilution phases (Figure 3c,d).

4.5 | Calculated regional water loss from Uckermark kettle holes

Mean E/I ratios calculated from all 50 kettle holes in 2017 suggested average regional water losses of 26% (E/I = 0.26). In other words, 26% of total inflowing water to all of the kettle holes is lost each year. Assuming no inflow to the kettle holes, all of their

respective storage can be lost during approximately 3.5 years ($0.26 \times 3.5 \approx 1$). Percentage enrichments suggested an average iso-topic enrichment during kettle hole flow-through of 28.10%. Thus, the regional mean water loss during the 2017 February–August period was likely to be approximately 26.00–28.10%. Nitzsche et al. (2017) using the difference in LEL between a defined dormant and growth season in a similar method to the monthly LEL-based approach in present study proposed a regional water loss of 28.00% in both 2013 and 2014, advocating the findings of this study. More-over, Hayashi et al. (1998) found that summer evapotranspirative losses in Canadian prairie wetlands approximated 25.00% based on pan experiments, with a significant (75.00%) loss through infiltration and lateral, shallow groundwater flow to the sides of kettle holes in close agreement to findings of this study and again supportive of substantial lateral groundwater flow-through (Hayashi et al., 1998). The regional connection was already discussed by Kayler et al. (2018). They measured the isotopic signature along the Quillow stream. From upstream to downstream, the isotopic enrichment increases following the LEL of the kettle holes. There are over 1,100 kettle holes in the catchment. Due to the fact that the kettle holes are hydrologically connected to the shallow unconfined Weichsalien aquifers, the spatial isotopic pattern of the Quillow River discharge is affected. This takes place owing to the fact that a fraction of the streamflow discharge, recognized as base flow, is contributed by the shallow aquifer.

As illustrated by Figure 6, E/I ratios and hence kettle hole water loss and residence time vary largely between kettle holes. Typically, water loss-dominated kettle holes including puddle types showed shorter residence times of up to 1 year (1604_0). Previous estima-tions of kettle hole residence time have proposed short residence times for these water bodies (Lischeid & Kalettka, 2012). Studies of shallow groundwater-connected lakes for the similar pond systems in Wisconsin, USA, have shown highly variably pond residence times. Typically, residence times were as high as 12.7 years but
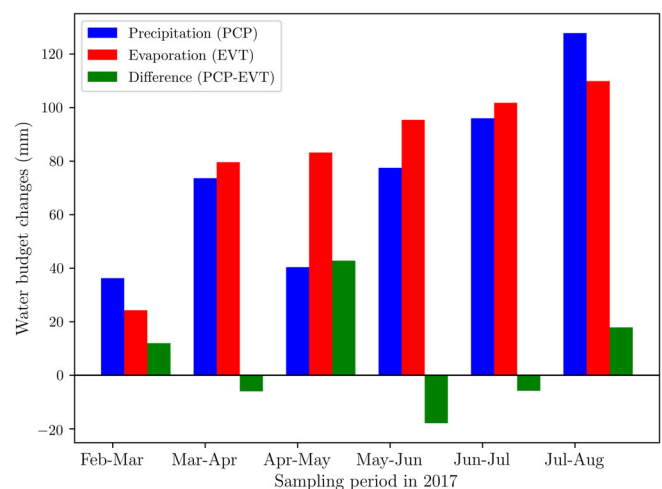
FIGURE 10 Water balance calculated from February to Aguste 2017 based on meteorological variables obtained from ZALF's station in Dedelow and lysimeter data

ranged to values as low as 1.6 years (Anderson & Cheng, 1993). A mean residence time calculated for Uckermark kettle holes based on 2013 and 2014 data has suggested a value of 5 years (Nitzsche et al., 2017). It is clear that this residence time based upon the calculation of E/I ratios can be variable on interannual time scales with a high dependence on meteorological conditions, particularly for water loss-dominated, puddle-type kettle holes. Following water loss, water gain was observed in 2017 from June to August. Using the LEL method to calculate water gain, a regional value of 14.00% was suggested from additions of summer precipitation influx. Comparing regional dormant and growth season LELs for Uckermark, Nitzsche et al. (2017) derived an estimation of refilling of 20% for the whole growth season.

Compared with different local-based techniques for estimation of residence time of water bodies such as slug tests and Darcy-based approaches, which are labour intensive and demanding techniques in terms of cost and data availability, the E/I values-based technique has different advantages over the mentioned methods. Indeed, the residence time can be readily and reasonably estimated by the E/I values, and it can be effectively and easily used for large scales.

However, because no isotopic fractionation occurs in water bodies of the kettle holes due to the transpiration effect of hydrophytes encircled the kettle holes, an underestimation of residence time and water loss, as estimated about 26%, is expected. To validate the water loss estimated in this study, there is a necessity of applying a fully integrated mechanistic surface–subsurface hydrological model such as HydroGeoSphere, given the fact that a proper parametrization of the hydrophyte belt surrounded the kettle holes can be implemented to this model. In fact, the vegetation buffering around the small water bodies can play an important role on the hydro(geo)logical processes owing to the fact that hydrophytes can take up a lot of water from the groundwater system, particularly during the growth season.

4.6 | Relationship between Landscape elevations of kettle holes and their E/I ratios and electrical conductivity

Investigation into relationships between kettle hole elevation and E/I ratio and electrical conductivity demonstrated a negative correlation (Figures 8 and 9). Student t tests calculated for elevation classes based on a one-tailed approach produced statistically significant results with p values <.05. For classes based on electrical conductivity, a p value of .0012 was calculated. A p value value of .026 was found also for E/I ratio-based elevation classes (Figure 9).

Based on total inflow to evaporation (I_{TOT}/E) calculated by an isotopic mass balance model by Isokangas, Rozanski, Rossi, Ronkanen, and Klove (2015), a poor connection between groundwater and 67 subpolar lakes in Finland was detected, although deeper flow paths from high-laying lakes towards low-laying lakes were characterized. Thus, the effect of lake's altitudes on establishing of subsurface interconnection could be identified.

The increase in E/I ratios and electrical conductivity among kettle holes with decreasing elevation may suggest a general trend to water loss-dominated and groundwater discharge behaviours. Heagle, Hayashi, and van der Kamp (2013) and Hayashi et al. (1998) found similar patterns in chloride for the kettle holes in the northern prairie region of North America. They found that kettle holes and wetlands located at higher topographic elevations tended to display low solute (particularly chloride) and thus salinity. They argued that this was due to kettle holes being located above the groundwater potential causing the shallow groundwater output of solutes from the kettle hole in a recharge-type scenario. Wetlands that were observed at lower topographic elevations on the other hand were shown to have higher solute and thus salinity contents. These were suggested to be influenced by inflowing solutes from higher kettle holes that accumulated in a shallow groundwater discharge-type environment (Hayashi et al., 1998; Heagle et al., 2013). Similar results were found for small mountain lakes in the Colorado alpine and in the forest land of Wisconsin whereby electrical conductivity was observed in both cases to be higher at lower elevations. Increases in electrical conductivity were hypothesized to result additionally from shallow groundwater flow-through entraining increased solutes from weathered material with decreasing height (Barsch & Caine, 1984; Kantrud, Krapu, & Swanson, 1989; Swanson, Caine, Woodmansee, & Kratz, 1988).

Using the results obtained within this study and findings from kettle holes located in the prairie region, a simplified conceptual model of Uckermark kettle holes is illustrated by Figure 11. This model is based upon the dominance of shallow groundwater flow-through from higher elevations to lower elevations, leading to increased solute concentrations and E/I ratios.

According to the proposed conceptual model (Figure 11), dissolved solutes are infiltrated into groundwater in higher kettle holes via flow-through with partial recharge and transferred via shallow groundwater flow-through to kettle holes occupying lower landscape elevations and hence concentrated in them by partial discharge. The increase in E/I ratio further supports this by suggesting a height transition from partially open, flow-through dominated to increasingly partially closed, water loss-dominated kettle holes with reduced height. This implies that kettle holes though predominantly flow-through dominated may show admixtures of recharge or discharge behaviours depending on landscape elevation. More work within this area is needed to be able to confirm this behaviour.

5 | CONCLUSION

The current study has been conducted with the purpose of pinpointing the hydrological processes that influence kettle hole water balance from February to August 2017 in the Uckermark of northern Brandenburg, Germany, where kettle holes are densely populated. The present investigation has taken advantages of stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δ^2H), and deuterium excess to shed lights on complex and sporadic interactions between kettle holes and the groundwater system. To that end, isotope mass balance model
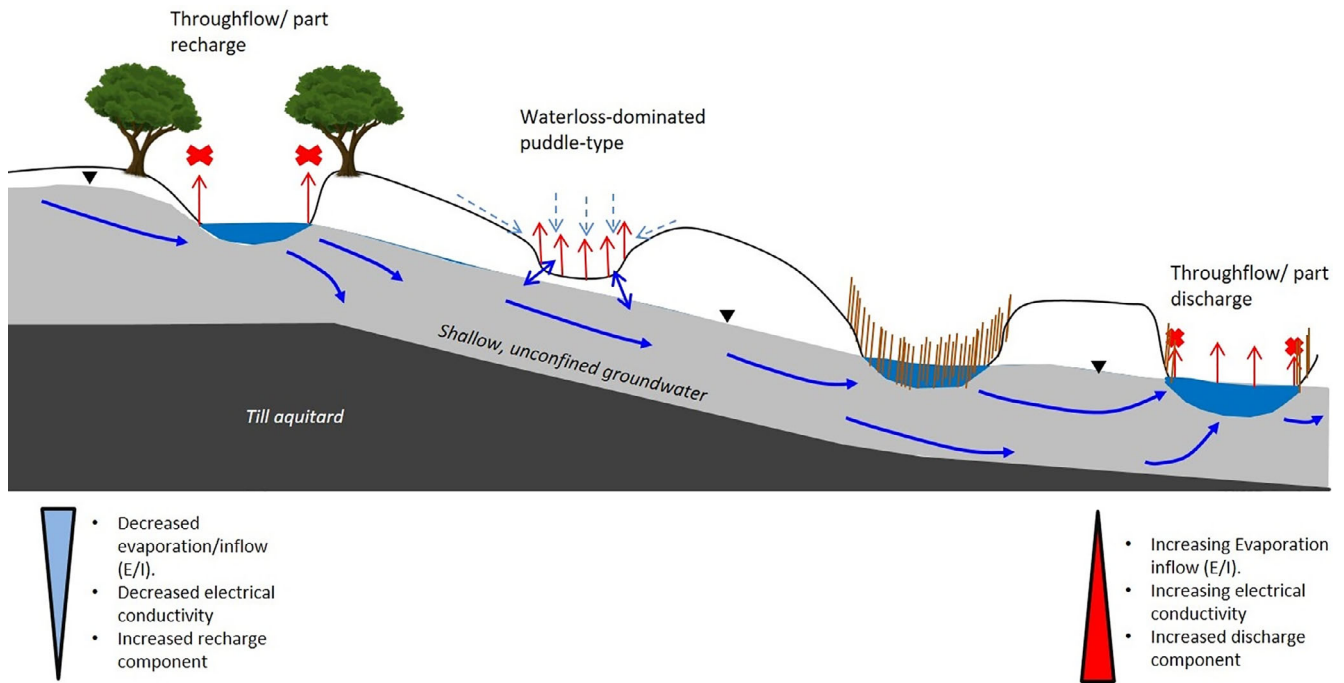
FIGURE 11 Conceptual model for the hydrologic connectivity between kettle holes across the Uckermark region of northern Brandenburg. Model is constructed from the data collected during this study and ideas from Hayashi et al. (1998) and Winter and LaBaugh (2003)

implemented in the "Hydrocalculator" programme was employed. Results indicated that isotopic composition of kettle holes has fluctuated both spatially and temporally, thereby representing distinct phases of dilution and enrichment being attributed to hydrological inflows of shallow groundwater, snow, rainfall, and evaporative loss. Moreover, findings revealed that evaporation/inflow (E/I) ratios changed annually, which may arise from the impacts of meteorological conditions on the depth of shallow groundwater. We identified that puddle-type kettle holes exhibited the highest E/I in comparison with the other kinds of the studied kettle holes. This might be associated with intimately interlocked linkage between puddle-type kettle holes and the shallow groundwater system, which per se is highly dependent upon the precipitation in terms of wet and dry spell periods. The obtained results demonstrated that water loss over Uckermark in 2017 can change from 26.00% to 28.10%. Moreover, based on the obtained results of this study and the system understanding gained from the applied approaches to kettle holes of the prairie region, a simplified but informative conceptual model was developed. The model illustrates that across the highest altitudes, the recharging kettle holes are dominant, where a lower ratio of E/I as well as a lower electrical conductivity is seen. Conversely, the lowest topographical depressions represent the discharge kettle holes, where a higher ratio of E/I and electrical conductivity can be observed. The kettle holes that exist in between, that is, the highest and lowest altitudes, are categorized as flow-through kettle holes in which the recharge takes place from one side and discharge from the other, depending upon the regional groundwater head gradient.

Based on the findings of this study, compared with the hillslope run-off and local meteorological conditions represented mainly by precipitation and evaporation, the regional shallow groundwater system may play the pivotal role in the processes taking part in the hydrology of the kettle holes in the Uckermark region. Ergo, to quantify and characterize these reciprocal interactions between kettle holes and shallow regional groundwater system, developing a high-resolution physically based hydrological model can be a viable approach; this objective should be taken into consideration for perspective studies for this region.

Therefore, previously conducted works in the field of kettle hole hydrology, which have been mainly undertaken in prairie pothole region in North America, could build our underlying assumption concerning the influence of landscape position on the hydrologic connectivity of kettle holes per se and their interactions with their respective adjoining shallow groundwater system. Our results showed that this assumption can be true for these kettle holes as well; however, further investigations are required using high resolution fully integrated mechanistic hydrological models to better quantify and characterize these hydrological processes (i.e., kettle hole–groundwater interactions) at a local scale. Due to a high abundance of kettle holes and high heterogeneity of landscape, the characterized processes obtained at a local scale should be upscaled to regional/landscape scale.

acting on behalf of the State Office of Environment, Health and Consumer Protection Brandenburg.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

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SUPPORTING INFORMATION

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