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Land-use and hydroperiod affect kettle hole sediment carbon and nitrogen biogeochemistry

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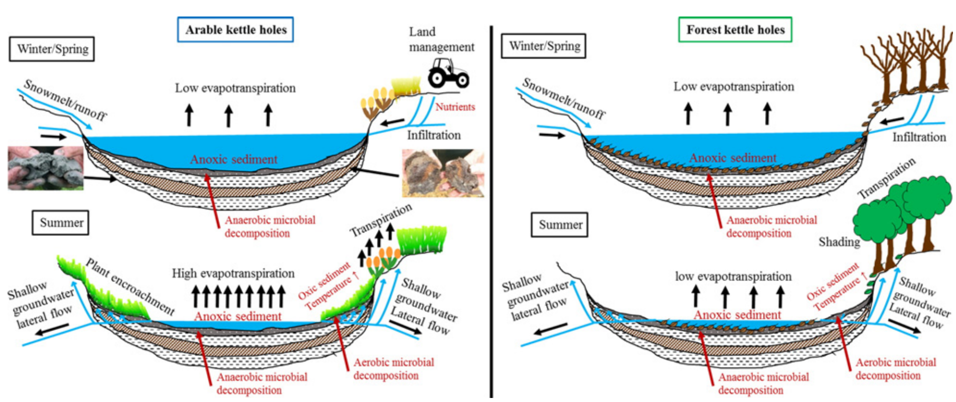
HIGHLIGHTS

- Kettle holes lie on the boundary of the aquatic and terrestrial domains.
- Surface sediments reflect surrounding land-use and management.
- Deeper sediments reflect past organic matter sources and the hydroperiod.
- The onset of evaporation and lateral flow partly determine kettle hole hydroperiod.
- Strong links between land use and hydroperiod drive kettle hole biogeochemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

Kettle holes are glaciofluvially created depressional wetlands that collect organic matter (OM) and nutrients from their surrounding catchment. Kettle holes mostly undergo pronounced wet-dry cycles. Fluctuations in water table, land-use, and management can affect sediment biogeochemical transformations and perhaps threaten the carbon stocks of these unique ecosystems. We investigated sediment and water of 51 kettle holes in NE Germany that differ in hydroperiod (i.e. the duration of the wet period of a kettle hole) and land-use. Our objectives were 1) to test if hydroperiod and land management were imprinted on the isotopic values ($\delta^{13}C$, $\delta^{15}N$) and C:N ratios of the sediment OM, and 2) to characterize water loss dynamics and kettle hole-groundwater connectivity by measuring the stable $\delta^{18}O$ and δD isotope values of kettle hole water over several years. We found the uppermost sediment layer reflected recent OM inputs and short-term processes in the catchment, including land-use and management effects. Deeper sediments recorded the degree to which OM is processed within the kettle hole related to the hydroperiod. We see clear indications for the effects of wet-dry cycles for all kettle holes, which can lead to the encroachment of terrestrial plants. We found that the magnitude of evaporation

Abbreviations: sp-type, semi-permanently water-filled kettle holes; t-type, temporarily water-filled kettle holes.

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Evaporation
Landscape functioning

depended on the year, season, and land-use type, that kettle holes are temporarily coupled to shallow ground water, and, as such, kettle holes are described best as partially-closed to open systems.

1. Introduction

The landscapes of northern America, central and northern Europe and northern Asia are populated by kettle holes (Kalettka and Rudat, 2006; Tiner, 2003), small (<1 ha) depressional wetlands of glaciofluvial origin. Land-use and management directly affect individual kettle holes, while site level geomorphology and climate conditions determine kettle hole hydroperiod, defined as the duration of the wet period of a kettle hole (Kalettka and Rudat, 2006; van der Kamp and Hayashi, 2009). The interactions between the hydrology, organic matter (OM) contributions, and land-use are inherently complex (Song et al., 2014); and how these interactions manifest in kettle hole biogeochemistry across a landscape is less understood (Premke et al., 2016).

The kettle hole water budget consists of winter and early spring inputs primarily driven by snowmelt and runoff over partially frozen soils, direct precipitation, and seasonal lateral flow (Gerke et al., 2010; Shaw et al., 2012; van der Kamp and Hayashi, 2009). Water losses are through evapotranspiration, spillover, and lateral shallow groundwater recharge (Berthold et al., 2004; van der Kamp and Hayashi, 2009). Kettle holes can be temporarily in contact with shallow groundwater potentially resulting in discharge or recharge from the groundwater (van der Kamp and Hayashi, 2009; Heagle et al., 2013). Kettle hole water levels are dynamic, often experiencing seasonal wet-dry cycles. However, for the NE region of Germany the timing of kettle hole water losses and their corresponding magnitudes are not well constrained.

These pronounced wet-dry cycles can lead to the complete drying and rewetting of sediments (Johnson et al., 2004) while others may stay submerged or partially submerged over the year. Strong water level fluctuations result in changes in OM dynamics and oxygen exposure during desiccation (Boon, 2006) that can alter microorganism communities or their carbon metabolism (Fromin et al., 2010; Reverey et al., 2016; Weise et al., 2016). During long-term wet conditions autochthonous primary production within the kettle hole can be an important OM source, while desiccation can lead to terrestrial plant encroachment into kettle holes, which may result in the formation of peat bodies (Gaudig et al., 2006). Thus, the dry-wet cycles impact the environmental conditions and affect OM sources that contribute to the sediment record.

Land management such as the general form of land-use, selection of crop species, fertilization and tillage have a large influence on terrestrial biogeochemistry and consequently for kettle hole surface sediments as well (Nitzsche et al., 2016). Furthermore, substantial material transfer from the surrounding terrestrial ecosystems is known to occur into kettle holes including inputs from plant biomass, soil particles via event based erosion, and nutrients (Frielinghaus and Vahrson, 1998; Gerke et al., 2010; Kleeberg et al., 2016). However, broad investigations of kettle hole biogeochemistry in the landscape context are few and we do not know the extent to which external (i.e. terrestrial) factors such as fertilization affect kettle hole internal OM turnover or how this is represented in the sediment column.

Kettle hole OM biogeochemistry is thus a function of these primary players: land-use, hydroperiod, and OM sources. We investigated 51 kettle holes with different hydroperiod and land-use by sampling sediment at several depths during one summer. The objectives of our study were, 1) to test if hydroperiod and land management were imprinted on the isotopic values ($\delta^{13}C$, $\delta^{15}N$) and C:N ratios of the sediment OM, and 2) to characterize water loss dynamics and kettle hole-groundwater connectivity by measuring the stable $\delta^{18}O$ and δD isotope values of kettle hole water over several years.

2. Material and methods

2.1. Study site

The study site is a 3.25 × 11.75 km (38.2 km^2) wide area and is located within the Quillow catchment (168 km^2; Nitzsche et al., 2016) of NE Germany. The study site comprises of approximately 290 kettle holes in topographic depressions, which were formed due to 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 proportions of land-use types across the study site are 74.4% arable, grasslands 10.4%, and forest 5.9%. Villages and single houses (4.5%) and larger stagnant water bodies of >1 ha (fens, lakes, reed dominated; 3.4%) are also dispersed over the area. Kettle holes make up around 1.4% of the area and are present in all land-use types (Fig. 1), and the proportion of stagnant water bodies (kettle holes, moors, reed-dominated, lakes) and streams largely decreases from NW to SE (Fig. SI1 in Supplementary information). The application of chemical fertilizers is common in the area since the second half of the 19th century and slurry application is common since 1970 (Neyen, 2014; Nitzsche et al., 2016). The landscape relief is moderately rolling ranging in elevation from 40 to 112 m a.s.l. The climate is subhumid with a mean annual temperature of 8.6 °C and mean annual precipitation of 495 mm as determined per year between 1992 and 2015 (AgroScapeLab Quillow, Dedelow, E 013°48′12″, N 53°21′59″). The mean annual temperature was 8.0 °C in 2013, 9.4 °C in 2014 and 9.1 °C in 2015. The mean annual precipitation was 446 mm in 2013, 561 mm in 2014 and 414 mm in 2015.

2.2. Sampling design

We sampled 51 kettle holes for sediments from the middle July to the end of August 2013. We based our kettle hole selection on: 1) size class, ensuring that we covered the range of different size classes following the classification of Kalettka and Rudat (2006), 2) land-use type (arable fields, grassland, forest), 3) distribution (we ensured to cover the entire study area), and 4) targeting at sampling kettle holes of different hydroperiod. We classified the kettle hole hydroperiod after several years of observation (2013–2015). We defined kettle holes as semi-permanently water-filled (sp-type) when they were water-filled during all water sampling campaigns from 2013, 2014 and 2015, and those that dried out at least one time over all sampling campaigns were classified as temporarily water-filled (t-type). Consequently, we sampled 13 sp-type and 24 t-type kettle holes in arable fields, 3 sp-type and 3 t-type kettle holes in forests, and 2 sp-type and 6 t-type kettle holes in grasslands (Table SI1 in Supplementary information). Sampled kettle holes were predominantly of edge type (42) with *Phalaris arundinacea*, minor full-reed (7) dominated by *Phragmites australis* and wood type (2) (see the classification of Pätzig et al., 2012) (Table SI1).

To capture the sediment spatial variability within kettle holes, three undisturbed sediment cores were taken by a gravity corer (UWITEC, Austria, i.d. 60 mm) in a transect from a shallow location (ca. 40 cm) to the deepest site (ca. 80 cm). If a kettle hole was dry (no water present in the sediment), we used a soil auger (Eijkelkamp, Netherlands, 2 cm ø). We took surface sediments (0–2 cm; presented earlier in Nitzsche et al., 2016), and deeper sediments (2–75 cm) from each kettle hole. The deeper sediment layer, according to Kleeberg et al. (2016) spans the last ca. 120 years.

From deeper layers, we sampled a mineral-dominated sediment and an organic-rich counterpart (e.g. a peat horizon) provided sufficient

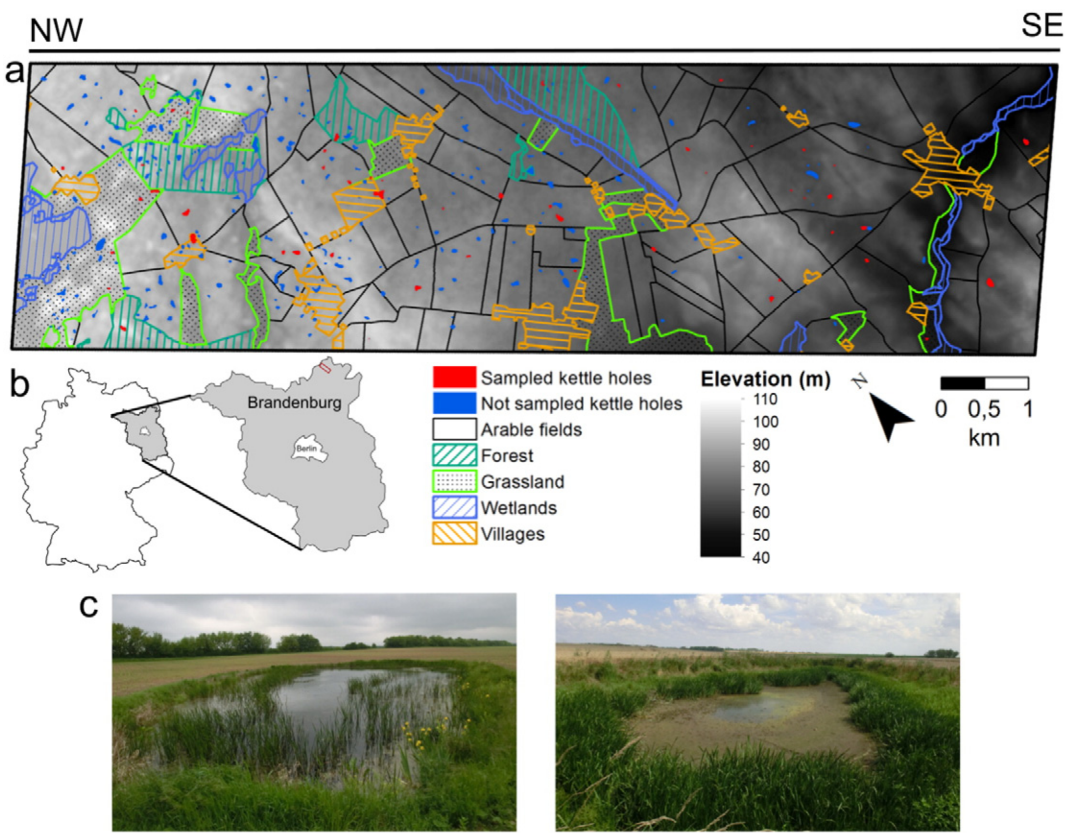

Fig. 1. Study site (a), the location of the study site (red rectangle) in NE Germany (b) and photographs of a temporarily water-filled (t-type) kettle hole in July 2013 (left) and the same kettle hole in July 2014 (right) (c). Sampled kettle holes (n = 51) (red) out of approximately 290 being present in the sampling area underlain by a shaded relief map (in m a.s.l.) and with covers, showing the land-use in which a kettle holes is present (a). Note that in the figure, the study site (a) has been rotated by 40°.

material was present. The one or two samples were usually taken over a 5 cm depth range (Table SI2). We combined the same sediment horizons from the three sampling points along a transect. Thus, it was possible for a single kettle hole to have two different deeper sediment samples, but this was not consistent across all kettle holes. In total, we collected 83 deeper sediment samples from which 32 kettle holes contained both a mineral and peat horizon, and 19 kettle holes that had only one sample. These samples can be further classified by hydroperiod: 27 samples were taken from sp-type and 56 samples from t-type kettle holes.

We took surface water samples from the center of the kettle holes, which were stored in 12 ml gas-tight exetainers (Labco Ltd. High Wycombe, UK) sealed with parafilm. We sampled during the growing season (July to August) in 2013–2015 ($n_{July/August\ 2013} = 45$; $n_{July\ 2014} = 23$; $n_{July\ 2015} = 20$) and additionally two times in the dormant season ($n_{December\ 2014} = 19$; $n_{April\ 2015} = 42$) (Table SI3). At the end of July 2014, we also sampled water (n = 20) for water chemistry related to evaporation (Cl^-, SO_4^{2-}, Ca, K, Na, Mg, P, Si). We also measured pH, electric conductivity and O_2 concentration in-situ with electronic probes (SenTix, TetraCon, and CellOx) directly in the surface water at the edge of the kettle hole.

2.3. Sample preparation

All samples were stored in gas-tight containers at 4 °C in dark conditions prior to preparation. Sediment samples were oven-dried at 65 °C for 48 h and subsequently ground to a powder. Water samples were filtered (0.45 μm cellulose acetate filter) before analysis.

2.4. Stable isotope analysis

We relied primarily on the isotopic signature ($\delta^{13}C$, $\delta^{15}N$) and C:N ratios of sediment OM to determine the source (e.g. terrestrial vs. aquatic) as well as the degree of microbial processing and identify potential land-management impacts (Andrews et al., 1998; Herczeg et al., 2001; Thevenon et al., 2012). Prior to carbon stable isotope analysis of sediment samples, 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 H_2O A0211) and the vapor was analyzed with a L2130-I Isotopic H_2O analyzer from Picarro (San Jose, CA, USA).

Stable isotope ratios are reported in delta notation (in ‰ units) after Eq. (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):

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

We used the ratios $^{13}C/^{12}C$ for $\delta^{13}C$, $^{15}N/^{14}N$ for $\delta^{15}N$, $^{18}O/^{16}O$ for $\delta^{18}O$ and $^{2}H/^{1}H$ for δD. Isotope values are reported relative to Vienna Pee Dee Belemnite (VPDB) for carbon, to N_2 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 ensured that the estimates of the isotopic values were precise to within <0.1‰ for $\delta^{13}C$ and <0.5‰ for $\delta^{15}N$. 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 $\delta^{18}O$ and <1.5‰ for δD.

2.5. Chemical analysis of water

Elemental concentrations (Ca, K, Na, Mg, P, Si) were analyzed via inductively coupled plasma atomic emission spectroscopy (ICP-OES) with an ICP-iCAP 6300 DUO (Thermo Scientific, Bremen). Sulfate (SO_4^{2-}) and Chloride (Cl^-) concentrations were measured via ion chromatography (Thermo Scientific Dionex, Bremen).

2.6. Evaporation in water bodies

There is a global relationship of $\delta^{18}O$ and δD of precipitation expressed by the equation $\delta^2H = 8 \cdot \delta^{18}O + 10$ – the Global Meteoric Water Line (GMWL) (Craig, 1961; Dansgaard, 1964). Evaporation leads to an enrichment of the heavy isotopes ^{18}O and ^2H in the water body due to smaller diffusivities in air (Gibson et al., 2005; Gonfiantini, 1986). This kinetic isotopic fractionation during evaporation leads to a deviation from the GMLW indicated by a decrease in the slope of this relationship and is best explained by the Craig-Gordon-model (Craig and Gordon, 1965). Evaporated water bodies plot to the right of the GMWL 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). The intersection point between the LEL and GMWL describes the source water, i.e. the weighted mean isotopic composition of the local precipitation (Gibson and Edwards, 2002).

Based on the $\delta^{18}O$ and δD isotope values of kettle hole water we calculated the evaporative water volume loss *f* from kettle holes sampled in the growing season (July/August 2013, 2014 and 2015) with the *Hydrocalculator* software developed by Skrzypek et al. (2015). *Hydrocalculator* allows for estimations of *f* based on the revised Craig-Gordon model (Horita et al., 2008) and includes modification of the Craig-Gordon model based on field studies, including sites from North America (Skrzypek et al., 2015), thus justifying its use in humid regions such as NE Germany. We assumed a non-steady-state hydrological regime of the kettle holes with no out- and inflows after filling was complete. For each year, we calculated *f* between beginning of April and the time of sampling in July. Though we did not take water samples in the beginning of April for each year (only in April of 2015), we chose this time as the time when the filling was expected to be complete and for the onset of evaporation based on daily potential evapotranspiration data for 2013 and 2014. We constructed the LEL based on the isotopic composition δ_L (‰) of kettle hole water at the time of sampling. To estimate the initial isotopic composition δ_P (‰) of kettle hole water we used the intersection between the LEL and local meteoric water line (LMWL; see below) for each year (Table SI4). In addition, we calculated *f* from April to July 2015 using the measured $\delta^{18}O$ and δD isotope values from our April 2015 sampling campaign as δ_P which allows for considering the deviation of April 2015 isotope values from the LWML (see below).

Mean temperature T (in °C) and relative humidity were obtained from a weather station in the center of the study area located 2 m above the water surface from one sp-type kettle hole. The weather station failed in the end of 2014, thereafter we used mean daily temperature and relative humidity from the ZALF AgroScapeLab Quillow station. We sampled monthly local rain using a ball-type collector (Kazahaya and Yasuhara, 1994). We used the rain isotopic composition (δ_{rain}) to construct the LMWL and calculate the mean $\delta^{18}O$ and δD of local precipitation between April and July. The stable isotopic composition of the ambient air moisture (δ_A) was determined based on stable isotopic composition of local precipitation and the slope of the LEL. An implicit assumption is that there is an equilibrium isotopic fractionation between δ_{rain} and δ_A, which is a function only of temperature. δ_A can also affected by relative humidity, wind speed, and direct sunlight over short time periods, but because our estimates are for two seasons, we assume daily fluctuations in these parameters have a small effect.

2.7. Statistical analysis

To test for statistical differences in $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of surface sediments with respect to land-use, hydroperiod and their interactions, we used a two-way ANOVA followed by a post hoc significance test (Tukey's HSD) after testing for normally distributed data with the Shapiro-Wilk test. We tested for differences in $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of deeper sediments with respect to hydroperiod, land-use, and TOC content by performing a nested ANOVA including the kettle hole in the error term of the model to account for the unbalanced sample size. We performed a three-way ANOVA followed by Tukey's HSD to test for significant differences in evaporative loss with respect to land-use, hydroperiod, and year sampled after testing for normally distributed data with the Shapiro-Wilk test. We used a generalized linear model (GLM) to test for significant differences in water chemistry data across land-use and hydroperiod types. We refrained from reporting p values of statistical tests for the evaporative loss *f* and water chemistry between grassland kettle holes and kettle holes of other land-use given the low *n* of two for grassland kettle holes. We used Moran's I to test for spatial autocorrelation of sediment $\delta^{13}C$ and $\delta^{15}N$, water chemistry data, and evaporative loss *f* in kettle holes from the different sampling periods. We used non-linear regression for curve fitting of deeper sediment $\delta^{15}N$ vs. C:N ratio. We calculated the Akaike's Information Criterion (AIC) to test whether a linear fit or a curve fit was better. We used a second order polynomial to fit the $\delta^{15}N$ and C:N ratio vs. depth for deeper sediments of sp-type kettle holes, and a local polynomial regression (loess) for the patterns of t-type deeper sediments. We applied linear regressions between the evaporative loss *f* of 2014 and water chemistry data, $\delta^{18}O$ vs. δD of kettle hole water, and $\delta^{13}C$ and $\delta^{15}N$ vs. the geographical distance (i.e. longitude × latitude). We used the Student's *t*-test to test for significant differences in mean slope of the growing season (July/August 2013, July 2014, July 2015) over the mean slope of the dormant season (December 2014, April 2015).

We used agglomerative clustering, a form of hierarchical clustering, to determine whether kettle holes reflect the hydroperiod and surrounding land-use based on their OM biogeochemistry. We performed an agglomerative (Euclidean distances using average linkage and standardized values) clustering using $\delta^{13}C$, $\delta^{15}N$ isotope data and molar C:N ratios of the surface sediments.

Agglomerative clustering is a common method to group similar samples and represent them in a dendrogram. This is achieved by creating and merging clusters that are made up of similar samples, while moving up in the hierarchy ('bottom-up' approach). To decide which clusters are merged, a distance metric is created as a measure for the dissimilarity between the samples and a linkage criterion is defined. The resulting dendrogram has the interlinkage distance (or height) on the y-axis that corresponds to the distance between clusters and allows for identifying similar clusters. All statistical analysis including the agglomerative clustering approaches were performed with R (version 3.1.1, R Foundation for Statistical Computing, Vienna, Austria, http://www.R-project.org/).

3. Results

3.1. Sediment $\delta^{13}C$, $\delta^{15}N$ and C:N data

We did not find any significant differences in surface sediment $\delta^{13}C$ with respect to land-use ($p = 0.57$) and hydroperiod ($p = 0.44$). In contrast, across all kettle holes, we found large differences in $\delta^{15}N$ with respect to land-use and hydroperiod (Fig. 2a; $p < 0.01$). Within arable fields, we found t-type kettle holes were significantly more enriched in ^{15}N compared to sp-type kettle holes by 2.1‰ ($p < 0.01$; Table SI5). Within grasslands, t-type kettle holes were enriched in ^{15}N by 2.8‰, and within forests by 3.3‰ compared to sp-type kettle holes, although the difference was not significant. Surface sediments from kettle holes in forests were significantly ($p < 0.01$) more depleted in ^{15}N compared to surface sediments in kettle holes from arable fields and grasslands. Overall, we found surface sediments to slightly decrease in $\delta^{15}N$ from SE to NW (Moran's I = 0.09, $p < 0.01$, $n = 51$). More precisely, surface sediments from kettle holes located in arable fields were weakly spatially autocorrelated (Moran's I = 0.18, $p < 0.01$, $n = 37$) in which the $\delta^{15}N$ decreased slightly from the SE to NW or by ca 0.6‰ ($r^2 = 0.26$, $p < 0.01$) for each unit of geographical distance (longitude × latitude).

Land-use was not significant in explaining the variation of $\delta^{13}C$, $\delta^{15}N$ and C:N ratios of deeper sediments. Sediment $\delta^{13}C$ values from t-type and sp-type kettle holes were similar (range of $\delta^{13}C$ from −27.7 to −28.9‰). $\delta^{15}N$ of sediments from t-type kettle holes (mean of 4.8 ± 0.3‰, $n = 56$) were consistently more enriched ($p < 0.01$) than sediments from sp-type kettle holes (mean of 3.1 ± 0.2‰, $n = 27$; Table SI6). Sediments from sp-type kettle holes had significantly ($p < 0.05$) higher C:N ratios (mean of 15.2 ± 0.9) than sediments from t-type kettle holes (mean of 13.1 ± 0.5).

In contrast to surface sediments, deeper sediments showed a clear tendency of an increase in $\delta^{15}N$ alongside a decrease in C:N (Fig. 2b). This trend is best explained by a non-linear function ($r^2 = 0.59$, $p_{coefficient} = 0.01$, $p_{exponent} < 0.01$), compared to a liner regression model ($AIC_{NLS} = 271$ vs. $ACI_{LM} = 281$). Both sediments from the t-type and sp-type kettle holes showed a decrease in $\delta^{15}N$ with depth ($r^2_{sp\text{-}type} = 0.02$; $r^2_{t\text{-}type} = 0.31$) (Fig. 3a). Similarly, C:N ratios from the t-type and sp-type kettle hole sediments increased with depth ($r^2_{sp\text{-}type} = 0.17$; $r^2_{t\text{-}type} = 0.30$) (Fig. 3b).

3.2. Kettle hole surface water $\delta^{18}O$ and δD data and evaporative loss f

We observed evaporative enrichment in kettle hole surface waters over all sampling periods (Fig. 4). The mean slope for the local enrichment line (LEL) for the late growing season (July/August 2013, 2014 and 2015) was 3.76, significantly lower ($p < 0.01$) than the mean slope (4.68) of the dormant season (December 2014 and July 2015 sampling campaigns). To estimate the water loss at the site scale, we first calculated the difference between the slopes of LELs (growing and dormant season) from the LMWL. We then subtract the difference between the normalized seasonal slopes and express this relative to the dormant season LEL, which results in an estimate of a site level evaporative loss (−28%) during our measurement period. Using a similar method but with reference to the growing season (instead of the dormant season), we can estimate how much water from the previous growing season contributes to the beginning of the next water year. On average about 20% of the kettle hole water volume has been refilled by shallow

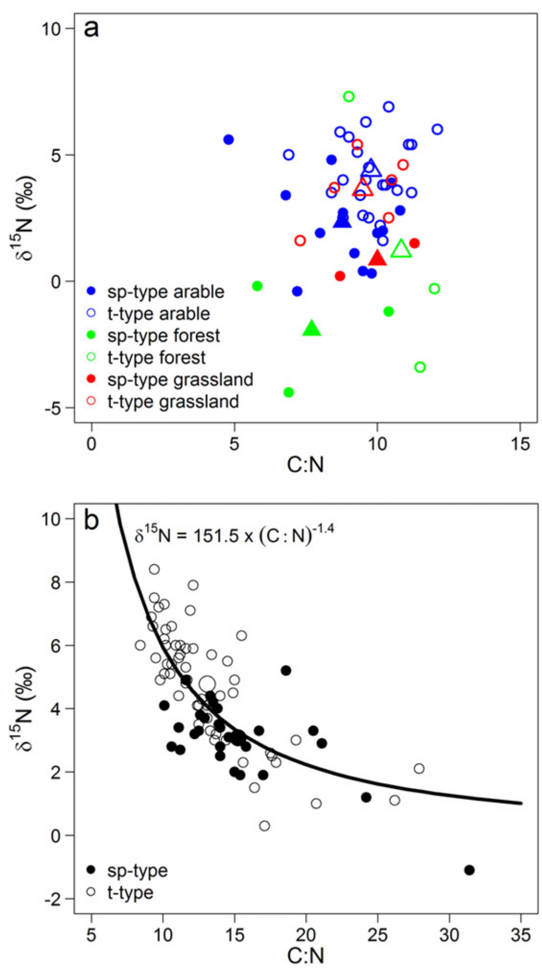

Fig. 2. Bi-plot of $\delta^{15}N$ (‰) vs. the C:N ratio for (a) surface sediments and (b) deeper sediments. Enlarged triangles (a) and enlarged circles and triangles (b) are the mean for each group. The black solid line in (b) represents a non-linear least square curve fit through all 83 deeper sediment samples.

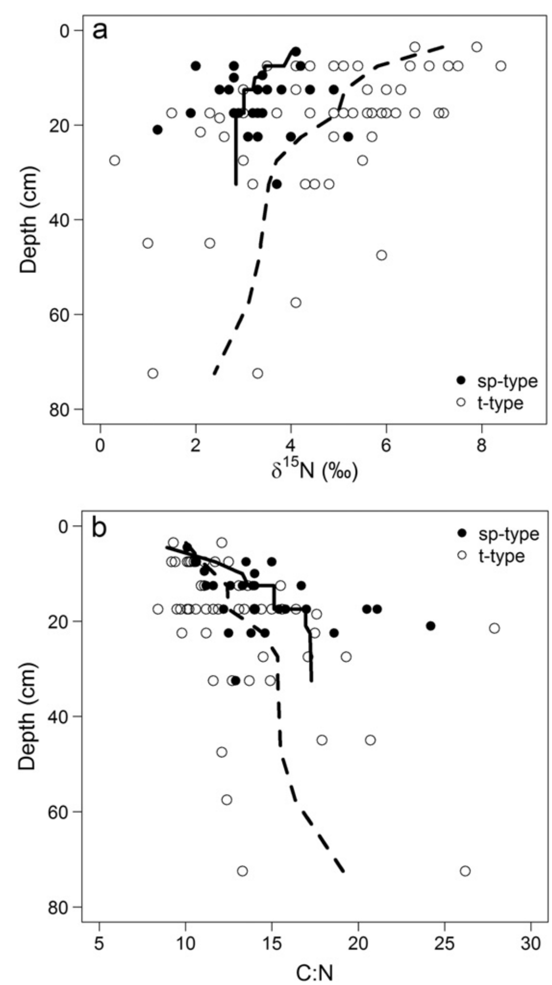

Fig. 3. Bi-plot of the $\delta^{15}N$ (in ‰) (a) the C:N ratio (b). vs. mean depth dimension for each deeper sediment sample (in cm). The black solid lines represent second order polynomial fit for deeper sediments of sp-type kettle holes ($n = 27$), and the black dashed lines local polynomial regressions (loess) for the patterns of t-type deeper sediments ($n = 56$). A total of 83 samples are shown because sometimes two samples per kettle hole were taken.

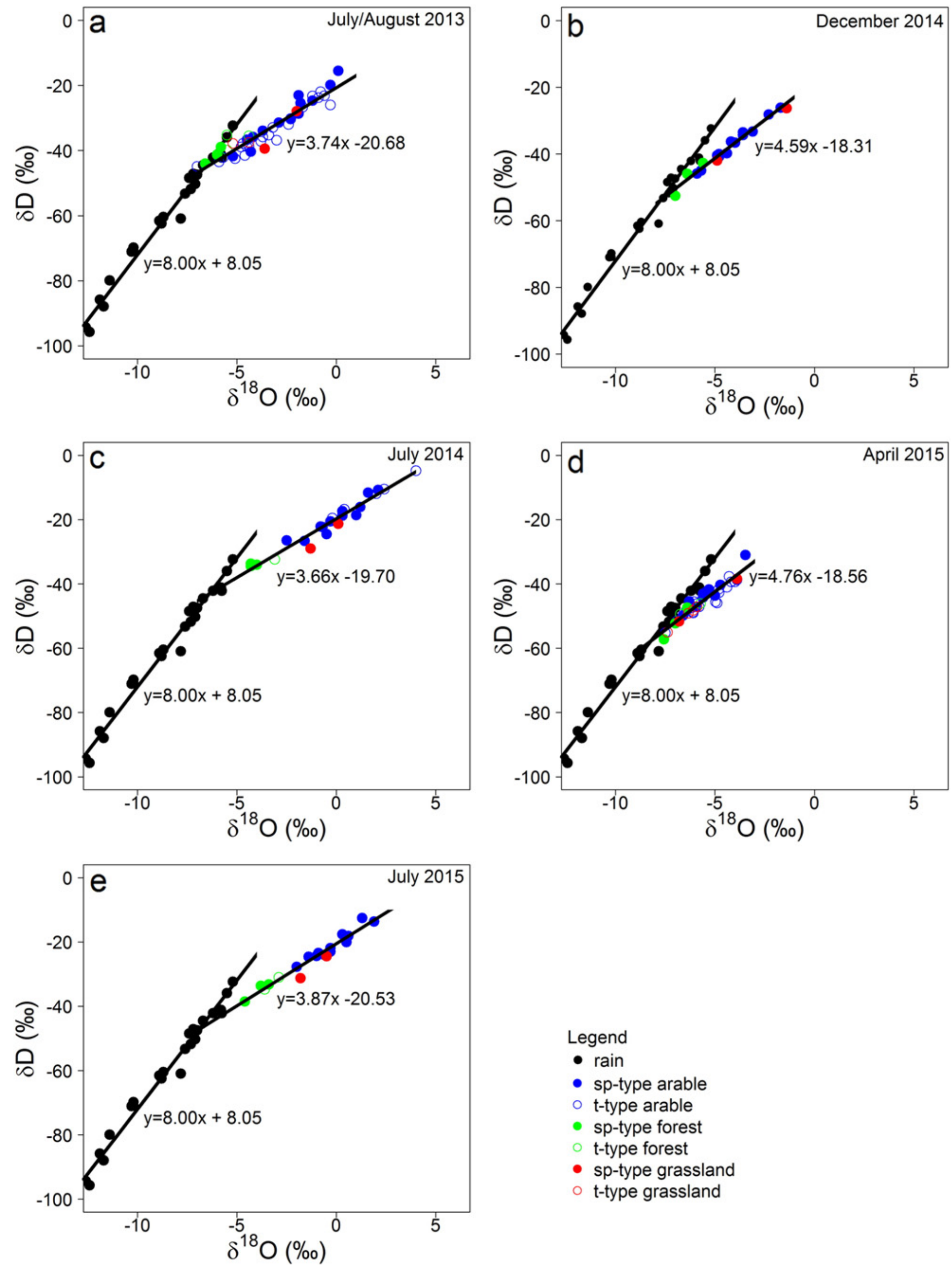

Fig. 4. Bi-plots of δD vs. $\delta^{18}O$ (in ‰) of kettle hole water from July/August 2013 (n = 45) (a), December 2014 (n = 19) (b), July 2014 (n = 23) (c), April 2015 (n = 42) (d) and July 2015 (n = 20) (e). Black solid circles depict rain water sampled monthly from August 2013 to July 2015. Two snow samples from winters 2014 and 2015 were also included in the regression line of the local meteoric water line (black solid line through rain water samples), but not shown because they were very depleted in the heavy isotopes.

groundwater or interflow, and suggests a mean kettle hole water residence time of about 5 years.

The calculated evaporative loss (*f*) values varied by the year sampled and kettle hole hydroperiod and land use. The t-type arable kettle holes had the greatest $\delta^{18}O$ and δD values (Table SI7) and the corresponding evaporative loss *f* averaged 56% in July 2014 (Table 1), which was higher compared to sp-type kettle holes (mean of 38%), although the difference was not significant. However, there were values of *f* that greatly exceeded the mean, for example, for two t-type and two sp-type kettle holes *f* was 60%, and for one t-type kettle hole in 2014 *f* was 75%, furthermore, some kettle holes were dry at the time of sampling indicating that rates for some kettle holes might have been higher. For example, in the 2015 growing season, only sp-type kettle holes could be sampled except for two t-type forests kettle hole. The sp-type kettle hole *f* estimates (mean of 23%) in arable land sampled in 2013 was significantly lower ($p < 0.01$) than the 2014–2015 growing season campaigns. Forest kettle holes were least affected by evaporation with $f < 20\%$, which was significantly lower compared to that of arable kettle holes ($p < 0.01$). The number of grassland kettle holes was too low for reporting representative values.

3.3. Surface water chemistry data

In-situ surface water parameters (pH, O_2, electrical conductivity) measured in the 2014 growing season were consistently lower for forest sp-type kettle holes compared to arable sp-type kettle holes (Table 2). Forest kettle holes also had lower concentrations (mg/l) of Cl^-, SO_4^{2-}, Ca, K, Mg, Na, but dissolved total phosphorous (DTP) and Si concentrations were both greater in forest kettle holes compared to arable kettle holes, but the difference was not significant. Furthermore, we found O_2

Table 1
Calculated average evaporative losses (f) ± SE (in %) for kettle holes.

Land-use	Hydroperiod	July/August 2013 (%)	July 2014 (%)	July 2015 (%)	April–July 2015 (%)
Arable	All	20 ± 2[a] (n = 35)	43 ± 4 (n = 17)	39 ± 2 (n = 13)	33 ± 2 (n = 13)
	t-Type	17 ± 2 (n = 22)	56 ± 8 (n = 5)	n.a.	n.a.
	sp-Type	23 ± 3 (n = 13)	38 ± 4 (n = 12)	39 ± 2 (n = 13)	33 ± 2 (n = 13)
Grassland	All	14 ± 4 (n = 4)	29 ± 8 (n = 2)	28 ± 5 (n = 2)	23 ± 3 (n = 2)
	t-Type	10 ± 1 (n = 2)	n.a.	n.a.	n.a.
	sp-Type	19 ± 7 (n = 2)	29 ± 8 (n = 2)	28 ± 5 (n = 2)	23 ± 3 (n = 2)
Forest	All	7 ± 2 (n = 6)	12 ± 2 (n = 4)	16 ± 5 (n = 5)	16 ± 1 (n = 5)
	t-Type	10 ± 2 (n = 3)	15 (n = 1)	18 ± 2 (n = 2)	16 ± 2 (n = 2)
	sp-Type	5 ± 1 (n = 3)	11 ± 0 (n = 3)	15 ± 2 (n = 3)	16 ± 1 (n = 3)

[a] Calculated f values after Eq. (1) represent mean values between f obtained each by $\delta^{18}O$ and δD.

to be significantly lower in forest kettle holes ($p < 0.06$). The concentrations of Cl^-, SO_4^{2-}, Ca, K, Mg, Na and Si in surface water from t-type kettle holes were consistently greater, but not significantly. Temporarily water-filled kettle holes had on average an electric conductivity that was significantly greater by 224 μs/cm than that of sp-type kettle holes ($p < 0.05$) and higher O_2 levels ($p < 0.06$). However, neither the electric conductivity, nor O_2 showed a correlation between with f for 2014. Instead, using all 23 sampled kettle holes in 2014, we found slight positive correlations between f and concentrations of Cl^- ($r^2 = 0.18$, $p < 0.05$), K ($r^2 = 0.2$, $p < 0.05$), Mg ($r^2 = 0.14$, $p < 0.05$) and a slight negative correlation with P ($r^2 = 0.18$, $p < 0.05$).

3.4. Agglomerative clustering

We performed an agglomerative clustering of surface sediment data ($\delta^{13}C$, $\delta^{15}N$, C:N ratio) to test whether kettle holes are distinguishable by their OM biogeochemistry. The agglomerative clustering yielded five different clusters with an agglomerative coefficient of 0.81 (Fig. 5). The clusters clearly separated kettle holes by hydroperiod (sp-type and t-type) and land-use (arable vs. forest). $\delta^{15}N$ was the core driver among the dataset, followed by C:N ratios. Clusters (C) C5 through C3, and a branch of C2 represent primarily t-type kettle holes. Cluster 5 (C5) is dominated by kettle hole sediments depleted in the heavy isotope ^{15}N, and consists primarily of forest kettle holes and one sp-type arable kettle hole. C4 represents one sp-type kettle hole that was classified by itself because the sediments had a high $\delta^{15}N$ value of 5.6‰, but low C:N ratio of 4:8. C3 consists of t-type kettle holes (4 arable, 1 forest) that have a greater $\delta^{15}N$ values than C4. C2 represents primarily t-type kettle holes (24), although one branch within C2 clusters near a branch of C1. C1 comprises of 14 kettle holes with a relatively low mean $\delta^{15}N$ of 1.5‰ and was dominated by sp-type kettle holes (n = 9). Grassland kettle holes clustered together with arable kettle holes from C1 and C2.

4. Discussion

We observed isotopic patterns in kettle hole sediment OM that are clearly related to the surrounding land-use and hydroperiod. Surface sediments were impacted the most by land management, while deeper sediment isotopic values and C:N ratios were closely related to the hydroperiod. The shallow ground water dynamics and evaporation were dominant hydrological processes that have potential feedbacks on OM contributions and environmental conditions. In the following, we discuss how the two primary drivers, hydroperiod and land-use, contribute to kettle hole sediment biogeochemistry and how we can use water isotope data to elucidate the development of the kettle hole water balance.

4.1. Surface sediments

For surface sediments, we found significant differences in isotopic composition between two core groups: forests and agriculture including grasslands. Differences due to land-use for all kettle holes were largely driven by $\delta^{15}N$ values. This pattern was especially strong in kettle holes in arable fields between hydroperiod types (Fig. 2a). Thus, we infer that activities in arable sites interact with the biotic and abiotic processes associated with hydroperiod to drive sediment C and N biogeochemistry. Previously, we found land use and management to have a profound effect on terrestrial biogeochemistry at our site (Nitzsche et al., 2016), most of which is related to management of crop fields.

Land management directly affects sediment biogeochemistry through OM source input. Slurry (organic fertilizer derived from animal manure) application is used widely in the study region, especially in the SE (Nitzsche et al., 2016) as confirmed by the spatial autocorrelation of $\delta^{15}N$ of surface sediments from arable kettle holes that we observe. This leads to the input of isotopically enriched OM and nutrients ultimately derived from slurry into kettle holes. Indirectly, nutrient run-off can cause eutrophication leading to seasonal anoxia in kettle holes, a phenomenon especially evident in sp-type kettle holes that can result in potential shifts in the isotopic signature of sediments. A seasonally anoxic water column reduces microbial degradation rate in general and favors anaerobic degradation, which can lead to no changes in $\delta^{15}N$ or a relative depletion of ^{15}N in the remaining OM (Lehmann et al., 2002; Menzel et al., 2013), possibly explaining why we observe lower $\delta^{15}N$ in surface sediments of sp-type kettle holes. On the other hand, seasonal anoxia can lead to greater denitrification, which is associated with enrichment of ^{15}N in the remaining dissolved nitrate (Teranes and Bernasconi, 2000), a process possible in sp-type kettle holes. Though we did not measure the $\delta^{15}N$ of nitrate, the low $\delta^{15}N$ in surface

Table 2
Elemental concentrations (mg/l) and pH, O_2 and elec. Conductivity of kettle hole water sampled in July 2014.

Land-use	Hydroperiod	pH	O_2 (mg/l)	Elec. cond. (μs/cm)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	P (mg/l)	Si (mg/l)
Arable	All (n = 17)	7.8 ± 0.2	5.9 ± 1.1	400 ± 41	23.6 ± 3.9	5.6 ± 1.7	52.3 ± 5.6	20.4 ± 2.7	10.4 ± 1.3	12.5 ± 2.1	0.4 ± 0.1	4.3 ± 0.9
	t-Type (n = 5)	7.6 ± 0.3	6.1 ± 2.9	513 ± 77	31.2 ± 8.0	5.4 ± 2.2	60.0 ± 7.4	26.5 ± 4.2	12.4 ± 2.9	15.3 ± 4.3	0.5 ± 0.2	7.4 ± 1.1
	sp-Type (n = 12)	7.9 ± 0.2	5.8 ± 1.1	353 ± 44	20.4 ± 4.3	5.7 ± 2.2	49.1 ± 7.2	17.8 ± 3.3	9.6 ± 1.4	11.3 ± 2.4	0.4 ± 0.1	3.0 ± 1.0
Grassland	sp-Type (n = 2)	8.2 ± 1.1	5.5 ± 5.2	249 ± 31	6.9 ± 2.4	1.6 ± 1.3	38.4 ± 14.5	11.0 ± 3.8	5.9 ± 0.2	7.2 ± 1.4	0.2 ± 0.1	0.6 ± 0.1
Forest	All (n = 4)	6.9 ± 0.2	1.3 ± 0.6	404 ± 124	10.2 ± 4.8	5.1 ± 2.2	57.2 ± 33.1	11.2 ± 1.2	6.1 ± 2.7	5.7 ± 2.3	1.1 ± 0.5	5.8 ± 1.8
	t-Type (n = 1)	7.5	3.0	755	24.4	10.7	153.3	12.1	13.4	12.3	0.4	10.3
	sp-Type (n = 3)	6.8 ± 0.2	0.7 ± 0.2	287 ± 60	5.5 ± 1.4	3.2 ± 1.7	25.1 ± 11.8	10.9 ± 1.6	3.7 ± 1.5	3.5 ± 0.6	1.3 ± 0.6	4.2 ± 1.4

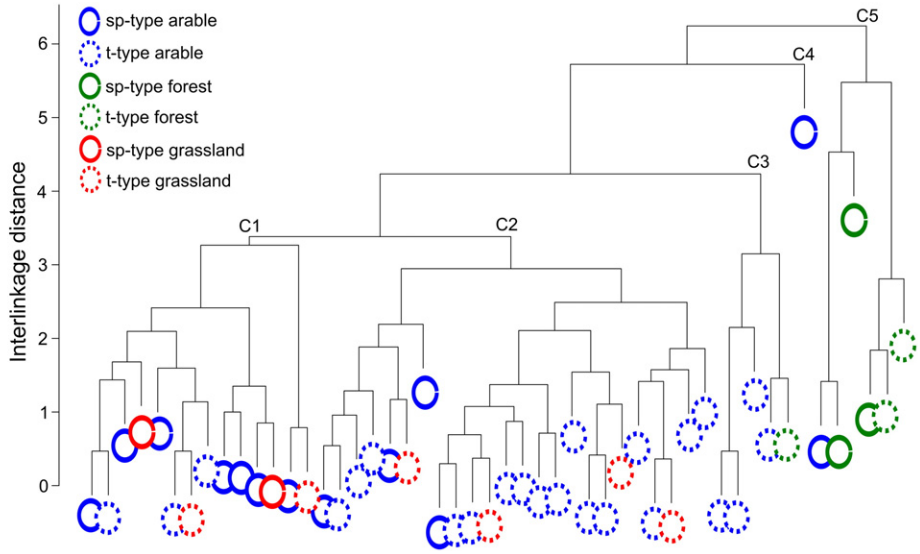

Fig. 5. Agglomerative clustering results of kettle hole surface sediment data (δ^{13}C, δ^{15}N, C:N).

sediments of sp-type kettle holes suggests that isotope fractionation due to denitrification is negligible.

Kettle holes within arable fields exhibit considerable variability among the hydroperiod types and for those that often fall dry or nearly dry, terrestrial plants are found mixed with communities that thrive under submerged or semi-submerged conditions (Nitzsche personal observation). The change in plant species associated with the hydroperiod (Euliss et al., 2004), is therefore an additional OM source that varies in isotopic composition (Badrian, 2015; Nitzsche et al., 2016) and can result in shifts in sediment isotopic composition. For example, *Phalaris arundinacea*, which was the most common plant at many kettle holes, has a δ^{15}N of 6.3 and a C:N ratio often >25 (Nitzsche et al., 2016). However, internal kettle hole OM sources, such as phytoplankton or other periphytic algae, may also contribute to the overall variability we observe in both hydroperiod kettle hole types. To obtain a deeper understanding of the biogeochemistry of surface sediments, more process-oriented research is needed that captures short-term inputs and losses.

Kettle holes present in forests and forest remnants had relatively low surface sediment δ^{15}N values (<0‰) and classified separately from the other kettle hole types, signifying C and N cycling processes that are different from the arable and grassland kettle holes. We infer that 1) anoxic conditions were particularly important in this land-use resulting in sediments more depleted in ^{15}N, and 2) the influx of beech litter (found in all forests at our site) was an allochthonous source of low δ^{15}N to the kettle holes. The reduction in O_2 may be caused by microbial decomposition of beech litter exhausting available O_2 as well as tree canopy cover preventing wind induced mixing of the water body. A decrease in O_2 concentration hampers microbial decomposition, and at suboxic conditions or in the absence of O_2, preferentially iron-bound P can be released from the sediment (Søndergaard et al., 2003; Spears et al., 2007); conditions that we observed in our forest kettle holes in July 2014. Beech leaf litter, a major OM contributor to forest kettle holes, has a δ^{15}N of -4.5 ± 0.4‰ at our site (Nitzsche et al., 2016) and, in addition to anoxic conditions, can help to explain the shift in sediment OM isotopic signal.

4.2. Deeper sediments

Based on the isotopic and C:N results, land management effects were not detectable within sediment OM from deeper depths. This concurs with previous research on kettle hole sediment stratigraphy within the same region which found low levels of heavy element concentrations derived from chemical fertilizers and pesticides in sediment cores (Kleeberg et al., 2016). Historically, intensified land management practices began near the end of the first half of the 20th century (Neyen, 2014), and given that our samples are constrained to the last 120 years (Kleeberg et al., 2016), management effects may be imprinted in the deeper sediment record from our study but at nominal levels.

The δ^{15}N and C:N of the t-type sediment OM from the deeper strata were significantly different from sp-type kettle holes pointing to potentially distinct environmental conditions that may affect decomposition. In the absence of large contributions of OM resulting from land management, we infer that internal cycling from microbes drives these patterns (Kramer et al., 2003; Paul and Clark, 1996). Microbes preferentially utilize the lighter isotopes ^{12}C and ^{14}N during decomposition increasing the stable isotope values of the remaining OM (Dijkstra et al., 2008). Microbial decomposition may be enhanced during longer dry periods, expected for the t-type kettle holes, as oxygen availability is high, especially in the surface near parts of the sediment (Boon, 2006; Reverey et al., 2016; Weise et al., 2016). The pattern in δ^{15}N vs. C:N suggests that the environmental conditions in the t-type kettle holes such as variations of aeration and temperature (Johnson et al., 2004) during dry-wet cycles contribute to stronger OM turnover (Hulthe et al., 1998; Mikha et al., 2005). The analyses we present in this study is, however, limited by our sampling design in that we did not perform a complete stratigraphic analysis such as Kleeberg et al., 2016, and further research that includes dating will add certainty to the inferences we draw here.

Interestingly, the δ^{15}N values of the sediments in t-type kettle holes drive the curve of the relationship between δ^{15}N and C:N (Fig. 2b). Lake sediment studies have found a similar trend but with depth (e.g. Esmeijer-Liu et al., 2012), and the relation between soil δ^{15}N and C:N is depicted as linear (Craine et al., 2015). Our data are novel in that and we find this pattern across a landscape (i.e., not a single kettle hole) and across different hydroperiod types. We hypothesize that OM samples in which the C:N values remained approximately constant (C:N < 7) experienced the recycling of OM within microbial communities (i.e., maintaining metabolic stoichiometry) while the isotopic signature increased with the degree of recycling. This pattern can also be observed in the data of Craine et al. (2015). The curvature in the relationship may, therefore, indicate a threshold at which new inputs are restricted to microbial communities; for example, the stabilization of OM via organo-mineral associations has been shown to potentially preserve OM from microbial decomposition (Lalonde et al., 2012; Vogel et al., 2014).

Deeper layer sediment OM C:N ratios were often >15 and the layers contained peat. These buried organic horizons are clearly protected from complete decomposition and much of the material collected in these layers still appeared plant-like. This is supported by lower $\delta^{15}N$ values and higher C:N ratios in the deeper sediment horizons of the t-type kettle holes (Fig. 3), indicating less microbial processing downward, possibly because the terrestrial OM was quickly buried by eroded soil particles (Frielinghaus and Vahrson, 1998; Kleeberg et al., 2016). The $\delta^{15}N$ might also be low because of atmospheric deposition. Atmospheric N isotopic composition has been becoming depleted in the heavy isotope over time due to anthropogenic emissions (Hastings et al., 2009; Holtgrieve et al., 2011). Wet deposition with low $\delta^{15}N$ in nitrate and ammonium was suggested as a potential impact on peat layers in Northern Finland leading to more ^{15}N depleted isotope values toward the surface (Esmeijer-Liu et al., 2012). However, in the deeper sediments present in our study the opposite trend occurs in which $\delta^{15}N$ values are lower in the deepest sediments (where we would expect higher values if deposition was important) suggesting that wet deposition has little to no effect on the deeper sediment OM.

4.3. Kettle hole hydrology

Overall, we found that the kettle holes of different land-use types and hydroperiod fell along an local enrichment line (LEL). Thus, the kettle holes are reflecting a similar source water and climate response (e.g. relative humidity, potential evaporation), confirming the findings of Thomas et al. (2012) regarding minor climate variability in the region. We also captured strong intra-annual patterns during our study. For example, winter 2012/2013 was characterized by substantial snowfall and temperatures below freezing resulting in snow accumulation on adjacent fields until the beginning of April. A substantial volume of meltwater relatively depleted in ^{18}O contributed to the isotopic source of 2013 sampled kettle holes via infiltration from the surrounding soil. This affects not only the isotopic signal of the source water but also the evaporation patterns by increasing the water volume and subsequently increase heat storage capacity (Abtew and Melesse, 2012) reducing the effect of evaporative fractionation. Thus, the initial conditions (isotopic composition and water volume) of the kettle hole, as predicated by snow levels and snowmelt contributions, constrain evaporative loss.

We used the isotopic enrichment of water in each kettle hole as a proxy for the fraction of water evaporated for two periods (winter–summer) over three years. We captured the onset of evaporation in the kettle holes between our April and June sampling, thus constraining the time point at which evaporation impacts the isotopic signature of water, and presumably, the water budget. We found that evaporative loss could be as little as 7% to as much as 75% based on the year, season, and land-use type. From a landscape perspective (i.e., estimates based on slopes of evaporative enrichment lines), we estimate that kettle holes experience an evaporative loss of 28%. We also found electric conductivity, Cl^-, Ca, Na, K, Mg and Si concentrations to be higher in t-type kettle holes, thus confirming evaporation is more dominant in t-type than in sp-type kettle holes. Evaporative loss f, explained 14 to 20% of the variation in Cl^-, K, Mg and P concentrations in 2014. However, these correlations indicate that internal biogeochemical processes, such as carbonate precipitation, leaching and re-dissolution of salts during wet-dry cycles and transpiration, may have greater importance in the cycling of these elements at our site (Berthold et al., 2004; Dogramaci et al., 2015).

While we found evaporation rates can be relatively high, evaporation alone cannot explain the complete dry-out of some of the kettle holes. Lateral groundwater flow to the wet margins of the water body is a dominant water loss for wetlands (Ferone and Devito, 2004; Gerke et al., 2010; Hayashi et al., 1998). For instance, Hayashi et al. (1998) found that shallow groundwater lateral flow could explain 75% of the total water loss. The magnitude of this flow can even be enhanced when the water is taken up by plants from the vegetation belt and the crop fields, for transpiration (Hayashi et al., 1998; van der Kamp and Hayashi, 2009; Woo and Rowsell, 1993). Since both lateral groundwater flow and evaporation contribute to kettle hole water loss, we can state that most of these kettle holes are partially-closed to open systems. Similar shallow water bodies have been found to be in contact with the shallow groundwater over the year and either discharge or recharge groundwater depending on the season (Euliss et al., 2004; Heagle et al., 2013; van der Kamp and Hayashi, 2009).

At our site, water transfer between the kettle hole and surrounding soil is strong particularly during the dormant season in which 20% kettle hole water volume is refilled. However, contact to the shallow groundwater can weaken during the growing season, in which case evaporation from the kettle hole water body and transpiration of plants in the surrounding vegetation belt most likely dominate kettle hole water loss. T-type kettle holes, in particular, might have a stronger linkage to the groundwater system. In this case, when the groundwater level decreases, the t-type kettle hole water table decreases concomitantly, and when the groundwater level rises again, so does the water table in these kettle hole types. Future research of kettle hole hydrology will need to address groundwater connectivity as well as vegetation transpiration losses in the late summer season to fully understand the kettle hole water budget.

4.4. Links between kettle hole biogeochemistry, hydroperiod, and land-use

Kettle holes lie at the nexus between land-use, hydrology, and aquatic-terrestrial ecology. Understanding the role of each over time is requisite to characterizing their biogeochemical function across this landscape. Our data show 1) how land-use can influence kettle hole biogeochemistry through actions such as slurry application and erosion, 2) how hydrology and plant communities interact resulting in peat layers; and 3) how the hydroperiod regulates important environmental conditions such as oxygen availability triggering aerobic decomposition.

Essential to characterizing kettle hole biogeochemistry is the observation that t-type kettle holes are fundamentally different than sp-type. However, assigning a kettle hole to one hydroperiod class or another is very subjective given the length of time kettle hole sediments integrate. In order to test for long-term differences in kettle hole biogeochemistry, we performed a data driven classification on surface sediments that was not constrained by our original observational classification. The clustering analysis revealed that kettle hole biogeochemistry is different for those which are more likely to be water filled or not over time. Furthermore, we are not surprised by the range in hydroperiod implicated by the clustering results given that the sediments are integrating shifts in hydroperiod over a relatively long time span. To the contrary, the fact that we do see a separation in the sediments that correspond to our hydroperiod classification provides strong evidence of the important role hydroperiod plays as a driver of kettle hole biogeochemistry. Future studies may build on such a classification to include deeper sediments as well.

5. Conclusion

We have provided evidence that kettle hole hydroperiod is a predominant driver of OM turnover and biogeochemistry. By analyzing shallow and deep sediment we captured both current and past conditions. We recognize that our research strategy to capture many different types of kettle holes across a large spatial extent does not provide the temporal resolution to capture past conditions with high accuracy; however, the findings and patterns from our study are robust and highly relevant to kettle hole biogeochemistry. The surface sediments reflect recent OM inputs and short-term processes, including management and land-use effects, while deeper sediments record different longer-term patterns of hydroperiod and the degree to which OM is processed. We found that kettle holes currently deemed sp-type, in the past also experienced prolonged drying and possible terrestrial plant encroachment that developed into peat layers over time pointing to the feedbacks between hydroperiod and plant communities. Interestingly, the deeper layer sediments from the t-type kettle holes did not show an increase in decomposition relative to the sp-type kettle holes. The change in environmental conditions (i.e., aeration/redox potential changes) during past dry periods may not have shifted enough to induce significant decomposition of the peat layers in the t-type kettle holes. Thus, the potential for kettle holes to sequester carbon remains high even under changing environmental conditions. We found kettle holes within the t-type or sp-type hydroperiod to exhibit similar hydrological patterns over the year. Evaporation was greatest in the t-type kettle holes on average, which, along with lateral flow, contributes to changes in redox and potential plant encroachment. The initial hydrological conditions are determined by larger climate controls (e.g., flood or drought) and winter precipitation, which modulate the role of lateral groundwater flow and evaporation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.09.003.

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