Title: Ephemeral kettle hole water and sediment temporal and spatial dynamics within an agricultural catchment

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Abstract:

Kettle holes are glacially created ponds that form within landscape depressions and are numerous across young moraine landscapes. Kettle hole water budgets are based primarily on winter precipitation and therefore undergo pronounced short-term changes in water level fluctuations. Little is known about kettle hole sediment biogeochemistry in NE Germany, especially with regards to hydroperiod. Our objective for this study was to link the abiotic influences demarked by the evaporative isotopic signal from kettle hole water and solute chemistry to sediment organic matter turnover imprinted in the sediment $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values. From the 20 kettle holes we sampled, 19 of these completely dried out but on different dates. This dynamic was partially explained by longitudinal and elevational changes over the catchment area illustrating regional controls of kettle hole water balance. At the scale of an individual kettle hole, we estimated evaporation explained up to 38% of water volume loss. The changes in water levels were weakly related to differences in surface sediment elemental N and C concentrations between kettle hole edge and center positions. These dynamics were primarily driven by redox conditions, Ca^{2+} , and several nutrient concentrations (DOC, TDN, TDP, and ammonium) in the water column. While we did not detect differences in the surface sediment $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, the $\delta^{15}\text{N}$ signature in relation to the C:N ratio highlights the advanced decomposition state of surface sediment OM in temporarily water filled kettle holes.

Introduction:

Small wetlands and ponds without a drainage point along the surface to downstream water bodies are often considered to be geographically isolated from upland and aquatic ecosystems (Marton et al., 2015). The classification is broad, encompassing many wetland geomorphologies, and does not necessarily represent wetland function since small water bodies and wetlands often share ecological connections, especially hydrological connectivity through groundwater (Leibowitz 2003). Subsurface connectivity depends on the geohydrological conditions, but when connectivity does exist, important geochemical solutes can be transferred potentially influencing sediment carbon (C) and nitrogen (N) biogeochemical cycling. The connectivity of isolated wetlands to groundwater and surrounding soil water (e.g., interflow) is potentially very important, but how connectivity is modulated spatially or temporally is most likely site dependent.

In NE Germany, the landscape is populated by kettle holes that are estimated to number between 150,000 to 300,000 (Kalettka and Rudat, 2006). Glacial fluvial in origin, kettle holes are small ponds ($<0.01 \text{ km}^2$) that form within landscape depressions. Evidence exists that shows kettle holes are not connected to groundwater (Kalettka et al., 2001; Gerke et al., 2010) or at a minimum, a hydrologic connection exists only during certain times in the growing season (Lischeid et al., 2016). The perimeter of kettle holes also changes rapidly with hydroperiod and given that the area occupied by temporarily water-filled kettle hole types (herein referred to as temporary kettle holes) is large, we might expect large spatial variation in organic matter (OM) turnover within the kettle hole vicinity. Earlier work hypothesized temporary kettle holes, those that dry out over the year, to have rapid OM turnover (Nitzsche et al., 2017), presumably due to the changes that occur with water level fluctuations including shifts in oxygen levels or the relative proportion of allochthonous or autochthonous sediment OM sources (Reverey et al., 2016). Based on this research, the temporary kettle hole hydroperiod types exhibited the highest rates of OM turnover compared to those that contained water over the season, but the patterns could not be generalized to the rest of the catchment given the small areal representation and the different land-use types in which the kettle holes were located.

While kettle hole hydroperiod is considered a dominant driver of water quality and water levels (Berthold et al., 2004; Gołdyn et al., 2015) as well as sediment biogeochemistry (Nitzsche et al., 2017), the potential connectivity of kettle holes or other isolated water bodies to groundwater can also have an impact on water quality (Rains et al., 2006). Whether a water body is strictly precipitation fed or part of a groundwater flow through network will in part determine the inflow and outflow of nutrients (e.g., NO_3^- , NH_4^+ , PO_4^{3-} , etc.) and their residence time in the water body. Additionally, changes in sediment redox status and water temperature that occur with water level fluctuations, will simultaneously affect nutrient demand by microbial communities (Weise et al., 2016), thereby influencing rates of denitrification or sedimentation and subsequent nutrient residence times (Marton et al., 2015). Thus, an understanding of kettle hole hydro-biogeochemical dynamics requires both a characterization of connectivity at the larger catchment scale, to gain insight into potential contributions from the extended catchment network, and at the local scale, to observe conditions that may lead to nutrient uptake and storage.

Potential connectivity between groundwater and geographically isolated water bodies within a catchment should be detectable across the landscape based on patterns in water chemistry and changes in sediment biogeochemistry. Across the Quillow catchment in NE Germany, we sampled 20 temporary kettle holes located in agricultural fields for characteristics related to hydrology, solute chemistry, and sediment biogeochemistry. Our objectives were to, 1) understand the regional controls on water levels of temporary kettle hole, 2) test if solute concentrations give any indication to the evaporation and hydrological connectivity, and 3) test if changes in water level height, and any subsequent changes in water quality, are related to spatial differences in surface sediment carbon (C) and nitrogen (N) turnover.

Methods:

Site description

The study site is located within the Quillow catchment (Fig. 1) and is part of the complex hummocky young ground and terminal moraine landscape typical for NE Germany (Nitzsche et al., 2016). The study site comprises of kettle holes in topographic

depressions formed by the delayed melting of buried dead ice blocks after the discontinuous retreat of the Weichselian glaciers approximately 12,000 to 10,000 years ago. The climate is sub humid with a mean annual temperature of 8.6°C and mean annual precipitation varies between 350 and 750 mm yr⁻¹. Altitude decreases from 100 m a.s.l. in the west of the catchment to 20 m a.s.l. in the southeast (glacial valley of the Ucker River). Correspondingly, regional groundwater flow is directed to the east/southeast; the Quillow is the main drainage recipient of the region. The Quillow stream is a western tributary to the Ucker, which discharges into the Baltic Sea 50 km further north (Merz and Steidl, 2015). The mean discharge of the Quillow catchment is 1.5 L s⁻¹ km² y⁻¹ which corresponds to 47 mm y⁻¹ during our sampling campaign (C. Merz, *personal comm.*).

Sampling design

Longitudinally across the catchment, we selected 20 temporary type kettle holes located in agricultural fields for observation. The kettle holes are classified as “storage” or “shore-overflow” types according to (Kalettka and Rudat, 2006), and have been observed to historically dry-out over the year (Kalettka *personal observation*). We measured kettle hole water chemistry and oxygen and hydrogen stable isotopes over the growing season on days 120, 141, 167, 211, and 252 of the year (DOY). For each sampling campaign, approximate 1L water was collected from the center of the kettle hole at approximately 10cm depth. For the water isotope analysis ($\delta^{18}\text{O}$, δD), 12ml was filtered (0.45 μm , cellulose acetate) into a gas tight glass container. For the water quality analysis, 250 ml of filtered water was collected in polyethylene containers.

Sediments were sampled from each kettle hole (n=20) at the beginning of the season. All study positions were submerged when sampled. We subsampled three points along the edge and three points in the center with a gravity corer (UWITEC, Austria, i.d. 60 mm). The top two centimeters were removed since they consisted of recently deposited, poorly decomposed OM, after which five centimeters were collected into a container (sediment horizon of 2 to 7 cm). The subsamples were combined for a single edge and center sample per kettle hole. Crops and vegetation present in the fields around the

kettle holes at the time of sampling were winter wheat, sugar beet, rapeseed, corn, and grasslands.

Sample analysis

From the water samples we measured pH (ProfiLine pH 3110 with a SenTix 60, WTW sensor), electrical conductivity (ProfiLine Cond 3110 with a TetraCon 325, WTW sensor), dissolved oxygen concentration (ProfiLine Oxi 3205 with a Cellox 325, WTW sensor) and redox potential (ProfiLine pH 3110 with a SenTix ORP, WTW sensor).

Water temperature was measured simultaneously with pH. For each sampling campaign, we recorded the water level measured by a gauge installed at the center of the kettle hole.

K^+ , Na^+ , Ca^{2+} , total dissolved P (TDP) was analyzed by ICP-OES (iCAP 6300 DUO, Thermo Fisher). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were analyzed on a Shimadzu TOC-V/TN and. Nitrate and ammonium were measured photometrically (San++ Continuous Flow Analyzer (CFA), Skalar).

Isotope analyses

Prior to carbon stable isotope analysis of sediment samples, roots were removed by hand and inorganic carbon was removed from all sediment samples by acid fumigation according to Harris et al. (2001). Sediment samples were weighed into tin capsules and combusted in an elemental analyzer (Flash HT, Thermo Scientific, Bremen, Germany).

Stable isotope ratios of sediments were measured with a Thermo-Scientific, Delta V Advantage isotope ratio mass spectrometer (Bremen, Germany). Stable oxygen and hydrogen isotope ratios of kettle hole water were measured via cavity ring down spectrometry (CRDS). Water samples were vaporized at 110°C (Isotopic H₂O A0211) analyzed with an L2130-I Isotopic H₂O analyzer from Picarro (San Jose, CA, USA).

Stable isotope ratios are reported in delta notation (in ‰ units) after equation (1), where the ratio R of the heavy isotope to lighter isotope in a sample is referenced to an international standard (Brüggemann et al., 2011):

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \cdot 1000. \quad (1)$$

Isotope values are reported relative to Vienna Pee Dee Belemnite (VPDB) for carbon, to N₂ in air for nitrogen and to Vienna Standard Mean Ocean Water (SMOW) for oxygen and hydrogen. Isotopic calibration for EA-IRMS measurements was to IAEA-CH-6 (sucrose), USGS40 (L-glutamic acid) and IAEA-N-1 (ammonium sulfate). Analysis of internal laboratory standards that were placed within each analytical run, ensured that the estimates of the isotopic values were precise to within <0.1‰ for δ¹³C and <0.5‰ for δ¹⁵N. Total organic carbon and total nitrogen concentrations (in wt%) of sediment samples were also obtained by EA-IRMS measurements. Repetitive measurements of laboratory standards with the Picarro yielded a precision of <0.1‰ for δ¹⁸O and <1.5‰ for δD.

Ancillary data

In addition to the kettle hole water, we sampled groundwater from a well (80m depth) located in Dedelow, a nearby town (Fig.1). An artesian well was also sampled nearby (36 m depth). For three of the sampling campaigns, water from the Quillow was sampled at three points (Fig.1) and was analyzed for water isotopes.

We used groundwater chemistry (K⁺, Na⁺, Ca²⁺) data available from Merz and Siedel (2015) to place kettle hole water chemistry in regional context. We used data available at two points along opposite ends of the Quillow. The data from these gauges were assembled over several years (2001-2011), but were not measured at the same point or day each year. We thus used the average over the data range rather than providing a time series.

We obtained weather data for calculating potential evaporation (PET), air temperature, and precipitation from a nearby weather station provided by the German weather service (DWD, station 7351). We calculated PET using the model presented by Allen et al. (1998):

$$ET_o = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + (1 + 0.34u_2)} \quad (2)$$

where R_n is net radiation ($\text{MJ m}^{-2} \text{d}^{-1}$), G is soil heat flux density ($\text{MJ m}^{-2} \text{d}^{-1}$), T air temperature ($^{\circ}\text{C}$), u_2 is wind speed (m s^{-1}) at 2m height, e_s is the saturation vapor pressure (kPa), e_a is the actual vapor pressure, Δ is the slope of the vapor pressure curve ($\text{kPa } ^{\circ}\text{C}^{-1}$), and γ is the psychrometric constant ($\text{kPa } ^{\circ}\text{C}^{-1}$).

Evaporation estimates

Evaporation leads to an enrichment of the heavy isotopes ^{18}O and ^2H in the water body due to their smaller diffusivities in air compared to the respective lighter isotopes (Gibson et al., 2005; Gonfiantini, 1986). This kinetic isotopic fractionation during evaporation leads to the remaining water to deviate from the local meteoric water line (LMWL) (Craig and Gordon, 1965). A LMWL is created by collecting precipitation (rain and snow) over the year and implementing the δD and $\delta^{18}\text{O}$ data in a least squares regression. We sampled monthly rain using a ball-type collector (Kazahaya and Yasuhara, 1994) located at the field station and at another site toward the stream source (Fig.1). Evaporated water bodies plot to the right of the LMWL and cluster on a local evaporation line (LEL), which is indicated by a slope commonly ranging between 4.0 and 5.5 for water bodies (Gibson et al., 2008). We quantified the LEL of each kettle hole over the growing season.

We calculated fraction evaporated f (eq.3), for each sampling campaign based on the water isotope data following the methods of Nitzsche et al. (2017) and Skrzypek et al. (2015):

$$f = 1 - \left[\frac{(\delta_L - \delta^*)}{(\delta_P - \delta^*)} \right]^{\frac{1}{m}} \quad (3)$$

Briefly, the method requires the initial isotopic content of the kettle hole (δ_P) and the final isotopic composition (δ_L), a limiting isotopic composition (δ^*), the slope of the local evaporation line, mean temperature T (in $^{\circ}\text{C}$), and relative humidity. The enrichment slope (m) is a function of the relative humidity and isotope kinetic fractionation (see Skrzypek et al. 2015 for full model description). We assumed that the temporarily filled kettle holes water budget relies solely on precipitation, thus we used the average precipitation isotopic values for the year as an estimate for the initial isotopic

composition δ_P (‰) of kettle hole water. The stable isotopic composition of the ambient air moisture (δ_A) was based on stable isotopic composition of local precipitation and the slope of the LEL.

Statistics:

Data were checked for normality using a Shapiro-Wilk test. We ran a linear mixed-effect (lme) model to test for regional controls over the water table height using the *lme4* library (Bates et al., 2014). We included elevation, longitude, and latitude. Random error terms included kettle hole and day of year. The significance of the final model was determined by a likelihood ratio test (Pinheiro and Bates, 2000). An lme model was used to investigate the effect of the calculated percent evaporation on water table height. To compare the LEL slopes we used a general least square model (gls) including a kettle hole identification interaction term. We used a paired Wilcox signed rank test to compare kettle hole sediment sampled from the center versus edge. We analyzed differences between center and edge sediment C and N (Δ) with water quality for each sampling date using partial least squares regression (PLS). A core tenant to this argument is that sediment isotopic signatures and elemental N and C content is in part driven by the loss of water due to evaporation and groundwater recharge over time along with the corresponding changes in water chemistry (i.e., salinity) and water nutrient concentrations (C, N, P). All analyses were performed in R (R Core Team, 2014).

Results:

Environmental variables

The sampling campaigns coincided with the rise and fall of evaporative demand (Fig. 2). All but one kettle hole went dry by the end of the sampling period although the kettle holes that did dry out did so at different rates (Fig. 3). We cannot report the exact date the kettle hole dried out, but by DOY 167, 8 kettle holes dried out, by DOY 211 another 5 dried out and another 6 by the end of the sampling period. We group the kettle holes according to the dry-out dates (DOY 167, DOY 211, DOY 252) of their hydroperiod to further summarize the data.

In testing for the regional controls over kettle hole water levels, only longitude and elevation were significant ($P < 0.05$) variables in explaining variation in water height at the catchment spatial scale. Kettle holes that were at a higher elevation and were further west in the catchment, tended to dry-out slower. Latitude was not significant. Fraction evaporated was also a significant factor ($P < 0.05$) when included in a separate model.

Slopes of kettle hole LELs had a range in values from 4.5 to 7.8 that varied in correlation strength (Table 1). The LEL slopes were not significantly different from each other. Across all kettle holes the LEL had a slope of 5.03 and an intercept of $-16.8 \delta D$ ($r^2 = 0.95$, Figure 4). The Quillow river samples from three different locations (Fig. 4, inset) show enrichment in the heavy isotopes over time. The initial values of the upstream samples were enriched in the heavy isotope relative to downstream locations. Groundwater samples fell on the LMWL. Based on the water isotope data, the proportion of kettle hole water evaporated had a range from -3 to 71% (Fig. 5). Evaporation was lower in April (DOY 120) and reached near maximum values in June (DOY 211). The hydroperiod grouping was not significantly related to the evaporation estimates (ANOVA, $p < 0.2$).

For visualizing the water quality data (conductivity, Ca^{2+} , K^+ , Na^+ ; Table 2) we used the hydroperiod groupings along with historical ground water data from the region (Fig. 6). Electrical conductivity values of the early dry-out (DOY 167) and the late dry-out (DOY 252) hydroperiods remained close to the upstream groundwater estimate. Electrical conductivity of the intermediate dry-out kettle holes (DOY 211) decreased over the sampling period. These patterns for the early and late dry-out hydroperiods were consistent for the Ca^{2+} concentrations as well, both were close in value with the upstream groundwater values. Ca^{2+} concentrations for the intermediate dry-out kettle holes were constant over the three sampling dates. Potassium (K^+) of all kettle hole hydroperiod groups was greater in concentration than the groundwater values. The late dry-out kettle holes (DOY 252) tended to have the lowest K^+ concentrations ($p < 0.01$). Na^+ concentrations were largely within the upstream and downstream groundwater values. Both early and intermediate dry-out kettle holes had a tendency to increase in Na^+ concentration over time.

Carbon and nitrogen concentrations

Isotopic values between the center and edge sediments were not significant. However, differences between paired center and edge N (median= 1.8 ‰) and C (median= 0.2 ‰) elemental concentrations were significant ($p < 0.01$), in which sediments from the center contained larger concentrations of both C and N.

To link sediment biogeochemistry to water quality we analyzed the differences in sediment C and N (ΔC , ΔN) between kettle hole center and edge to different water quality indicators using PLS for each sampling period (Figure 7). The variance explained by the first component increased from near 41% at DOY 120 to 91% by the last sampling date (Table 3). The second component explained at most 17% of the variation (for DOY 141) and we therefore do not emphasize these results for the exploratory analysis. The correlation between ΔN and the water quality tended to be stronger than ΔC . With regards to kettle hole hydroperiod, the strength in correlation with kettle hole water height decreased with time. Early in the season (DOY 121), nutrients such as nitrate and TN, along with water temperature, were highly correlated ($r^2 > 0.6$) with the first component for. On DOY 141, elevation and oxygen, better correlated with component 1. Midseason, on DOY 167, elevation, redox, conductivity, DOC, Ca^{2+} , and Na^+ were highly correlated with the first component. On DOY 211, the day with highest explained variance, redox, ammonium, DOC, TN, Ca^{2+} , K^+ , and TP were most correlated with component 1.

Discussion:

The overall goal of this research was to understand the regional controls on temporary kettle hole water levels and to relate these changes in water levels to spatial differences in surface sediment C and N concentrations and stable isotope signatures. At the catchment scale, both longitude and elevation were significant in explaining the decrease in kettle hole water levels, but at the local scale, evaporation was a better predictor. Kettle hole water loss is thus controlled by both local and regional controls during the growing season, however, the water chemistry and sediment isotopic values

point to different water contributions and environmental effects related to the hydroperiod.

1) Solute concentrations as a function of groundwater and evaporation

Almost all of the kettle holes dried out over the experiment confirming the temporary classification and substantiating the assumption that we might observe evapoconcentration of the kettle hole water solutes. The kettle hole water solute concentrations were highly variable but the seasonal conductivity, Na^+ , and Ca^{2+} patterns largely fell within the groundwater concentrations. In cases of strong evapoconcentration, solute concentrations and conductivity increase (Rains et al., 2008), which we did not observe. Solute concentrations were also independent of water level height. Taken together, these results suggest a strong coupling to surrounding water sources, such as interflow or shallow groundwater. Our findings are consistent with Lischeid et al., (2017), who suggested that groundwater solutes discharge into kettle holes and that the high solute concentration in kettle holes was evidence for a hydraulic connection between kettle holes and a shallow groundwater system.

Concentrations of K^+ , however, were greater than typical groundwater levels and the kettle holes with shorter hydroperiods tended to have significantly greater concentrations relative to the longer hydroperiod kettle holes. Surrounding agricultural soils, especially clay rich horizons, are hypothesized to contribute to these elevated K levels through erosion and leaching (Gerke et al., 2010; Kleeberg et al., 2016; Merz and Steidl, 2015), although we cannot explain why K^+ is retained longer and at higher concentrations within the kettle holes. In general, land managers have long recognized the heterogeneity in solute concentration and conductivity across the landscape by planting sugar beets in areas of high conductivity (Fig. S1) and cornfields at relatively higher elevations with lower conductivity.

Evaporation was highest in the early summer with the average kettle hole evaporative loss amounting to 38% of the kettle hole water volume, ca. 5200 m³ of water, consistent with estimates from temporary kettle holes in this area (Nitzsche et al., 2017).

Furthermore, the kettle holes with the shortest hydroperiods tended to have the largest

estimates of evaporative loss. Overall, the evaporation estimates were not related to the regional estimates of PET during the same period suggesting that evapo-transpiration is a function of local microclimate and vegetation transpiration for each kettle hole (Hayashi et al., 1998; Burba et al., 1999). Transpiration, however, does not result in a shift of the kettle hole water isotopic signature and thus represents a water loss unaccounted for by the evaporation estimates (Gibson et al., 2002). If we assume phragmites and typha species with an LAI of 1, (Westlake et al., 2009), then we might expect a maximum water loss of $125\text{ m}^3\text{ d}^{-1}$ at a stomatal conductance of approximately $100\text{ mmol m}^{-2}\text{ s}^{-1}$ (von Rein et al., 2016). Since macrophytes were not present in every kettle hole, this transpirational loss is a gross overestimate; yet, losses due to transpiration have the potential to be large over the season.

The evaporation estimates did not correlate with the solute concentrations either, providing further evidence that the solute concentrations are more likely related to groundwater and interflow contributions (Gerke et al., 2010). Kettle hole discharge of isotopically enriched water appears to be greater in the upstream sector of the catchment, a pattern we observed in stream water samples that fell on the LEL. There are over 1100 kettle holes in the catchment, the majority lying in the west, representing an area of ca. 5.5 km^2 . Based on the catchment wide water budget, the mean kettle discharge is estimated at ca. $3.5\text{--}5.5\text{ L s}^{-1}$ and therefore contributes on the order of 2-5%, depending on catchment location, of the Quillow discharge (ca. $105\text{--}205\text{ L s}^{-1}$). Thus, it is likely that these other evaporated sources are contributing as well to the spatial isotopic patterns in the Quillow. For example, since the enriched water isotope signal was sustained throughout the season, it is also possible that different near surface aquifers (Weichsalien and Weichsalien-Saalien) contribute to the isotopic patterns.

Another explanation of the relatively enriched stream isotopic values might be the spatial distribution of water age (Orlowski et al., 2016). Water tends to remain in storage until sufficient through-flow is achieved usually occurring during high rainfall events (Hrachowitz et al., 2016). The water that enters the stream tends to be dampened in isotopic values compared to the isotopic signal of precipitation, suggesting that water introduced to the stream originates from subsurface water pools (Kirchner,

2003). At our site, significant water inputs occur during spring wet up and water input is generally fairly low (ca. 500 mm). This implies that pulse rainfall events are not the mechanism behind the enrichment of stream water over the season, but rather subsurface water contributions to the stream as well as the hydrologically connected kettle holes in the catchment. Future research will need to account for potentially different isotopic values of the aquifers as well as to develop models that can estimate contributions of kettle hole water to the stream water over the hydrological year.

2) Hydroperiod influence on sediment biogeochemistry

We found the N and C elemental concentrations were lower at the sediment edge relative to the center, exemplifying the spatial heterogeneity in OM turnover induced by the processes associated with the hydroperiod of these kettle hole types. The changes in redox conditions, temperature, and other factors associated with sediment dry-out along the kettle hole edge most likely results in conditions that enhance microbial decomposition and accelerate biogeochemical cycles (Weise et al., 2016, Revere et al., 2016; von Rein et al., 2016a). It is also likely that input in the form of leaf litter from nearby terrestrial vegetation occurs (Nitzsche et al., 2016) as well as possible overlaps in microbial communities (Bardgett et al., 2001) or shift in their dynamics (von Rein et al., 2016b). These results highlight the importance of the spatial impact the temporary kettle hole types have on biogeochemical cycles of this landscape.

We also considered the change in water quality with relation to the spatial differences between center and edge in sediment C and N. Through this exploratory analysis we learned that the late summer water quality explained the most variation and is likely due to a number of reasons. First, the kettle holes that still contained water until late summer were most likely similar to each other, thus sharing a similar response to water quality. Moreover, increasing redox levels were positively correlated with the spatial differences (i.e., center vs. edge), which is consistent with an increase in microbial decomposition as more oxygen becomes available. In this case the areas near the edge is exposed earlier to these conditions and thus are more strongly affected compared to the center. Total dissolved nitrogen, on the other hand, was negatively correlated with the spatial differences. Lower concentrations in total nitrogen, as well as ammonium and

nitrate, suggest that the shift in redox accelerated nitrification, which was then followed by algal uptake or perhaps leaching into groundwater (Lischeid and Kalettka, 2012).

The sediment isotopic variability was large and any differences between the edge and center sediments were not detectable. This large isotopic variability is similar to what was found for surface (0-2 cm) and deeper (2-75 cm) sediments in kettle holes from a larger survey of kettle hole hydroperiod types (Nitzsche et al., 2017). We placed our sediment samples in the previously found relationship between sediment OM $\delta^{15}\text{N}$ and C:N of deeper sediments (Fig. 8), which aligned to these previous results. Nitzsche et al (2017) hypothesized that the curvature in the relationship was due to enhanced microbial turnover. The kettle holes we studied here also fall on the steep slope of the curve providing further evidence of the high rate of OM turnover of these kettle hole types.

Conclusion

Kettle holes in NE Germany are not geographically isolated wetlands and water quality is largely controlled by shallow groundwater or interflow. Questions remain concerning why there are spatial differences of stream water quality that reflect evaporative effects over the season. Is this a function of local shallow aquifers or is this a function of water retention times? We show evidence of spatial differences in C and N within a kettle hole where kettle edges have more rapid OM decomposition that is most related to the many environmental changes that occur as water levels recede and sediments are exposed to oxidizing conditions.

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Table 1. Individual kettle hole (KH) local enrichment line slope, intercept, and R².

KH ID	Slope	Intercept	R ²
183	7.1	-10.8	0.99
187	6.3	-10.2	—
190	5.5	-17.0	0.99
235	6.5	-9.6	—
236	4.7	-18.8	0.88
287	5.0	-17.6	0.98
313	4.5	-17.6	0.72
394	4.8	-18.1	0.97
606	5.6	-16.6	0.99
639	6.6	-12.3	—
671	4.5	-18.4	0.94
1162	4.7	-19.3	0.92
1189	5.2	-17.0	0.99
1228	5.6	-14.3	0.99
1316	7.3	-9.4	—
1599	7.8	1.8	—
1604	4.5	-18.7	0.94
1797	5.9	-12.3	0.99
2489	6.1	-11.9	—
2544	5.4	-15.0	0.99

* Kettle holes with less than three samples are indicated by a dash (—) in the R² column

Table 2. Water quality of kettle holes with different hydroperiods (H.P.1, H.P.2, H.P.3) over the study period.

DOY	120			141			167		211
	H.P. 1‡	H.P. 2‡	H.P. 3‡	H.P. 1	H.P. 2	H.P. 3	H.P. 2	H.P. 3	H.P. 3
pH	7 (± 0.2)	7.7 (± 0.3)	7.4 (± 0.3)	7.1 (± 0.2)	8 (± 0.4)	7.5 (± 0.3)	7.2 (± 0.2)	7 (± 0.2)	7.2 (± 0.2)
T (°C)	10.4 (± 0.5)	12 (± 0.8)	12.3 (± 1)	15.8 (± 0.3)	16 (± 0.9)	15.8 (± 0.6)	17.1 (± 1.2)	15.8 (± 1)	16.3 (± 1)
Redox (mV)	55.7 (± 19.7)	145.3 (± 12.3)	160 (± 10.1)	100.7 (± 26.6)	159.3 (± 10.5)	215.9 (± 17.7)	74.4 (± 32.6)	102.2 (± 24.8)	88.3 (± 28.8)
O ₂ (mg L ⁻¹)	6.5 (± 0.7)	10 (± 2.4)	9.5 (± 1.8)	7.6 (± 1.9)	10.5 (± 2)	9.9 (± 1.7)	6.3 (± 1.9)	6.2 (± 1.7)	5.4 (± 1.3)
NH ₄ (mg L ⁻¹)	0.1 (± 0.1)	NA	0.1 (± 0.1)	0.5 (± 0.4)	0.1 (± 0.1)	0.1 (± 0.1)	0.1 (± 0.1)	0.1 (± 0.1)	0.7 (± 0.4)
NO ₃ (mg L ⁻¹)	0.1 (± 0.1)	0.1 (± 0.1)	1.5 (± 1.4)	0.2 (± 0.1)	0.1 (± 0.1)	0.1 (± 0.1)	0 (± 0)	0 (± 0)	NA
DOC (mg L ⁻¹)	33.8 (± 6.2)	27.1 (± 6.6)	27.9 (± 5.4)	48.6 (± 9)	33 (± 7.4)	25.7 (± 3.6)	40.6 (± 8.2)	32.5 (± 3.9)	33.3 (± 3.7)
N _t (mg L ⁻¹)	3 (± 0.6)	1.9 (± 0.4)	3.3 (± 1.4)	4.2 (± 0.9)	2.3 (± 0.5)	1.8 (± 0.3)	2.6 (± 0.5)	2 (± 0.3)	3.6 (± 0.5)
P _t (mg L ⁻¹)	0.7 (± 0.4)	1.1 (± 1)	0.1 (± 0.1)	1 (± 0.4)	1.6 (± 1.1)	0.2 (± 0.1)	2.1 (± 1.1)	0.4 (± 0.3)	0.3 (± 0.1)

‡n= 8 for H.P. 1, n= 5 for H.P. 2, n= 6 for H.P. 3

Table 3. PLS analysis results of differences between kettle hole sediments sampled at the edge and center (ΔC , ΔN) with water quality over study period. .

	Day of Year			
Correlation with 1 st component	120	141	167	211
Longitude	0.36	0.26	0.26	0.36
Elevation	0.53	0.63	0.62	0.07
pH	0.19	0.48	-0.36	0.06
T	0.64	0.26	-0.45	0.15
redox	0.31	0.30	0.69	0.91
O ₂	0.17	0.60	0.22	0.04
Conductivity	-0.55	-0.58	-0.89	-0.53
NH ₄ ⁺	-0.01	-0.57	-0.17	-0.82
NO ₃ ⁻	0.61	-0.58	—	-0.61
DOC	0.21	0.04	0.66	0.85
TN	0.62	-0.25	0.54	-0.97
Ca	-0.55	-0.57	-0.78	-0.61
K	0.09	0.06	0.22	0.74
Na	-0.23	-0.43	-0.63	0.21
TP	0.21	0.16	0.24	0.67
Water Height	0.62	0.52	0.50	0.09
Correlation with response variables				
ΔN	0.75	0.60	0.64	0.98
ΔC	0.61	0.56	0.67	0.92
Variance explained				
r ²	0.47	0.34	0.43	0.91

Figure 1. Quillow catchment (168 km²) study area in which 20 kettle holes (three and four digit numbers) were sampled for water and sediments. The stream water was sampled at three points along the Quillow stream (Q1, Q2, Q3), rain water collectors are depicted by triangles, the two wells from Merz and Steidl (2015) are represented by red triangles, and the village Dedelow is indicated by a star. Different land use types are depicted across the fields in the 2015 water season.

Figure 2. Precipitation and potential evapotranspiration (PET) during the sampling period in the Quillow catchment, NE Germany. Precipitation (mm) events are depicted by light gray lines, PET (mm/d) by a continuous gray line, and sampling days are indicated by black vertical lines.

Figure 3. A) Individual kettle hole water level decrease over the study period. Each line and color-symbol pair trace the water level decrease across the sampling dates (i.e., the values are not continuous) for a single kettle hole ($n=20$). B) Kettle hole elevation with relation to hydroperiod grouping. The grouping corresponds to the sampling campaign for which there was no surface water remaining for collection ($n=19$, two kettle holes overlap in elevation within the DOY 167). The precise dry out event may have occurred between campaigns.

Figure 4. Deuterium (δD) and oxygen ($\delta^{18}O$) isotopic biplot of kettle hole, stream, and groundwater samples. Kettle holes were grouped according to their hydroperiod patterns: open circles dried out by DOY 167, blue circles DOY 211, and red circles by DOY 252 including one kettle hole that did not dry out by the end of the study. Triangles represent samples drawn from the Quillow stream at three positions over three sampling dates between April and June. The open triangles are samples from the upstream position, the grey from midstream, and the yellow downstream. Lines to emphasize the trend of enrichment over time connect the positions. Black diamonds are samples from groundwater. The black solid line traversing the entire figure is the local meteoric water line and the dotted line through the samples is the local enrichment line. The figure inset shows the Quillow river isotopic patterns independent of the kettle holes. The open triangles are samples from the upstream position, the grey from midstream, and the yellow downstream.

Figure 5. Proportion of evaporated water by collection date. The proportion of evaporated water was calculated using the water isotope data (δD , $\delta^{18}O$) collected over the growing season.

Figure 6. Kettle hole water quality over the growing season in the Quillow catchment, NE Germany. Kettle holes are grouped by hydroperiod in which triangles (n= 8) had the shortest, squares an intermediate hydroperiod (n= 5), and circles the longest (n=6). Means and standard errors are displayed for kettle hole values. Groundwater conductivity and concentration levels typical for upstream (solid line) and downstream (dashed line) of the Quillow are included as a reference.

Figure 7. The multivariate PLS analysis of differences between kettle hole sediments sampled at the edge and center (ΔC , ΔN) and water chemistry at different dates over the growing season.

Figure 8. Curve-linear relationship between sediment $\delta^{15}\text{N}$ and C:N ratios. Data from this study are listed as center and edge. The data from Nitzsche et al. (2017) are indicated by open and closed black and white symbols and are samples taken from a depth of 2-75cm. The hydroperiod types are semi-permanent (sp-type) and temporary (t-type), a classification based on a statistical clustering analysis.