Author´s response (HESS-2016-374)

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1. Point-by-point response to review 1

1) Generally speaking, the structure of this manuscript is more like a hydrogeological survey report or groundwater resource summary, not a research article. Why did you do this study?

We are sorry that the reviewer got this impression but disagree with the reviewers rating of the MS. Indeed, the paper presents an in-depth and thorough analysis of the subsurface. This requires among others also a hydrogeological survey. However, we claim that this is by far not enough to reach the goals of our study:

- Understand the hydraulic and biogeochemical functioning of the subsurface in a so far not adequately addressed setting (thin-bedded carbonate-siliciclastic aquifer bedrock) provided by the Hainich CZE.
- Explore the links and feedbacks between surface and subsurface.
- Demonstrate that a holistic approach that considers the surface and subsurface factors is indispensable for the mechanistic understanding of the coupling of surface and subsurface compartments, fluid dynamics, biogeochemical element cycling and ecology in the critical zone.

The extent to which we have analyzed the subsurface goes far beyond a classical hydrogeological survey for two major reasons:

(1) We consider and reconstruct all subsurface compartments, i.e., the soils sensu strictu, the unsaturated and the saturated bedrock in depth and combine it with the actual type of land management.

(2) We present and put in action a novel and comprehensive multi-method approach that combines geological, hydrogeological, hydrogeochemical, pedological, structural geological, mineralogical, and geophysical tools and methods to assess the effective hydraulic and transport structures of the subsurface compartment and to explain the state and evolution of the groundwater chemistry.

With this multi-method approach, we provide

- a detailed aquifer stratigraphy for understanding horizontal and vertical connectivity
- a geological and pedological mapping of aquifer outcrop areas for the localization of preferential infiltration zones, as vertical infiltration is highly minimized by argillaceous confining beds
- a determination of soil hydraulic conductivities and grain size distributions/soil texture properties
- a mapping of the types of land management as well as of relief landforms/slope positions
- the analysis of groundwater quality in different slope positions and aquifer storeys by means of multivariate statistics

We further stress the point that – based on our multi-method approach - the actual spatial distribution pattern of the hydrochemistry observed in the different groundwater “clusters” is controlled by the residence time and the interactions of both (I) the infiltrating precipitation and seepage with the interfaces in soils and (II) unsaturated and saturated bedrock formations.We are convinced that this novel, comprehensive and synoptic approach is indispensable for interpreting groundwater quality in essentially all groundwater systems and that without this multi-method-approach these quite distinct and synoptic results would not have been reached. Although there are a small number of published examples characterizing aquifer vulnerability/human impact, none of these studies characterizes pristine groundwater quality in comparison with aquifer stratigraphy, soil hydraulic properties and land management in a hillslope groundwater catchment. We revised the manuscript to make theses aims clearer to the reader.

What scientific questions are answered in this paper?

The guiding scientific question is: What are the essential and necessary information to be gathered in order to understand the factors that control the hydraulic and biogeochemical functioning of the subsurface and to explore the links and feedbacks between surface and subsurface as a function of land use. An additional aspect we aimed for to address is the specific setting provided by the Hainich CZE. It represents a widely distributed, yet scarcely described and in previous publications not adequately addressed setting of thin-bedded mixed carbonate-siliciclastic strata in hillslope terrains. Theses settings provide groundwater reservoirs with importance as drinking water supply and a significant geographical distribution not only in Europe (e g. "Germanic Triassic", Khuff formation (Middle East)).

The author listed three aims in the introduction part, but it seems the authors are trying to address so many issues in one manuscript, and bring difficulties for readers to follow up. The first aim is obviously not a science question but more like a geological background by the survey. The second and third aims are significantly different. Also, it's very important to highlight the research purposes and the novelties in the title, abstract and conclusion parts. Therefore, the detail demonstration of the connections between these two aims is highly expected. I actually suggest the authors to focus on one aim only in the paper.

Once again, we are sorry that the reviewer got this impression. We tried to counteract that by rearranging the manuscript to clarify why we approached the scientific questions in that way. Of course, the multi-method-approach has many aspects. In the revised paper we emphasized the need and explained in more detail the relations and links of the different aspects in view of the aims of the MS. For example, we present the relationships between surface and subsurface influences on hydrogeochemistry in the introduction, discussion and conclusion chapters. We substantiated with our dataset how close groundwater quality is linked to the recharge area characteristics.

We also clarified the goals and research questions in the introduction. The paragraph now reads (page 3, line 28 ff.):
The goals of our study are to (1) understand the hydrogeological and biogeochemical functioning of the subsurface in a so far not adequately addressed setting provided by the Hainich CZE, (2) explore the links and feedbacks between surface and subsurface, and (3) to demonstrate that a holistic multi-method-approach, that considers the surface and subsurface factors, is indispensable for the mechanistic understanding of the coupling of surface and subsurface compartments, fluid dynamics, biogeochemical element cycling and ecology in the critical zone.
To reach these goals, the following research questions are answered:
(I) How is the critical zone comprised and connected in the hillslope setting of a thin-bedded, mixed carbonate/siliciclastic succession? (II) How do spatial arrangement, particularly outcrop patterns and geostructural links (karst features like caprock sinkhole lineaments) impact compartment connection, (intrinsic vulnerability) and groundwater quality? Do groundwater quality in contrasting summit/midslope and footslope wells reflects surface influences?" And finally: (III) what are the main control parameters for groundwater quality? What are the reasons for particular hydrogeochemical conditions within the multi-storey/hillslope aquifer system?

2) Because it is a research article instead of report, the authors are expected to explain why Hainich CZE is important and interesting to study. Are there any special geological characteristics? I'm not familiar to the hydrogeological setting in Germany, but I assume that carbonate-rock structures are widely distributed. Is Hainich CZE a typical karst aquifer in Germany? All of those are necessary to be fully illustrated in the manuscript.

We agree and have changed the MS accordingly. We introduced a section on the Hainich CZE within the introduction which illustrates its importance and relevance to the greater scientific community. This section now reads as follows (page 4, line 23 ff.):

The Hainich CZE is a multifarious environmental laboratory for multiscale geo- and bioscience research, as
(1) both, the so scarcely described geological setting (alternations of marine thin-bedded limestones and marlstones) and the hillslope relief/sloping aquifer configuration are common and widely distributed
(2) the monitoring plot and well transect (see Küsel et al., 2016) provides a unique access to the multi-layered aquifer system of the common setting
(3) it represents a rare anthropogenically low-impacted (non-contaminated) cultural region in central Europe with a very extensive type of land management during the last centuries, allowing the investigation of natural (surface) signal transformation in the pristine aquifer systems and of ecosystem functioning
(4) the geostructural and lithological properties were found to be predictable and thus enable the tracking of biogeochemically cycling and quality development within single aquifer storeys
(5) the Hainich it is a regionally important groundwater recharge area in Thuringia (Fig. 1) and an example of peripheral groundwater supply for water deficient sedimentary basins (Rau and Unger, 1997; Hiekel, 2004)

We have exemplified the details of the geological setting, which is widespread and common, but scarcely described in literature, in more detail. We added important information on the geological characteristics. The paragraph now reads as follows (page 4, line 2 ff.):

The Hainich Criticial Zone Exploratory covers 430 km² of a hillslope subcatchment of the Unstrut river in northwestern Thuringia, Central Germany (Fig. 1). It is bounded by the recipient Unstrut river and the distribution area of the Upper Muschelkalk formations. The Hainich represents a NW-SE orientated geological anticline that is developed topographically as a low mountain range with a steep western, and a moderately inclined eastern flank (Jordan and Weder, 1995). The study area is located at the eastern flank of the Hainich hillslope, thtat shows a geostructural buildup with NE dipping strata in the direction of the syncline of Mühlhausen-Bad Langensalza (Kaiser, 1905; König, 1930; Patzelt, 1998; Wätzel, 2007). A tectonical uplift, faulting and tilting of strata is assumed for the Late Cretaceous in analogy to the surrounding horst structures Thüringer Wald (in the S) and Harz (in the N; compare to Voigt et al., 2004; Kley and Voigt, 2008). The outcropping strata in the study area comprise sedimentary rocks (Middle/Upper Muschelkalk and Lower Keuper - subgroups of the Middle Triassic). According to the German stratigraphy (Deutsche Stratigraphische Kommission, 2002), the Diemel formation (Middle Muschelkalk), Trochitenkalk, Meissner, and Warburg formation (Upper Muschelkalk) and the Erfurt formation (Lower Keuper) outcrop in the study area. The Upper Muschelkalk subgroup, which hosts the target aquifers of the Hainich CZE, is organized by bio- and lithostratigraphic marker beds (Ockert and Rein, 2000; Kostic and Aigner, 2004). Previous studies hydrostratigraphically organize the Upper Muschelkalk subgroups into a Hainich Transect Lower Aquifer Assemblage (HTL) and a Hainich Transect Upper Aquifer Assemblage (HTU; Küsel et al., 2016).The area belongs to the Cfb climate region (C: warm temperate, f: fully humid, b: warm summer) according to the Köppen-Geiger classification (Kottek et al., 2006) and exhibits a leeward decline in areal precipitation and increasing mean air temperature

from the Hainich ridge (> 900 mm/y; 7.5-8 °C) to the Unstrut valley (< 600 mm/y; 9-9.5 °C; long term average 1970-2010, TLUG, 2016). The intensively investigated study area is limited to a 29 km^2-subarea of the Hainich CZE, that surrounds the soil and groundwater monitoring transect (Küsel et al., 2016).

3) The authors used more than half of the words in this manuscript to introduce and describe the field works and data collections. Again, I would recommend the authors to focus on the discussion of statistical analysis (PCA and cluster analysis) of geochemistry data, and address the effect of karstification and hydrological stratigraphy on groundwater quality/hydrogeochemistry (section 4.2).

As we introduced a new and contrasting aquifer stratigraphy of a common, but barely addressed setting, we decided for a comprehensive method and results presentation. Nevertheless, we summarized and abbreviated the site description and methods chapter (together 2742 words) and extended the results (2725 words) and discussion (4030 words). We agree that a focused discussion of groundwater quality is necessary. Thus, we extended the discussion of geochemical data in the discussion:

- In chapter 5.1.2 (page 12, line 14 ff.), groundwater chemistry was discussed in the context of the aquifer configuration and groundwater development.
- Groundwater flow directions (5.2.5, page 15, line 5 ff.) are interpreted by means of hydrogeochemistry, karst phenomena and the knowledge of local geology.
- Finally the provenance of groundwater from different hierarchical clusters was interpreted (5.3, page 15, line 40 ff.).

4) The authors mentioned the effects of fault zones on groundwater chemistry with dissolution-enlarged fractures. Hydraulic conductivity through the faults in karst aquifer can be larger in several magnitudes, due to the dissolution of carbonate-rock dissolution. Does dissolution play a more important role rather than faults? More explanations are expected.

The study area is characterized by old NW-SE orientated fracture systems that are described in regional literature as preferential flow paths. This fracture system is now described in the following text passages:

Second order relief elements are also the two NW-SE oriented lineaments of more than eighty caprock sinkholes (which are passive karst phenomena) with up to 80 m in diameter (page 7, line 30 ff.).

Two contact springs in the recharge area (Grauröder Quelle, Ihlefeldquelle) and two karst springs in the discharge area (Kainspring, Melchiorbrunnen, coupled to NW-SE oriented fault zones, …(page 10, line 26 ff.).

As caprock sinkholes are arranged in lineaments (Fig. 2 A) parallel to regionally known fault orientations, it is very likely that they are coupled to the penetration of surface/subsurface water at fracture zones (compare to: Smart and Hobbs, 1986; Worthington, 1999; Klimchouk, 2005), that promote preferential recharge (Smart and Hobbs, 1986; Suschka, 2007) (page 13, line 20 ff.).

Our descriptions of dissolution-enlarged fractures are limited to our drill cores material which had been recovered from wells which had not been drilled directly into fault zones. Our assumption that fractured/more permeable rocks are predisposed to a stronger karstification, resulting in a greater overall permeability in fault/fracture zones was added to the discussion chapter 5.2.5 and reads as follows (page 15, line 19 ff.):

Zones with enhanced fracture indices (fractures/m drill core) in well sites H3 as well as consistent Fe/Mn-oxide fracture

walls in all aquifer storeys of this site points to a quick and cross-formational descending flow of oxygenated groundwater (thus with low Fe/Mn mobility; Hem, 1985) via vertical master joints (term: Dreybrodt, 1988; Ford and Williams, 2007) close to potential fracture zones. This is supported by higher concentrations in Na+, K+, NO3-, Cl- and TOC in the deeper site of H3 compared to the shallower well of this site, related to agriculture and fertilizing (Matthess, 1994; Kunkel et al., 2004). Cross-formational descending flow in shattered or fractured rocks is assumed to take place in fracture zones (Worthington, 1999; Goldscheider & Drew, 2007), tracked by lineaments of caprock sinkholes (Mempel, 1939; Hoppe, 1962; Smart and Hobbs, 1986; Jordan and Weder, 1995).

Fracture zone-related cross-formational flow is also discussed in chapter 5.3 (page 16, line 16):
Oxygenated groundwater in both aquifer storeys (thus with low Fe/Mn mobility; Hem, 1985) and a high degree in rock fracturing and fracture mineralization with Fe-/Mn-oxide minerals (aquifer storeys moM-9/8/7 and 6), point to a vertical penetration with near surface groundwater via fracture zones through all aquifer storeys. Enhanced concentrations in Na+, K^+, NO_3^-, Cl^- and TOC (Fig. 7) are likely related to agriculture and fertilizing (Matthess, 1994; Kunkel et al., 2004) around the sinkhole lineaments. As nitrate, which is generally derived from agricultural fertilizers (Agrawal et al., 1999; Jeong, 2001), is still present in the deep aquifer waters of site H3, vertical bypassing through master joints (term: Dreybrodt, 1988; Ford and Williams, 2007), must be faster than the denitrification process. Quick infiltration is here mostly related to the preferential sinkhole recharge, as the soils (Luvisol/Cambisol, both with low-conductive subsoils and a high degree in lateral soil interflow) in the outcrop zones bear only moderate to poor soil hydraulic conductivities. In general groundwater in the discharge of exceptionally highly conductive preferential recharge spots can reflect surface signals, even in stratified aquifer/aquitard successions. These zones are therefore suggested to be of uppermost importance for groundwater protection.

In our thin-bedded mixed carbonate-siliciclastic setting, karstification effects are not very distinct (in comparison with classical karst/unconfined karst). Karst/dissolution phenomena are limited to formations with very high limestone-marlstone ratio (here: Trochitenkalk-formation). Other parts of the stratigraphic succession may be regarded more or less as fracture aquifers. We highlighted this important information in the results. The paragraphs of chapter 4.3.1 and 4.3.2 are formulated as follows:

The 7 m thick Trochitenkalk formation (moTK) with thick (5 30 cm), gray, coarse bioclastic limestones (mainly rudstones with the rock-forming fossil Encrinus liliformis) forms a carbonate-rock-fracture aquifer with minor karstification (intrastratal karst according to Ford and Williams, 2007) (page 9, line 11 ff.).

Limestones in the Meissner formation are fracture aquifers and their rock matrices are predominantly composed of calcite and trace amounts of dolomite, quartz, illite and feldspar (page 9, line 25 ff.).

Flow paths are predominantly fractures and matrix porosity is lower than 5 % in all stratigraphic intervals. Although it is of karst-fracture type with partially solution-enlarged fractures, the karstification and the development of conduits is limited and concentrated at the formation´s very base (page 9, line 42 ff.).

The Meissner formation (moM) contains limestone-fracture aquifers which are interbedded marlstone-aquitards on the decimeter to meter scale. Limestones of this formation are almost exclusively fracture aquifers with very little matrix porosity, concentrated at certain thickly bedded limestone marker beds (page 10, line 5 ff.).

On the other hand, dual-permeability hydrological characteristics are commonly observed in karst aquifers. The authors should address some literature citations of flow properties in karst aquifer in the introduction.

We agree with the reviewer that dual-permeability flowpaths are typical for classical/massive karst sites. Obviously we failed to distinguish our thin-bedded carbonate-karst setting from classical karst sites. Thus, we highlighted these differences in the manuscript title, abstract and introduction.

Aquifer configuration and geostructural links control the groundwater quality in thin-bedded carbonate/siliciclastic alternations of the Hainich CZE, Central Germany (manuscript title)

This CZE represents a widely distributed, yet scarcely described setting of thin-bedded mixed carbonate-siliciclastic strata in hillslope terrains (page 2, line 8 ff.).

Here, the bedrock of fractured, mixed carbonate-/siliciclastic alternations represents a widely distributed, yet scarcely described geological setting (page 3, line 26 ff.).

Dissolution-related conduits are very limited and matrix porosities are very low (5 %). We added this information to the results (chapter 4.3.2):

Flow paths are predominantly fractures and matrix porosity is lower than 5 % in all stratigraphic intervals. Although it is of karst-fracture type with partially solution-enlarged fractures, the karstification and the development of conduits is limited and concentrated at the formation´s very base (page 9, line 42).

As groundwater flow properties are not in the scope of our study, we changed the title of the manuscript to:
Aquifer configuration and geostructural links… (manuscript title)

We do not agree with the reviewer, that literature citations of flow properties are necessary in the introduction, as it is not on-topic to the following aspects discussed within the introduction:

- Near surface groundwater quality is strongly related to the percolation of water through soils, the unsaturated zone and the aquifers Groundwater quality is hereby mainly controlled by bio/geochemical fluid-rock/soil interactions in these compartments (compare to page 3, line 2 ff.).
- A holistic investigation of both surface and subsurface is necessary for understanding groundwater quality. Although there are comprehensive studies published (i.e. Gleeson et al., 2009), these studies do not discuss pristine groundwater quality (compare to page 3, line 15 ff.).
- As a mixed carbonate-/siliciclastic setting, Hainich CZE represents a widely distributed, yet scarcely described geological setting (see page 3, line 26 ff.).

We thus described groundwater flow modes in the discussion. The paragraph now reads as follows (page 12, line 36 ff.):

Within the aquifer-aquitard-sandwich, fast conduit groundwater flow, which is typical for karstified carbonate rocks (Wong et al., 2012), likely takes place in the moTK-1 and partially in the moM-1 aquifer storeys, whereas slow diffusion in slightly fractured, thin aquifers beds is anticipated in the moM-2 to moM-9 aquifer storeys. Confined diffuse flow is considered

laminar and takes place in interparticle pores and fractures of dense limestones with low primary porosity (Smart and Hobbs, 1986). This results in the well oxygenated moTK-1 and moM-1 groundwaters and a significant oxygen consumption/deficiency (coupled to the mobility of Fe2+ and Mn2+-ions and the low mobility of NO3- and SO4- ions) in the moM-2 to 9 groundwater, resulting in completely different milieu conditions for the biogeochemical processes and for the life in the subsurface as well.

5) The authors might not have enough data, especially the historical data before the beginning of sampling. But it is interesting to see any trends of geochemistry data variation along time, with changes of land use type and anthropogenic factors.

As the fluctuations of groundwater levels and hydrogeochemical data is very dynamic and complicated (with respect to seasonality, rainstorm events and response times), we decided to present this issue in a second research article (in preparation). Nevertheless, we agree with the reviewer that a brief description of groundwater fluctuations is desirable and added a chapter (4.4.3) to the results (page 11, line 12 ff.). The chapter now reads:

4.4.3 Fluctuations of groundwater levels and quality

Groundwater levels are confined in footslope wells. In the wells of site H5, groundwater rises 30 m (H53), 50 m (H52) and 70 m (H51) higher than the base of the screen section. Fluctuations of groundwater levels in our monitoring wells range from 1-3 m in the hilltop recharge area (well site H13) to more than 25 m in the groundwater transit area (well site H5). The groundwater level fluctuations show a strong seasonality with annual highstands (March to April) and lowstands (October to December). Monitoring wells of different sites and screen depths differ in average concentrations of the major solutes. These spatial differences are generally higher than the seasonal fluctuations in the wells. An exception to these conditions are marked seasonal fluctuations of Ca^{2+} (monitoring well H31/41), Cl^{-} (H52/53), K^{+} (H41), Mg^{2+} (H41), Na^{+} (H31/41), Si^{4+} (H41) and SO_4^{2-} (H31/41).

And a discussion of the effect of contamination/pollution/human factors to data is desired.

Hainich CZE is a rare non-contaminated region in Central Europe without villages, waste disposal sites or industry within the groundwater recharge area. Like vulnerability studies (investigating the impact of potential anthropogenic hazards), we used comparable tools/methods for exploring soil hydraulic properties, aquifer configuration and land management. In contrast to "anthropogenic hazard studies", our focus lies on the reconstruction of the subsurface structure by utilizing pristine groundwater quality data.

Influences of land management on groundwater quality is now described in a separate chapter (5.2.3), that now reads as follows (page 14, line 19 ff.):

5.2.3 Influences of land management in the recharge area on groundwater quality

The forest areas as a source of groundwater from catchment-near summit/shoulder wells are confirmed by their aquifer outcrop areas (moTK-1, moM-1) within the managed (and partly unmanaged) forest. In contradiction, we detected potentially agriculture-related substances (NO_3^-, K^+, Cl^-) in the wells drilled to all aquifer storeys in midslope location wells (H31/41), although these groundwater types are recharged mainly within the forest (up to 96.5 % forest). These surface signals are interpreted to be related to the cropland and village areas within the preferential recharge zones with sinkhole lineaments. Anoxic groundwater in aquifers (moM8/9) partially recharged from outcrop areas with agricultural and village land use, are likely attributed to microbial oxygen depletion resulting from the degradation of organic carbon or oxidation

of inorganic electron donors. For shallow wells in valleys (H42/43/4S), lateral soil water inflow with high organic/fertilizer load towards the valley provide an alternative way for the enhancement of oxygen depletion. Much lower NO_3^-, K^+, Cl^- concentrations in the footslope wells (H52/53) are likely a consequence of the argillaceous caprocks that increase in thickness towards the footslope.

Moreover we added a new chapter that deals with the intrinsic vulnerability of the recharge area (5.4). It reads as follows (page 17, line 19 ff.):

5.4 Assessment of vulnerability factors

The configuration of the aquifer system in the hillslope setting also controls the groundwater resource vulnerability. With our multi-method investigation of the different subsurface compartments, we also revealed factors of the areas´ intrinsic vulnerability. Characteristics of intrinsic vulnerability are solely controlled by hydrogeological properties of the aquifer and overburden (Vrba and Zoporozec, 1994), and integrate the inaccessibility (i.e. by low-permeable cover strata) of the saturated zone and the attenuation capacity (retention, turnover) of the overburden (Adams and Foster, 1992).

The stacking of aquifers/aquitards, the coverage with caprocks and the lateral continuity of strata reduces the overall dominating disperse infiltration and, thus the intrinsic vulnerability. Threatening of single aquifer storeys or assemblages is predominantly controlled by fractures/faults (valleys) or karst phenomena bypassing the protective cover of soils and unsaturated zones (Fig. 8). A moderate degree of physical filtering by the narrow fractures, which are the predominant flow paths, is assumed. Also the claystone and marlstone interlayers bear a certain filtering of contaminants by retention. The preferential recharge/outcrop zones of the aquifer storeys are characterized by generally highest vulnerability. However, these zones, located in the summit to upper midslope of low mountain ranges, are mostly covered by forest. Generally, the summit position of outcrop zones of the main aquifer storey (moTK-1) lowers the risk for contamination, paradoxically, due to the thin soils that prevented lasting agricultural use and settlements. Further zones of higher vulnerability are located in the discharge of sinkhole lineaments or fracture zones that bypass surface water or drains directly into the aquifers. A mapping and structural investigation of these geostructural links will be recommended for (i.e.) proper dimensioning of drinking water protection zones. In comparison to classical karst sites (i.e. massive carbonates) with pronounced karst phenomena, (Doerfliger et al.,1999, Witowski et al., 2002), our portrayed setting shows an overall low to moderate vulnerability, that is locally elevated by inherent factors (outcrop zones) and inherited features (i.e. karstification of the underlying Middle Muschelkalk subgroup).

6) In the end of section 4.2, the authors classify three modes of subsurface water flow in the karst aquifer. I would say the lineaments of sinkholes are not necessarily due to flow through open faults. Is there a possibility that bedding parallel in either unconfined and confined aquifer can cause lineaments of sinkholes as well? Probably just track the faults/fracture zones from geological map/structure survey.

We agree with the reviewer that a proper definition of caprock sinkholes is necessary for the interpretation of fault related flow. The paragraphs concerning caprock sinkholes now read as follows:

Second order relief elements are also the two NW-SE oriented lineaments of more than eighty caprock sinkholes (which are passive karst phenomena) with up to 80 m in diameter. Caprock sinkholes are mostly exhibited on local ridges. A second and parallel lineament of three shallow elongated (uvala-like) karst depressions with a horizontal extent of up to 400 m crosses the lower Hainich hillslope (page 7, line 30 ff.)

The second route for preferential recharge is related to the lines of caprock sinkhole lineaments, which can be tracked over more than four kilometers in the midslope between transect locations H2/3 and H4. The origin of these sinkholes does not lie in the karstification of the Upper Muschelkalk strata itself, as the combination of aquifer fracture networks (tight conduits) and stabilizing, insoluble aquitard beds do not cause sufficient mass deficits that will allow hanging wall collapses. Here, caprock sinkholes are related to mass deficits by subrosion in the underlying evaporite rocks with gypsum and halite (Mempel, 1939; Malcher, 2014). As caprock sinkholes are arranged in lineaments (Fig. 2 A) parallel to regionally known fault orientations, it is very likely that they are coupled to the penetration of surface/subsurface water at fracture zones (compare to: Smart and Hobbs, 1986; Worthington, 1999; Klimchouk, 2005), that promote preferential recharge (Smart and Hobbs, 1986; Suschka, 2007). Although dissolution of soluble rocks is limited within the target aquifers of this study, it is reasonable, that collapse structures are accompanied by enhanced rock fracturing and permeability (page 13, line 15 ff.)

As the aquitard interbeds highly reduces vertical flow connections, outcrop zones of the aquifer storeys as well as caprock sinkholes act as important preferential infiltration pathways which are typical for hillslope recharge zones. Since caprock sinkholes remain dry, even directly after precipitation events, high infiltration rates can be assumed for these structures (page 15, line 8 ff.).

We also tracked the lines of sinkholes and displayed these lineaments in Figure 2A (page 31). These zones are also included into the input dataset of the recharge potential map (Fig. 8 page 37). Mapped caprock sinkholes and uvala-like depressions are orientated in the same direction of NW-NE striking faults and to the geological fold axis (Hainich ridge, respectively), we interpret these linear features as fracture zones.

7) Discussion 4.3 has weak relevant to the statistics analysis result. I don't think the authors have enough data to discuss karstification dissolution, so I recommend removing it.

We agree with the reviewer and removed the chapter.

8) To be honest, I didn't get the key points in the conclusion part. The authors do not need to mention the results of mapping and survey in the conclusion part. I suggest the authors to summarize the results of data analysis and emphasize the relationships. It might be better to make the statements by bullet points.

We agree with the reviewer. The new paragraph is listed by bullet points and reads as follows (page 18, line 6 ff.):

- *Low-permeable marlstone beds within a marine succession of high lateral continuity represent a number of aquitards that cause a multi-storey hydrostratigraphy of the Upper Muschelkalk formations.*
- *As a multi-storey hydrostratigraphy exhibits limited vertical percolation, the outcrop zones of dipping aquifer storeys become very important as preferential surface-recharge areas for inputs of matter and energy.*
- *Diffuse fracture flow dominates over karst/conduit flow in the mixed/multi-layered lithology. Subsurface water flow predominantly takes place in bedding-plane parallel mode / in stratabound fractures of the limestone beds and it is trackable from the recharge areas along the storeys.*
- *From summit to footslope positions, travel distances and presumably groundwater ages generally increase. For the individual storeys however, travel distances to monitoring wells decrease in the downslope direction, whereas their groundwater ages very likely increase due to lower fracturing and higher retention. In the same direction, surface controls (i.e. nutrient input) decrease and subsurface controls (water-rock-interaction) increase.*
- *Compared to more vulnerable settings (i.e. massive carbonate karst, open karst), the mixed carbonate-siliciclastic alternations exhibit moderate intrinsic vulnerability. This is due to lateral continuity of low permeable interbeds,*

soil covers and caprocks, of which the latter successively increase in thickness towards the footslope. Areas downstream the caprock sinkhole lineaments (and likely transverse valleys) are likely more threatened by anthropogenic (mostly agricultural) input.

- *The quality of groundwater resources with peripheral hillslope recharge benefits from extensive land management or, ideally (managed/unmanaged) forest coverage and reveals the importance of recharge area protection.*

2. Point-by-point response to review 2 (hess-2016-374-RC3)

The study is based on a very sound data set, the manuscript reads well and the joint discussion of the different data and their synthesis to conceptual model is appealing. But as it stands it remains a very sound and thorough study of a single case, because the authors miss quite obvious opportunities to address more generic questions.

The study is on the one hand a comprehensive characterization of the subsurface structure of the Hainich CZE and also includes many general aspects which are transferable to other aquifer systems. We are sorry that the reviewer got the impression of missing generic questions. Thus we highlighted the thin-bedded mixed carbonate-siliciclastic rocks forming thin aquifer storeys. This important and very frequent hydrogeological setting of carbonate-/siliciclastic-rock alternations in hillslope terrain is no described in depth in the literature.

We added factors of intrinsic vulnerability (chapter 5.4, page 17, line 19 ff.) that reads as follows:

5.4 Assessment of vulnerability factors

The configuration of the aquifer system in the hillslope setting also controls the groundwater resource vulnerability. With our multi-method investigation of the different subsurface compartments, we also revealed factors of the areas´ intrinsic vulnerability. Characteristics of intrinsic vulnerability are solely controlled by hydrogeological properties of the aquifer and overburden (Vrba and Zoporozec, 1994), and integrate the inaccessibility (i.e. by low-permeable cover strata) of the saturated zone and the attenuation capacity (retention, turnover) of the overburden (Adams and Foster, 1992).

The stacking of aquifers/aquitards, the coverage with caprocks and the lateral continuity of strata reduces the overall dominating disperse infiltration and, thus the intrinsic vulnerability. Threatening of single aquifer storeys or assemblages is predominantly controlled by fractures/faults (valleys) or karst phenomena bypassing the protective cover of soils and unsaturated zones (Fig. 8). A moderate degree of physical filtering by the narrow fractures, which are the predominant flow paths, is assumed. Also the claystone and marlstone interlayers bear a certain filtering of contaminants by retention. The preferential recharge/outcrop zones of the aquifer storeys are characterized by generally highest vulnerability. However, these zones, located in the summit to upper midslope of low mountain ranges, are mostly covered by forest. Generally, the summit position of outcrop zones of the main aquifer storey (moTK-1) lowers the risk for contamination, paradoxically, due to the thin soils that prevented lasting agricultural use and settlements. Further zones of higher vulnerability are located in the discharge of sinkhole lineaments or fracture zones that bypass surface water or drains directly into the aquifers. A mapping and structural investigation of these geostructural links will be recommended for (i.e.) proper dimensioning of drinking water protection zones. In comparison to classical karst sites (i.e. massive carbonates) with pronounced karst phenomena, (Doerfliger et al.,1999, Witowski et al., 2002), our portrayed setting shows an overall low to moderate vulnerability, that is locally elevated by inherent factors (outcrop zones) and inherited features (i.e. karstification of the underlying Middle Muschelkalk subgroup).

We also compiled a recharge potential map (Fig. 8, page 37), that comprehensively displays recharge options for selected aquifer storeys.

Furthermore, we added general aspects of this aquifer type to the conclusions (page 18, line 6 ff.) that now reads:

- *Low-permeable marlstone beds within a marine succession of high lateral continuity represent a number of aquitards that cause a multi-storey hydrostratigraphy of the Upper Muschelkalk formations.*

- *As a multi-storey hydrostratigraphy exhibits limited vertical percolation, the outcrop zones of dipping aquifer storeys become very important as preferential surface-recharge areas for inputs of matter and energy.*
- *Diffuse fracture flow dominates over karst/conduit flow in the mixed/multi-layered lithology. Subsurface water flow predominantly takes place in bedding-plane parallel mode / in stratabound fractures of the limestone beds and it is trackable from the recharge areas along the storeys.*
- *From summit to footslope positions, travel distances and presumably groundwater ages generally increase. For the individual storeys however, travel distances to monitoring wells decrease in the downslope direction, whereas their groundwater ages very likely increase due to lower fracturing and higher retention. In the same direction, surface controls (i.e. nutrient input) decrease and subsurface controls (water-rock-interaction) increase.*
- *Compared to more vulnerable settings (i.e. massive carbonate karst, open karst), the mixed carbonate-siliciclastic alternations exhibit moderate intrinsic vulnerability. This is due to lateral continuity of low permeable interbeds, soil covers and caprocks, of which the latter successively increase in thickness towards the footslope. Areas downstream the caprock sinkhole lineaments (and likely transverse valleys) are likely more threatened by anthropogenic (mostly agricultural) inputs.*
- *The quality of groundwater resources with peripheral hillslope recharge benefits from extensive land management or, ideally (managed/unmanaged) forest coverage and reveals the importance of recharge area protection.*

In general, for mixed carbonate-/siliciclastic rock alternations that are prone to develop multilayered aquifer systems, both the aquifer configuration (spatial arrangement of strata, hillside cutting, outcrop positions) and the related geostructural links (preferential recharge areas, karst phenomena) are major controls of impacting surface and subsurface factors. For the studied type of thin-bedded carbonate aquifer setting, we were able to demonstrate, that a comprehensive investigation of aquifer connectivity in the transit/discharge area as well as soil cover and land use in the recharge area is mandatory and must be rated indispensable for a thorough understanding of the state and evolution of groundwater quality (page 18, line 25 ff.).

Furthermore, the characterization appears not so holistic. With respect to the treatment of the soil, the assessment steps barely beyond a soil standard survey.

In comparison to published examples, our study focuses on the assessment of groundwater quality by interpreting aquifer outcrop areas, aquifer stratigraphy, soil texture/thickness.

To increase the perceptibility of our holistic approach, we adapted our manuscript as follows:

- A soil map compiled on the basis of relief type, slope angle, surface geology and land use. Calibration of soil groups and soil texture/soil thickness was carried out by using our soil survey data (Figure 2B, page 31).
- Soil hydraulic conductivities (Ks) and grain size analysis measured on all relief positions and soil groups were be added to the dataset. The data is presented in Figure 3 (page 32). Spatial distributions of soil Ks are shown in Figure 8 (page 37). The additional paragraph concerning soil-Ks now reads as follows (page 8, line 30 ff.):

  4.2.2 Soil hydraulic properties

  Average (median) soil hydraulic conductivities (Ks) of the five major soil groups infer, that Cambisols and Luvisols (1.3 to 1.5 10-4 m/s) form the most conductive soil cover in the study area, followed by Rendzic Leptsols and Chromic Cambisols (2.5 to 5* 10-5 m/s) and Stagnosols (about 6* 10-7 m/s; Table 1, Fig. 3 and 8). Topsoils of Chromic Cambisols are considerably more conductive than those in Rendzic Leptosols and*

Luvisols. Generally subsoils are less conductive than topsoils of the same location. Soil hydraulic conductivities (Ks) are essentially uncorrelated with the soil texture (i.e. correlation Ks vs. Median grain size: Spearman r2 = + 0.17). Soil thickness is uncorrelated to the slope gradient (r2 = -0,24 and barely better if slope positions are correlated individually).

- A groundwater recharge potential map was constructed (Figure 8, page 37). The related paragraphs in the results and discussion chapter now read as follows:

4.4.4 Recharge potential map (page 11, line 22 ff.)
The recharge potential is here defined as a qualitative measure of the probability for infiltration, percolation and groundwater recharge. The maps (Fig. 8) visualize potential spatial variation in infiltration-recharge, waiving spatiotemporal variable conditions like precipitation characteristics and antecedent soil moisture. The recharge area maps of two selected aquifer storeys (Fig. 8A and 8B) show the largest recharge potential for their outcrop areas on the Hainich hillslope. Increasing overburden thickness is accompanied with a drastic decrease in recharge potential towards the NE. With respect to the relief position, greatest recharge potential is assumed for local valleys and in the extension of sinkhole lineaments, although these areas show increased soil thicknesses. In areas with greater thickness of the overburden strata, valleys are considered as areas of preferential recharge. A slightly higher recharge potential is assumed for pasture and cropland areas compared to forests. The same holds for the flat summit/culmination and upper slope areas while the slopes of transverse valleys show greater surface water runoff.

5.2.4 Utilization of the recharge potential for interpreting groundwater quality (page 14, line 32 ff.)
Due to the recharge potential map (Fig. 8), thick, limestone-dominated aquifer storeys in the deeper sections of the hydrostratigraphy (i.e. moTK-1) are mainly recharged in their outcrop areas and subordinarily in sinkhole lineaments and transverse valleys. Within these areas, Ah-Cv soils (i.e. Rendzic Leptosol) and fractured limestone bedrocks offer the highest recharge potential. A drastic decrease in recharge potential with increasing overburden strata is confirmed by low concentrations in surface-related substances (i.e. NO_3^-.Cl^- , K^+) in well sites H1/2/4/5 for the aquifer storey moTK-1. Increasing concentrations of ions, which are related to the dissolution of the carbonate (aquifer) bedrock (Ca^{2+},Mg^{2+}, HCO_3^- and Sr^{2+}) point to a chemical evolution of groundwater in the direction of discharge (H1 to H5). A moderate to high recharge potential combined with cropland/pasture areas) in the recharge direction of site H3 is reflected by increased concentrations in TOC, NO_3^-.Cl^- , K^+, Na^+ and O_2 (Fig. 6 and 8). Aquifer storeys with thin-bedded limestone-marlstone alternations (i.e. moM-8, Fig. 8) generally show a lower recharge potential in their aquifer outcrop zones, compared to thick, limestone-dominated aquifers (moTK-1), which is related to thicker soils and a high marlstone-limestone ratio. This is reflected in the groundwater quality of moM-8 wells (H42/43/53) with low Eh and low concentrations in O_2, pointing to slow flow velocities and long residence time within the argillaceous soils and marlstone-dominated and thinly fractured bedrocks.

For a more holistic analysis of land management and soils in the aquifer outcrop area, these issues were displayed in form of an additional diagram (Fig. 5, page 34) and a new chapter was added to the results section:

4.3.3 Land use types and soils within the outcrop zones of aquifer storeys (page 10, line 11 ff.):

The outcrop zones of the two lowermost aquifer storeys (moTK-1, moM-1) are predominantly covered by forest, whereas the outcrop zones of stratigraphically higher storeys show mixed types of land management including, forest, cropland and pasture (Fig. 5 A) Within the aquifer outcrop zones, the four major soil groups (Rendzic Leptosol, Leptic Cambisol, Cambisol and Chromic Cambisol) are present in different spatial proportions (Fig. 5 B). Significant proportions of Luvisol cover the outcrop areas of moM-7, moM-9 and moTK-1. Stagnosol and Colluvisol are restricted to the outcrop area of mm, moTK-1 and moM1-4. The grain size classes of subsoils show a slight trend of increasing silt content towards the outcrop zones of stratigraphically higher aquifer storeys (moTK-1 to moM-9). Argillaceous soils occur frequently in moM-4 to moM-6. Pure clay as subsoil category is restricted to moM-2 to moM-7 (Fig. 5 C).

I thus encourage the authors to extend their analysis by addressing more generic questions using the beautiful data they have at hand. I hope the authors will find the following points helpful to further optimize their study for the reader and to fully explore the potential of their effort.
An obvious question that could be addressed is how much of the proposed experimental and monitoring effort is needed to come up with such a comprehensive assessment or how much of the information can be left out before without changing the quality of the conceptual model. This question could be easily addressed by taking the presented insights as the best guess of the unknown truth and stepwise leaving out increasing amounts of for instance their hydro chemical data (in space and or in time) and perform the same multivariate analysis.
We agree with the editor, that this issue is necessary for the reader. Thus, we touched this issue in the conclusions. However, a full analysis of this question is a topic of ongoing research within the D03 project of CRC AquaDiva. The additional paragraph in the conclusions now reads (page 18, line 27 ff.):

For the studied type of thin-bedded carbonate aquifer setting, we could to demonstrate, that a comprehensive investigation of aquifer connectivity in the transit/discharge area as well as soil cover and land use in the recharge area is mandatory and must be rated indispensable for a thorough understanding of the state and evolution of groundwater quality. Linking groundwater hydrochemistry mostly to surface factors such as land use would result in a contradiction, as groundwater chemistry does not reflect the type of land use in immediate proximity to the wells. Furthermore, footslope wells´ hydrochemistry is strongly impacted by aquifer stratigraphy, karst phenomena input and the cross-formational ascent of sulphatic groundwater that could not be evaluated without spatial lithostratigraphical data. A geostructural investigation and mapping is essential for the localization of aquifer outcrop areas and the assumption of stratigraphy-controlled flow directions. In case the soils group and the type of land use would have been neglected, discrimination between influences by natural and anthropogenic controls would have been ambiguous. If the dataset included hydrochemistry and multivariate statistics only, the interpretation of this dataset would have been ambiguous, also as different chemical surface/subsurface sources result in similar hydrochemical compositions.
Recent studies of the CRC AquaDiva focus on signal transit and transformations of surface signals. This is for instance applied to surface-sourced organic matter and microorganisms (Küsel et al., 2016, Schwab et al., 2017, Lazar et al., 2017) to further investigate subsurface connectivity, surface-subsurface interactions and functions of microbial life in groundwater environments. Further CZ exploration should also aim the investigation of deeper strata connection by regional groundwater flow, hydraulic properties and proportions of unsaturated zones and matter processing within.

The characterization of the soil is compared to the characterization of the deeper subsurface rather descriptive and follows mainly standard mapping approaches. I wonder whether any data on permeability and infiltrability where

collected?

Among others, soil thickness data and soil hydraulic conductivities (duplicate measurements from 16 sites, 2 depths) were added to the dataset. The new paragraph reads as follows (page 8 line 30):

4.2.2 Soil hydraulic properties

Average (Median) soil hydraulic conductivities (Ks) of the five major soil groups infer, that Rendzic Leptsols and Chromic Cambisols (2.5 to 5 10^{-5} m/s) form the most conductive soil cover in the study area, followed by Cambisols, Luvisols (1.3 to 1.5* 10^{-4} m/s) and Stagnosols (about 6* 10^{-7} m/s; Table 1, Fig. 3 and 8). Topsoils of Chromic Cambisols are considerably more conductive than those in Rendzic Leptosols and Luvisols. Generally subsoils are less conductive than topsoils of the same location. Soil hydraulic conductivities (Ks) are essentially uncorrelated with the soil texture (i.e. correlation Ks vs. Median grain size: Spearman r^2 = + 0.17). Soil thickness is uncorrelated to the slope gradient (r^2 = -0,24 and barely better if slope positions are correlated individually).*

Furthermore, the chapter on soils in the results section was extended. This paragraph now reads (page 8, line 13 ff.):

4.2.1 Soil distribution and soil development

Soils cover the entire landscape with major soil series developed from carbonate rocks ("carbonate soil series": Rendzic Leptosols to Chromic Cambisols), siliceous rocks ("siliceous soil series": Luvisols, Stagnosols) or alluvial sediments (WRB and German soil groups: Table 1). Culmination areas and adjacent shoulder positions are covered with Cambisols. Small plateaus and spurs between transverse valleys in shoulder positions exhibit Chromic Cambisols which grade into Cambic Regosols on the shoulder and Calcaric Regosols on the midslope. Chromic Cambisols are also found in local depressions and old caprock sinkholes. Rendzic Leptosols occur in form of narrow patches in western crestal areas (close to well H11). Luvisols are coupled to the spatial distribution of loess loam in the central and eastern midslope/footslope areas. In case of a very thin loess loam cover, soils are developed as Pelosol-Cambisol and Cambisol. Fluvial soils cover the central parts of headwater areas and the complete valley floor in the lower parts (in the northeast) of the study area. Colluvisols occur at the margins of local valley flanks in the shoulder and midslope area (Fig. 2 B). Typical sequences of two superimposed soils comprise (I) Chromic Cambisols (paleosols) developed from marlstones and (II) Luvisols developed from loess loam (with windblown loess sedimentation after the formation of soil (I) (Fier, 2012). Average soil thicknesses are 21 cm (for Rendzic Leptosols), 32 cm (Rendzic Leptosol-Cambisol transitions), 66 cm (Cambisols), 54 cm (Chromic Cambisols), 71 cm (Luvisols), 132 cm (Fluvisols), 91 cm (Stagnosols) and 78 cm (Colluvisols). Subsoils show higher average clay and fine silt content compared to the topsoils of the same soil group (Fig. 3).

Even if, not the analysis of the available soil types lacks behind its potential to infer on recharge areas. The latter depend on the ks, retention properties and apparent preferential pathways and the spatial pattern thereof. Even if the latter were not mapped, one could use a pedo transfer function to estimate ks and compile a geostatistical analysis with interpolation or even conditional simulation. This would yield an estimate on potential hot spots for recharge.

We carried out soil hydraulic conductivity measurements as well as a grain size analysis for all soil groups and all types of land management. Correlations between soil hydraulic conductivities and mapped quantitative soil texture properties (i.e. median grain size, clay content, soil grainsize class) was not possible, as the soil hydraulic conductivities are uncorrelated to the soil texture in our study area. For this reason, a quantitative map of hydraulic conductivities (Ks) was not possible with the actual dataset. Instead of a Ks-map, we decided to display a recharge potential map (chapter 5.2.4) that considers the following parameters, which is described in the following section (page 7, line 14 ff):

3.9 Groundwater recharge potential map

For the determination of preferential zones for infiltration/recharge, we calculated qualitative maps of the recharge potential (compare to Muir and Johnson 1979; Shaban et al., 2006; Deepa et al., 2016) in ArcGIS 10.3 by a weighted linear combination of surface/subsurface properties that influence water infiltration and percolation. The input raster datasets and the respective weight factors were chosen based on expert knowledge and the best fit to measured soil hydraulic conductivities: aquifer storey overburden thickness (40 %), type of bedrock (limestone-dominated vs. marlstone-dominated strata; 15 %), soil classes (15 %), fracture/karst zones (10 %); vegetation and type of land management (10 %), soil thickness (5 %) and slope angle classes (5 %).

Technical details:

- Generally the figure caption are very brief.

We added more detail to all figure captions. The new figure captions read as follows (page 28 line 2 ff.):

Fig. 1. Location of the Hainich CZE (a + b): Prominent karst springs in the Hainich CZE are coupled to NE-SW orientated fault zones (b; modified from Mempel, 1939 and Jordan and Weder, 1995). (c): Geological setting of the eastern Hainich hillslope with monitoring wells of the research transect, accessing Upper Muschelkalk target formations (mo); Data sources: DEM ©GeoBasisDE/TLVermGeo, Gen.-Nr.: 7/2016.

Fig. 2. (A): Types of land management, outcrop zones of aquifer storeys, sinkhole lineaments, potential fracture zones and measurement points for soil hydraulic conductivities. Aquifer storeys which are lower in stratigraphy outcrop in higher positions on the Hainich hillslope. The AquaDiva well transect H1 to H5 (also shown) covers hillslope regions from the summit (H1) to the footslope (H5). (B) Conceptional soil map showing calculated soil groups and mapped calibration data points. Signatures of the mapped soil profiles represent the grain size class (soil category) of the topsoil. Interpolated isolines of mapped soil thickness show increasing thickness towards the NE and towards the transverse valleys.

Fig. 3. Physical properties of topsoil/subsoils and parent rocks of the four major soil groups. (A): Median frequencies of the fine grain size fractions (clay + fine silt) showing increasing proportions towards the bedrock, respectively. (B): Median soil hydraulic conductivities of soil groups showing higher median soil hydraulic conductivity in Chromic Cambisols and Luvisols compared to the Rendzic Leptosols and Cambisols and general decreases in hydraulic conductivity towards the subsoil. The error bars describe the root of the estimation variance of the average.

Fig. 4. Graphical correlation of marlstone/claystone intervals in gamma-ray logs, biostratigraphic limestone marker beds (grainstones/rudstones) and the degree of karstification (red bars and red scale bar below: solution-enlarged bedding planes to karst breccia). The geological aquifer correlation is cross-checked with the hierarchical clustering of hydrochemical parameters.

Fig. 5. Surface and subsurface properties of the aquifer outcrop zones (moTK-1 to moM-9) on the Hainich hillslope. Area sizes are related to the 29 km2 area of this study. (A): Absolute abundances of land management types in the preferential recharge areas of the aquifer storeys. The two basal aquifer storeys are characterized by the largest aquifer outcrop areas and the highest amounts of forest within these areas. Agricultural land management increases towards the higher aquifer storeys (moM-2 to moM-9). (B): Relative abundances of soil groups within the aquifer outcrop zones showing high diversitiy in all aquifer outcrop zones depending on slope positions and quarternary loess loam/alluvial clay coverage, (C): Grain size groups of the topsoils and subsoils in the aquifer outcrop zones.

Fig. 6. Stratigraphic succession of the Upper Muschelkalk with stratigraphic marker beds (left), a gamma-ray log, aquifer assemblages HTL/HTU, aquifer storeys moTK-1 to moM-9 and the average chemical compositions of monitored groundwater (left: ions of carbonate/sulphate minerals; middle: redox-sensitive ions; right: ions which are potentially related to the type of land management). The color code of hierarchical clusters is identical to Fig. 4.

Fig. 7. Principal component analysis (PCA) biplot for the complete parameter set (a) and for the limited parameter set (b) without redox related parameters. Five clusters can be distinguished in both parameter sets. Samples within the clusters are identical for both PCA plots. Factor loads for PC1 and PC2 are displayed as labels of the x/y-axis as well as the sequence of factor loads for individual components. The color code of hierarchical clusters is identical to Fig. 4.

Fig. 8. Recharge potential maps for the two contrasting aquifer storeys moTK-1 (upper map) and moM-8 (lower map). The recharge potential is a qualitative indicator for infiltration and percolation towards selected aquifer storeys. The brighter the output color, the higher the recharge potential. Aquifer outcrop zones show highest recharge potentials, followed by sinkhole lineaments and (NE-SW orientated) transverse valleys. Recharge potential decreases drastically with increasing thickness of overburden strata towards the NE. Datapoints of field measurements are displayed in the left map (moTK-1 recharge potential) and color-coded with respect to their soil hydraulic conductivity; Data sources: DEM ©GeoBasisDE/TLVermGeo, Gen.-Nr.: 7/2016.

Fig. 9. Average groundwater chemistry of the hierarchical clusters 1-5 (left: groundwater wells and aquifer storeys within the clusters). First column: parameters related to the carbonate-CO2-equilibrum, 2nd column: dissolved O2, redox potential and redox-sensitive ions, 3rd column: ions which are potentially related to land management, 4th column: ions related to the dissolution of either carbonate/sulphate or clay minerals. The error bars describe the root of the estimation variance of the average. The colour code of hierarchical clusters is identical to Fig. 4.

Fig. 10. Conceptual cross section of the Hainich hillslope showing the overall geological structure with the ten aquifer storeys illustrating preferential aquifer recharge zones in the summit to midslope region as well as the discharge direction. Lineaments of caprock sinkholes crossing the potential groundwater flowpath represent potential zones for descending or ascending cross-formational flow and also the mixing of different types of groundwater.

Figure 4: how much variance is explained by the first two principle components? I didn't find it in the text, would be nice to provide it here.

The information has been added (page 10, line 42 ff.):

According to the PCA of the complete parameter set, the first two components (PC1 plus PC2) explain 54.9 % (variances of PC1: 34.6 % and PC2: 20.4 %), and according to the parameter set without redox sensitive parameters PC1 plus PC2 explain 62.1 % (variances of PC1: 35.4 % and PC2: 26.8 %) of the total variability, respectively.

- I guess the color code in Figure 5 represent the cluster in Figure 4. Would be helpful to add that to the caption, also of Figure 6.

This was done accordingly (Figure 6 page 35, Figure 7 page 36, Figure 9 page 38).

- Figure 7. Is the error bar the standard deviation of the sample or the root of the estimation variance of the average. I guess the latter is more appropriate to infer on significant differences.

The error bar represented the standard deviation. Obviously we missed to mention this in the figure caption. After checking

both methods, we are confident, that the root of the estimation variance of the average is more appropriate. We changed the graph and figure caption, accordingly (Figure 9 page 38)

- The reference in the section 4.1 (infiltration properties) is not the most recent one, particularly not with respect to preferential flow. Furthermore, this part is rather descriptive and could possibly be written without the data you have.

We agree and changed the paragraph as suggested. The paragraph now reads (page 13, line 27 ff).:

The spatial distribution of the soil groups reflect the outcrop zones of limestones/marlstones (Greitzke and Fiedler, 1996; Brandtner, 1997; Rau and Unger, 1997) and the succession of aquifer storeys in the summit/shoulder area of the hillslope which exhibits little quarternary rocks coverage and thin soils (Rendzic Leptosol, Chromic Cambisol) with favorable infiltration properties in the aquifer outcrop areas of moTK-1 and moM-1/6/8. Thicker relictic Chromic Cambisols which are formed by intensive decarbonatization (Rau and Unger, 1997; AG Boden, 2005) are restricted to accumulations in former depressions (i.e. caprock sinkholes) on shoulder regions of the hillslope (moTK-1 and moM-1 outcrops). Besides these depressions, Chromic Cambisols with low hydraulic conductivities are typically the subsoil layer of sequences with two layer superimposed soils, resulting in lateral soil interflow (Ali et al., 2011) as it is observed in the shoulder and midslope region during the measurement of soil hydraulic conductivities. Soils on unfractured marlstone/claystone aquitards are typically Calcaric Regosols and Stagnosols with low hydraulic conductivities of both, soils and parent rocks. According to our dataset, soil thickness is primarily controlled by the slope gradient of transverse valleys with increasing soil thickness and water storage options towards the center of valleys. As a result of the increasing coverage of parent rocks by loess loam from the regional midslope to the footslope, (related to solifluction of windblown dust; Kleber, 1991; Bullmann, 2010), loess loam becomes the dominating soil substratum in the outcrop areas of aquifer storeys moM 7-8-9. In this area, Luvisols cover local ridges and Luvisol-Stagnosol-transitions (related to the continuous vertical clay relocation (Rau and Unger, 1997) cover local valleys, whereas older caprock sinkholes are either filled by colluvisols or with loess loam, leading to either poor or very good infiltration/recharge properties. In the same context, Bachmair et al. (2009) considers the role of micro-depressions in soils as one of the major factors for preferential recharge.

More actual literature has been added. The revised paragraph now reads as follows (page 12, line 3 ff):

Although median grain size, grain size sorting and the standard devitation of grain size fractions is comparable in all soils, "carbonate series soils" (Rendzic Leptosol and Chromic Cambisol) offer higher hydraulic conductivities than "siliceous series soils" (Cambisol, Luvisol, Stagnosol) by one order of magnitude. Soil hydraulic conductivities (Ks) are uncorrelated to soil texture properties. For this reason a linear transfer function (Ks vs. median grain size or grain size category) for extending the 16 Ks measurements to the 271 mapped soil profiles was not possible with the actual dataset. A low correlation between Ks and texture is related to strong influences of soil structure and aggregation (Totsche et al., 2017) rather than texture on Ks. Structural parameters are for instance the content and proportion of macro and microaggregates, a hierarchical aggregate system, the presence and frequency of secondary pores and anthropogenic changes like former plough traces or traces of forestry machines. Bachmair et al. (2009) for instance identify tillage-related macropores as a main factor for deep infiltration into cropland soils, whereas surface littler layers inhibit infiltration in forest soils. Moreover preferential infiltration through biomacropores (i.e. earthworm borrows, root channels), that bypass the soil matrix are of great significance in aggregated and argillaceous soils with low matrix conductivity for the infiltration during heavy rain events (Deurer et al., 2003; Weiler and Naef, 2003; Blouin et al., 2013). Klaus et al.,(2013) identify vertical

macropores of anecic earthworms as a major flow control in a hillslope tile drain system. Wienhöfer and Zehe (2014) additionally consider loose, litter-rich topsoils, lateral preferential pathways, preferential pathways at the soil-bedrock surface and bedrock topography.

3. List of all changes made in the manuscript (HESS-2016-374)

- We changed the title of the manuscript by focusing on the scientific questions and the geologic situation with thin bedded mixed carbonate/siliciclastic rocks as it was proposed by reviewer 1.

- The abstract was reformulated as it was suggested by reviewer 1 by focusing on the novelties of the comprehensive approach as well as on the major research outcomes (interpretation of groundwater quality by means of hydrostratigraphy, preferential infiltration zones and land management as well as soil hydraulic properties in the groundwater catchment).

- The introduction now includes published examples for comparable comprehensive investigations and their application for vulnerability assessment / for understanding groundwater chemistry. The special geological characteristics of the study site were highlighted in the introduction as proposed by reviewer 1. Moreover, the uniqueness and the capacities of Hainich CZE were explained in the introduction.

- All study aims were reformulated (as suggested by reviewer 1) to highlight scientific questions that are to be explained by this study. All three study aims are now connected to each other (structure of the critical zone, groundwater quality controls, and spatial variations of surface impact).

- The site description was condensed into one chapter that is now located between the introduction and the methods chapters, as proposed by reviewer 2. The definition of groundwater assemblages, defined by former publications (HTU/HTL) are mentioned in the site description, only, and not in the results and discussion chapter.

- The methods chapter was re-organized by sub-chapters (3.1 to 3.8). Hydrogeochemical methods, which are regarded to be more relevant in this study (hydrogeochemistry, statistical analysis) are grouped at the beginning of the methods chapters. The methods chapter was complemented by the newly added methods (measurement of grain size, measurement of soil hydraulic conductivities, and construction of the conceptual soil map).

- General chapters concerning relief and land management were reduced in supplementary information. A short explanation of caprock sinkholes was added to the relief chapter (3.1). The results chapter was re-organized in surface properties (4.2) and subsurface properties (4.3). Soil distribution and soil development is now described in the results chapter in a briefer style. Soil hydraulic properties which are necessary for understanding recharge potential are added to the results (4.2.2) as well as the geological outcrop zones (4.2.3).

- As soil characterization is rather descriptive (as it is remarked by reviewer 2), grain size data of 16 soil sites (up to 6 samples/Profile) and soil hydraulic conductivities are measured at 16 sites (2 depths/profile) were added to the results (4.2.1 Soil distribution and soil development; 4.2.2 Soil hydraulic properties). Moreover, soil mapping was complemented by a conceptual soil map.

- The hydrostratigraphy chapter (3.2) was reorganized starting with the core log correlation and the ten newly defined aquifer storeys. Aquifer compartments of former publications are mentioned in a briefer way at the end.

- For a more holistic characterization of the groundwater catchment, we added grain size classes within the outcrop areas / capture zones of all aquifer zones and soil hydraulic conductivities to the results chapter (4.2.2, 4.3.3).

- The paradox situation of shallow, anoxic and deep, oxic aquifers was added to the results chapter (4.4.1) as well as the variances of principal components as requested by reviewer 2. A brief chapter concerning groundwater level and groundwater quality fluctuations was added to the results chapter (4.4.3) as requested by reviewer 1. This chapter is intentionally short; as these issues are discussed in detail within a second research article.

- The discussion chapter now starts with the aquifer structure interpreted by lithology (5.1.1), followed by the newly written chapter concerning structural and relief information evaluated by groundwater chemistry/hierarchical cluster analysis and principal component analysis (5.1.2).

- More generic questions like the controls on groundwater quality in groundwater catchments (5.3), influences of soil/soil hydraulic conductivity (5.2.2) and land management (5.2.3) on groundwater quality and a conceptualization in form of vulnerability classes was added to the manuscript.

- The discussion chapters are now focused on the discussion of statistical analysis of geochemical data as requested by reviewer 1. In addition to the enhancement of the existing chapter 5.3 (Controls on groundwater quality: interpretation of hierarchical clusters), we added a new chapter on hierarchical cluster interpretation (5.1.2 Structural and relief information evaluated by groundwater chemistry).

- Preferential recharge areas are interpreted in a new chapter (5.2.1) that explains the nature of caprock sinkholes and outcrop zone infiltration. Influences of soil properties (5.2.2) as well as types of land management (5.2.3) and their influence on infiltration are discussed in two chapters. References on preferential flow in chapter 5.2.2 (Influences of soils in the recharge area) are updated with more recent literature citations as requested by reviewer 2.

- Four modes of groundwater flow (5.2.5) are described in detail by interpreting groundwater chemistry and hydrostratigraphy. This includes the effect of fault zones on groundwater quality as well as some literature citation as it was desired by reviewer 1.

- The interpretation of groundwater provenance (5.3) by interpreting the hierarchical clusters of hydrogeochemistry was reorganized. The interpretation now compares more comprehensively (as requested by reviewer 2) surface (land management, soil hydraulic properties, soil chemistry) and subsurface influences (aquifer rock lithology and aquifer bulk rock mineralogy, length of flowpaths) with focus on the provenance of dissolved substances for interpreting hydrogeochemical patterns. Modes of groundwater flow are transferred to chapter 5.2.5.

- More general aspects of groundwater recharge and hydrostratigraphy in thin bedded carbonate-siliciclastic alternations were added to the conclusions. The additional chapter concerning vulnerability factors (5.4) as well as to the figure showing vulnerability classes were added the discussion. This chapter includes a brief discussion of intrinsic vulnerability as requested by reviewer 1. The associated recharge potential map contains the tracked faults and fracture zones from the observations of sinkhole lineaments and the geological map as proposed by reviewer 1.

- We removed the last chapter in the discussion, concerning the controls for variations in karstification (as proposed by reviewer 1) as this chapter is not directly related to the study aims.

- Conclusions were reformulated and now summarize the results of hydrostratigraphy, the interpretation of hierarchical clusters, the interpreted modes of groundwater flow and intrinsic vulnerability. Statements are listed with bullet points as proposed by reviewer 1.

- A short discussion of how much information/monitoring effort is necessary to come up with the actual conceptual model (as it is proposed by reviewer 2) is described at the end of the conclusions. This question is not discussed in detail, as it is a topic of ongoing research within the D03 project of AquaDiva.

- All figure captions are extended as it is proposed by reviewer 2. Also color codes and variances of principal components as well as estimated variances of the average are added to the figures/the text.

Figures:

- The map concerning soil groups and land management types was complemented by a conceptual soil map, interpolation lines of soil thickness and soil hydraulic conductivities (Ks). For a greater lucidity, the map was split into two thematic maps.

- Surface/subsurface properties of the aquifer outcrop zones were displayed in an additional graph showing the frequency of land management types, soil groups and grain size classes.

- Physical soil properties (abundances of fine grain size fractions and Ks) were displayed in an additional graph for Topsoil/subsoil and bedrock material.

- The groundwater classification (piper diagram) was removed, as the groundwater classification is fully described in the test.

- A recharge potential map for the moTK-1 and moM-8 aquifer storey was added.
  The former map of outcrop zones of all aquifer storeys, surface karst phenomena, groundwater isolines and rivers was removed.

~~Pedological and hydrogeological setting and subsurface flow structure of the~~ Aquifer configuration and geostructural links control the groundwater quality in thin-bedded carbonate~~-rock~~/siliciclastic alternations of the Hainich CZE, ~~Hainich in western Thuringia,~~ Central Germany

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Abstract

The quality of near-surface groundwater reservoirs is ~~to a large extent~~ controlled, but also threatened, by a manifold of surface-subsurface interactions. ~~land use and the properties of the soils in the recharge areas. Studies on groundwater quality and v~~Vulnerability studies, typically evaluate the variable interplay of surface factors (land management, infiltration patterns) and subsurface factors (hydrostratigraphy, flow properties) in a thorough way, but disregard resulting groundwater quality. Conversely, hydrogeochemical case studies that address chemical evolution of groundwater often lack ~~therefore, call for~~ a ~~thorough and holistic~~ comprehensive analysis of the structural buildup. ~~and hydraulic properties of the full range of surface and subsurface compartments involved in the interactions of water with immobile surfaces of the soils and rocks. This study~~ In this study, we aim to reconstruct the actual spatial groundwater quality pattern from a synoptic analysis of the hydrostratigraphy, lithostratigraphy, pedology and land use in the Hainich Critical Zone Exploratory (Hainich CZE). This CZE represents a widely distributed, yet scarcely described setting of thin-bedded mixed carbonate-siliciclastic strata in hillslope terrains. At the eastern Hainich low-mountain hillslope, bedrock is mainly formed by alternated marine sedimentary rocks of the Upper Muschelkalk (Middle Triassic) that partly host productive groundwater resources. Spatial patterns of the groundwater quality patterns of a 5.4 km long well transect are derived by principal component analysis and hierarchical cluster analysis. Aquifer stratigraphy and geostructural links were deduced from lithological drill core analysis, mineralogical analysis, geophysical borehole logs and from mapping data.~~provides a comprehensive characterization of the soils senso stricto, the unsaturated zone, aquifer stratigraphy and hydrochemistry in a hillslope karst environment of a carbonate rock subcatchment of the Hainich Critical Zone Exploratory (CZE). This CZE is located within the Upper Muschelkalk Formations in the Hainich low mountain range, Thuringia, central Germany. We investigated the~~ Maps of preferential recharge zones and recharge potential were deduced from a digital (soil) mapping, soil survey data and field measurements of soil hydraulic conductivities (Ks). ~~soils, surface geology, land use types and the infiltration properties based on a field survey.~~ By attributing spatially variable surface and subsurface conditions, we were able to reconstruct groundwater quality clusters that~~Aquifer stratigraphy, lithology and structure were analyzed based on drill core analysis, mineralogical analysis and geophysical borehole logs. Hydrogeochemical data from 15 permanent monitoring wells along a 5.4 km long hillslope transect were analyzed for major and minor ions, total and dissolved organic and inorganic carbon during a 4 year monitoring period and were statistically evaluated.~~

~~The geological succession of the interlayered and laterally continuous limestone (karst/) fracture aquifers and marlstone aquitards of the Upper Muschelkalk results in two main aquifer assemblages (HTL and HTU = Hainich transect lower/upper aquifer assemblage), which comprise ten previously undocumented individual aquifer storeys. The geologically inferred stratification of the subsurface was confirmed by principal component analysis and cluster analysis of groundwater chemistry. According to groundwater compositions within the HTL and HTU assemblages, there are 5 main clusters (2 in HTU and 3 in HTL).~~ reflect the type of land management in their preferential recharge areas, aquifer hydraulic conditions and cross-formational exchange via caprock sinkholes or ascending flow. Generally, the aquifer configuration (spatial arrangement of strata, valley incision/outcrops) and related geostructural links (enhanced recharge areas, karst phenomena) control the role of surface factors (input quality and locations) versus subsurface factors (water-rock interaction, cross-formational flow) for groundwater quality in the multilayered aquifer system. ~~Soil properties are related to infiltration rates and the initial chemistry of recharge waters. The reconstructed recharge zones for the aquifer storeys are characterized by predominantly forest land use on "carbonate series" soils and cropland/pasture land use on "siliceous series" soils, the latter developed from quarternary aeolian loess and alluvial valley fills.~~

~~Based on the local geological structure, aquifers in the lower positions of the litho/hydrostratigraphy (i.e. HTL) outcrop in higher slope positions, show greater catchment sizes and a greater limestone/marlstone-ratio. The latter leads to thin soils, low water retention potential and predominantly forest land use, resulting in presumably high groundwater recharge rates and little anthropogenic influence on groundwater quality. As the subsurface stratification enforces confined groundwater~~

flow, intrastratal karstification and the resulting hydraulic conductivity increases (and groundwater residence time decreases) with increasing bed thickness and limestone/marlstone ratio towards the lower portions of the stratigraphic succession. By implication, aquifers in the upper litho/hydrostratigraphic positions (HTU) exhibit small and partly agriculturally managed catchments with thick soils, low infiltration potential and, based on thinly bedded aquifer/aquitard successions, low hydraulic conductivities and long groundwater residence times. All in all, the Our investigation reveals general properties of alternating sequences in hillslope terrains that are prone to form multi-layered aquifer systems. This synoptic analysis is fundamental and indispensable for a mechanistic understanding of ecological functioning, sustainable resource management and protection. complex interplay of geological structure, lithology, soil group and land use type results in distinct hydrochemical, and presumably ecological conditions in the different aquifers.

Keywords

critical Critical zone, fractured rock aquifers, groundwater rechargesoil hydraulic conductivity, hydrostratigraphy, infiltration, intrastratal karst, lithostratigraphy, Muschelkalk, soilsvulnerability

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1 Introduction

Near-surface groundwater reservoirs are increasingly threatened by anthropogenic impact, like the intensification of agricultural land use and water production, while their ecological functioning is still rather unexplored. The holistic reconstruction of the subsurface architecture of carbonate-rock landscapes is mandatory to reveal their hydrogeological functioning for sustainable management and resource protection. Generally, tThe hydrogeochemical and (micro)biological compositions of shallow (< 200 m) groundwater bodies may be to a large extent controlled by thesystems is a result of biogeochemical processes and the fluid-rock/soil interactions while traveling through the overburden of the aquifers (Urich, 2002; Canora et al., 2008). The subsurface compartments that form the overburden are (from surface to subsurface) (I.) the soils sensu stricto, i.e. the rather thin (< 1-2 m), pedogenetically transformed, intensively rooted and enlivened uppermost parts of the Earth's crust, (II.) the partly water saturated, weakly weathered to almost unaltered rocks, and finally (III.), the water saturated rocks that may act as aquifers, aquicludes or aquitards. Infiltrating rain waterprecipitation, as the main component of groundwater recharge of surface near groundwater systems, first passes the soils., which are a source for mobile Thereby, the seepage collects among others, dissolved organic carbon (Guggenberger and Kaiser, 2003), colloidal and mineral, organic and organo-mineral suspended particles (Münch et al., 2002; Totsche et al., 2006, 2007; Schrumpf et

al., 2013; Gleixner, 2013) and even biota (Dibbern et al., 2014). as well as for fertilizers (Köhler et al., 2006) and pesticides from agriculture (Müller et al., 2003). The residence time of the seepage percolating water in the soils as well as in the unsaturated and saturated zones, regulates the chemical and biological quality by controlling the extent to which the partial equilibrium of the rate-limited dissolution, retardation and release processes is achieved (Weigand and Totsche, 1998; Münch et al. et al., 2002). Residence times and thus groundwater quality depend on various surface factors the (duration and intensity of precipitation, land management/vegetation, moisture content, water retention characteristics and the presence of macropores) and subsurface factors (i.e. soil thickness, hydraulic parameters and preferential flow paths).

However, subsurface factors are spatially very variable in fractured rock and carbonate-rock terrains (Cook, 2003) and their relative importance for recharge and groundwater quality is still poorly understood (Gleeson et al., 2009). Sustainable management and resource protection therefor call for a holistic investigation of surface/subsurface architecture and interactions for the reconstruction of the hydrogeological functioning and groundwater quality. Concepts for vulnerability assessment (Hölting et al., 1995; Goldscheider et al., 2000; Witkowski et al., 2003; Vías et al., 2006), for instance, already consider the variable interplay of surface/subsurface factors and compartments in a thorough way, but disregard the evolution of pristine groundwater quality. Conversely, hydrogeochemical case studies A number of papers present detailed studies of karst groundwater chemistry (i.e. Suk and Lee, 1999; Moore et al., 2009) often lack a comprehensive analysis of the structural buildup and composition of the entire compartments, whereas the important "biogeoreactor" of the overburden soils are vastly neglected., of interactions between karst groundwater and springs (Barberá and Andreo, 2012), or they present structural karst aquifer models with the simulation of groundwater flow (Dafny et al., 2010), whereas the overlying soils are not considered in these studies. Other studies that focus on flow path models in the unsaturated zone (Pronk et al., 2009) or on water balance and groundwater recharge, consider land use and soil groups (Steward et al., 2011; Allocca et al., 2014) but without a detailed description of aquifer structure/stratigraphy. Some studies assess the aquifer vulnerability by considering unsaturated zone lithology and hydraulic conductivities (Witkowski et al., 2003), yet leaving groundwater chemistry out of focus. Studies that include land use and soil groups (Pronk et al., 2009; Steward et al., 2011; Allocca et al., 2014), leaving typically leave groundwater chemistry out of focus. Up to now, a comprehensive characterization of the full range of surface and subsurface compartments, including the soils, the unsaturated zone and the detailed aquifer structure and stratigraphy is lacking. This holds in particular for karst landscapes that supply 25 % of the world's population with drinking water (Ford and Williams, 2007). The AquaDiva transect consists of multiple wells at five sites for groundwater monitoring, termed H1 to H5. Each site contains 1 to 4 drilled wells labeled with a suffix, for instance H51, H52 and H53. Site H1 (wells H11 to 14) and H2 (H21 to H23) are located in the upper hillslope region of the catchment, which is covered by forest. Sites H3 (H31/32), H4 (H41 to H44) and H5 (H51 to H53) are situated in the agriculturally used, middle and lower slope regions of the Hainich hillslope (Fig. 1).

In this study, we follow a holistic approach for reconstructing the pristine groundwater quality in the aquifers of the Hainich Critical Zone Exploratory (Hainich CZE) in central Germany. Here, the bedrock of fractured, mixed carbonate-/siliciclastic alternations represents a widely distributed, yet scarcely described geological setting. WeThis study presents such a holistic analysis synoptically characterize all surface and subsurface compartments involved in the flow of water and transport of matter in the subsurface of the Hainich CZE. of the subsurface compartments of the Hainich CZE involved in subsurface water flow, connecting the surface (impacted by land use) with the groundwater bodies. This includes the reconstruction of the aquifer recharge areas, characterization and mapping of land use types, soils and surface geology (including karst and fracture zones), litho/hydrostratigraphic core characterization and geophysical borehole logs as well as the statistical analysis of the groundwater composition. The goals of our study are to (1) understand the hydrogeological and biogeochemical functioning of the subsurface in a so far not adequately addressed setting provided by the Hainich CZE, (2) explore the links and feedbacks between surface and subsurface, and (3) to demonstrate that a holistic multi-method-approach, that considers

the surface and subsurface factors, is indispensable for the mechanistic understanding of the coupling of surface and subsurface compartments, fluid dynamics, biogeochemical element cycling and ecology in the critical zone.

To reach these goals, the following research questions are answered:

(I) How is the critical zone comprised and connected in the hillslope setting of a thin-bedded, mixed carbonate/siliciclastic succession? (II) How do spatial arrangement, particularly outcrop patterns and geostructural links (karst features like caprock sinkhole lineaments) impact compartment connection, (intrinsic vulnerability) and groundwater quality? Do groundwater quality in contrasting summit/midslope and footslope wells reflect surface influences?" And finally: (III) what are the main control parameters for groundwater quality? What are the reasons for particular hydrogeochemical conditions within the multi-storey/hillslope aquifer system? ~~The main aims of this study are (1) the characterization of subsurface architecture and flow paths, (2) the reconstruction and assessment of infiltration potential in the groundwater catchment, and (3) the influence of land use, soils, topography, lithology, geological structure and karstification on groundwater compositions. The results of this study provide the surface/subsurface framework and conceptual understanding of hydrochemistry for the Hainich CZE research site, which is unique for observing cultural landscapes on carbonate-rock aquifer systems in temperate climates (Küsel et al., 2016). The study is embedded within the collaborative research centre 1076 AquaDiva (www.aquadiva.uni-jena.de), that aims to explore the mutual dependency of the functional biodiversity of the subsurface compartments, controlled by land use, weather events, and especially on the role of the local geology for the functioning of the groundwater ecosystem (Küsel et al., 2016).~~

2 Site description

~~This study is embedded within the collaborative research centre 1076 AquaDiva (www.aquadiva.uni-jena.de), that aims to explore the mutual dependency of the functional biodiversity of the subsurface compartments, controlled by land use, weather events, and especially on the role of the local geology for the functioning of the groundwater ecosystem (Küsel et al., 2016).~~ The Hainich ~~CZE~~ Criticial Zone Exploratory ~~is part of the Hainich low mountain range and~~ covers 430 km² of a hillslope subcatchment of the Unstrut ~~R~~river in northwestern Thuringia, Central Germany (Fig. 1). It is ~~limited~~ bounded by the recipient ~~stream (~~Unstrut ~~R~~river~~)~~ and the distribution ~~zones~~ area of the Upper Muschelkalk ~~target~~ formations. The Hainich represents a NW-SE orientated ~~Hainich ridge is a~~ geological anticline that is developed topographically as a low mountain range with a steep western, and a moderately inclined eastern flank (Jordan and Weder, 1995). ~~The western flank of the Hainich is characterized by complex tectonics with NW-SE oriented grabens, bounded by normal faults that belong to the regionally important Eichenberg-Gotha-Saalfeld fault zone (Mempel, 1939; Patzelt, 1998).~~ The study area is located at t~~T~~he eastern flank of the Hainich hillslope ~~with the study area~~, thtat shows a ~~rather simple~~ geostructural ~~setup~~ buildup with NE dipping strata in the direction of the syncline of Mühlhausen-Bad Langensalza (Kaiser, 1905; König, 1930; Patzelt, 1998; Wätzel, 2007). A tectonical uplift, faulting and tilting of strata is assumed for the Late Cretaceous in analogy to the surrounding horst structures Thüringer Wald (in the S) and Harz (in the N; compare to Voigt et al., 2004; Kley and Voigt, 2008). The outcropping strata in the study area comprise sedimentary rocks (Middle/Upper Muschelkalk and Lower Keuper - subgroups of the Middle Triassic). According to the German stratigraphy (Deutsche Stratigraphische Kommission, 2002), the Diemel formation (Middle Muschelkalk), Trochitenkalk, Meissner, and Warburg formation (Upper Muschelkalk) and the Erfurt formation (Lower Keuper) outcrop in the study area. The Upper Muschelkalk subgroup, which hosts the target aquifers of the Hainich CZE, is organized by bio- and lithostratigraphic marker beds (Ockert and Rein, 2000; Kostic and Aigner, 2004).~~Although little is known about the exact uplift and exhumation age, (NW-SE) fault orientations and the position between the two large horst structures Thüringer Wald and Harz (low mountain ranges), uplifted in the Late Cretaceous (Voigt et al. 2004; Kley and Voigt, 2008), point to a similar history of uplift of the Hainich ridge in the Late Cretaceous.~~ Previous studies hydrostratigraphically organize the Upper Muschelkalk subgroups into a Hainich Transect Lower Aquifer Assemblage (HTL) and a Hainich Transect Upper Aquifer Assemblage (HTU; Küsel et al., 2016).

~~Groundwater flow is supposed to take place mainly in fractured hard rock aquifers and very subordinate in quaternary valley fills. The Hainich low mountain range is one of the regionally important recharge areas like the Dün, the Fahner Höhe or the Ettersberg in Thuringia (Fig. 1) and is also a typical example of peripheral groundwater supply for water deficient sedimentary basins (Rau and Unger, 1997; Hiekel, 2004).~~ The area belongs to the Cfb climate region (C: warm temperate, f: fully humid, b: warm summer) according to the Köppen-Geiger classification (Kottek et al., 2006) and exhibits a leeward decline in areal precipitation and increasing mean air temperature from the Hainich ridge (> 900 mm/y; 7.5-8 °C) to the Unstrut valley (< 600 mm/y; 9-9.5 °C; long term average 1970-2010, ~~Thüringer Landesanstalt für Umwelt und Geologie~~TLUG, 2016). The intensively investigated study area is limited to a 29 km^2-subarea of the Hainich CZE, that surrounds the soil and groundwater monitoring transect (Küsel et al., 2016).

The Hainich CZE is a multifarious environmental laboratory for multiscale geo- and bioscience research, as
(1) both, the so scarcely described geological setting (alternations of marine thin-bedded limestones and marlstones) and the hillslope relief/sloping aquifer configuration are common and widely distributed
(2) the monitoring plot and well transect (see Küsel et al., 2016) provides a unique access to the multi-layered aquifer system of the common setting
(3) it represents a rare anthropogenically low-impacted (non-contaminated) cultural region in central Europe with a very extensive type of land management during the last centuries, allowing the investigation of natural (surface) signal transformation in the pristine aquifer systems and of ecosystem functioning
(4) the geostructural and lithological properties were found to be predictable and thus enable the tracking of biogeochemically cycling and quality development within single aquifer storeys
(5) the Hainich it is a regionally important groundwater recharge area in Thuringia (Fig. 1) and an example of peripheral groundwater supply for water deficient sedimentary basins (Rau and Unger, 1997; Hiekel, 2004)

~~2~~ 3 Material and methods

For the detailed and synoptic analysis of the critical zone and the aimed reconstruction of the groundwater quality control factors, we apply a multi-method approach that comprises drill core and geophysical-log analysis, geological surveys, soil and groundwater samplings, soil hydraulic measurements and a statistical analysis of groundwater hydrogeochemistry.

~~**2.2 Data resources**~~

3.1 Groundwater well transect

The Upper Muschelkalk strata are accessed by a ~~AquaDiva~~hillslope transect that consists of multiple wells at five sites for groundwater monitoring, termed H1 to H5. Each site contains 1 to 4 drilled wells ~~labeled with a suffix, for instance H51, H52 and H53~~. Site H1 (wells H11 to 14) and H2 (H21 to H23) are located in the ~~upper hillslope~~summit/shoulder region of the catchment, which is covered by forest. Sites H3 (H31/32), H4 (H41 to H44~~3~~ and additional sweep well H4SB) and H5 (H51 to H53) are situated in the agriculturally used, ~~middle and lower slope~~midslope and footslope regions of the Hainich ~~hillslope~~low mountain range.

3.2 Hydrogeochemistry and hydraulics

Groundwater levels were recorded by permanently installed data loggers (Orpheus Mini, Ecolog 500/800, OTT Hydromet GmbH, Germany). Groundwater was sampled at least every four weeks over three hydrological years (Nov. 2013 to Oct. 2015) in 15 permanent monitoring wells (5.1 to 88.5 m final depth below surface) of five sites along the 5.4 km long well transect (Fig. 1) between 417 and 244 meters above mean sea level (masl). The groundwater ~~accessing~~ wells were ~~regularly~~

sampled with submersible motor pumps (MP1, Grundfos, Denmark) or, in the case of very low water levels with bladder pumps/bailers. The physicochemical parameters ~~temperature (T), pH, redox potential (Eh), electrical conductivity (temperature corrected at 25°C; EC 25) and dissolved oxygen (O_2)~~ of groundwater samples were measured on site using a flow-through cell, equipped with probes for temperature (T), pH (SenTix 980, WTW GmbH, Germany~~; manufacturer for all probes mentioned~~), electrical conductivity, temperature corrected to 25°C (EC 25)(TetraCon 925), redox potential (Eh) (SenTix ORP 900), ~~concentration of~~ and dissolved oxygen (O_2) (FDO 925)~~ and a multi-parameter meter (Multi 3430 IDS, WTW GmbH, Germany)~~. Hydrochemical analyses (duplicates) comprised major and minor ions (< 0.45 µm, PES filter) by ICP-OES (725 ES, Varian/Agilent, USA) and ICP-MS (Thermo Fisher Scientific, Germany; Thermo Electron, U.K.), acid and base neutralizing capacity by acid/base-titration, major anions (SO_4^{2-},Cl^-, NO_3^-, NO_2^-, PO_4^{3-}; PES filter < 0.45 µm) by ion chromatography (DX-120, DIONEX, USA), redox sensitive parameters (Fe^{2+}, NO_2^-, NH_4^+, HS^-) by colorimetry (DR/890, Hach, USA) and determination of carbon sum parameters (TOC, TIC, DIC, DOC; PES filter < 0.45 µm) by high temperature catalytic oxidation (multi 18 N/C 2100S, AnalytikJena, Germany). Groundwater was classified using a Piper plot (Piper, 1944) according to Furtak and Langguth (1967) and Kralik et al. (2005).

3.3 Statistical analysis

SPSS 22 (IBM Corp., USA) and Origin Pro 2015 (OriginLab Corp., USA) were used for descriptive and multivariate statistics of the hydrochemical data. This includes hierarchical cluster analysis (HC) for distinguishing hydrogeochemical groups independently from ~~geologically defined aquifer stratifications~~lithostratigraphy-based hydrostratigraphy. Two different parameter sets were statistically examined at the same number of groundwater analysis from three hydrological years. A complete parameter set (a), including all measured parameters, was chosen to ~~figure out~~identify the ~~control~~ parameters that control~~influencing~~ the hydrochemical compositions of the groundwater domains by means of Principal Component Analysis (PCA). As redox processes seems to be very distinct in the studied groundwaters (masking other processes), a limited parameter set (b) was defined that does not include ions which are strongly affected by redox processes. The complete parameter set (a) contains, EC-25, pH, ~~dissolved oxygen~~O_2, Eh, TOC, anions (NO_3^-, Cl^-, SO_4^{2-}), cations (Ca^{2+}, Mg^{2+}, $Mn^{2\text{ and }4+}$, K^+, Na^+, $Fe^{2\text{ and }3+}$, Zn^{2+}, Sr^{2+}, Ba^{2+}) and silica (Si^{4+}). The limited parameter set (b) includes EC-25, pH, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+, Zn^{2+}, Sr^{2+}, Ba^{2+} and Si^{4+}. Data preparation for HC includes a z-score normalization of concentrations. Strongly correlating variables (> 0.9) and constant values were excluded, outliers were eliminated (next neighbor method) and listwise deletion was carried out (according to Backhaus et al., 2016). Then, a euclidic distance measure was applied and five clusters were chosen based on the visual ~~observation~~ inspection of the scree plot elbow criterion (Cattell, 1966). The phenon line was chosen at a linkage distance of about 67. Thus, samples with a linkage distance lower than 67 were grouped into the same cluster. Finally, Ward´s method for clustering was applied (Ward, 1963).

3.4 Field survey

~~Characterization of the geological, hydrogeological and pedological situation as well as of the infiltration properties in the Hainich CZE was based on a field survey carried out in the intensively investigated subcatchment of the Unstrut River (Fig. 1).~~ 482 bedrock outcrops were ~~described within an area of 29 km^2 considering~~investigated for lithology, flow paths~~, (according to Dunham, 1962) and~~ karst features and the thickness of quarternary cover sediment. Strike and dip directions were constructed, based on the mapped boundary between two prominent formations (~~the most prominent limestone package~~ (Trochitenkalk/Meissner formation)~~, and the superposing limestone-marlstone alternations (Meissner formation).~~ ~~In the same area, a total of~~Soil profiles were described for 117 ~~soil profiles resulted from~~ ramcore drillings (GSH 27, Robert Bosch GmbH, Germany; 50 and 60 mm diameter, drilled to the bedrock; up to 5 m depths), ~~supplemented by~~and 154 supplementary soundings (Pürckhauer, 22 mm)~~ soil profiles. Ramcore drilling was done with an electrically powered motor hammer (GSH 27, Robert Bosch GmbH, Germany) up to depths of 5 meters to reach the host rock~~. ~~Soil mapping focuses on~~

~~the influence of geology, relief and land use on infiltration properties.~~ Soil description was carried out according to the German soil survey instruction (Bodenkundliche Kartieranleitung KA5, AG Boden, 2005) and the world reference base (WRB)-scheme (IUSS Working Group WRB, 2006). Soil colors were determined using a Munsell soil color chart. ~~Outcrop mapping was supplemented by the description of rubblestones on cropland, for distinguishing underlying loess loam, marlstone, dolomite and limestone. Strike and dip directions were constructed, based on the boundary between the most prominent limestone package (Trochitenkalk formation) and the superposing limestone-marlstone alternations (Meissner formation).~~

Soil hydraulic conductivities (Ks) were measured in two depths (10 and 30 cm) at 16 locations (duplicates) within the potential groundwater catchment area by using a Guelph-Permeameter (2800K1, Soilmoisture, USA). Soil hydraulic conductivities were calculated according to the equations in Elrick and Reynolds (1992, p. 320 ff.). Hydraulic conductivities for each site are calculated as the harmonic average of the topsoil and subsoil (or parent rock in Ah/C-soils). Mean values of hydraulic conductivities of soil groups are given as spatially weighted arithmetical means.

3.5 Analysis of drill cores and borehole logs

For the determination of the stratigraphic succession, aquifer properties and mineralogical indicators for groundwater flow, 395 meters of drill cores from twelve drillings were investigated. ~~Core~~Lithology, fractures/pores and rock weathering were described according to ~~description, based on~~ DIN EN ISO 14689-1 ~~(geotechnical classification of rock) comprised hydrogeological features like fractures and pores and a weathering index~~. We extended ~~it~~ this geotechnical rock classification to sedimentary structures, limestone classification (Dunham, 1962), pore classification (Lucia, 1983), ~~the~~ degrees of karstification, ~~the~~ aquifer types, fracture angles and fracture colors, as well as secondary mineralization on fractures~~, which are indicative for recent and past groundwater flow pathways~~. Additional information about stratigraphy, clay content, fracturing and groundwater inflow was revealed by analyzing geophysical open-borehole logs of ten drillings ~~from the upper to the lower slope~~ (site H1/2/3/4/5, Fig. 1). This included data on caliper, passive gamma-ray radiation, sonic velocity (delay time of sound waves), specific electrical resistivity of rocks, as well as the temperature and specific electrical resistivity of the well water. Gamma-ray curves are interpreted, based on the graphical ~~correlation~~ interpretation of high gamma ray peaks (marlstones) and intersections of gamma ray curves with an empirically defined~~-~~ "shale line", here at 90 API (separating limestones from marlstones). ~~The spatial correlation of marlstones presumes that basin centre marlstones are laterally more continuous than shallow water limestones (Aigner, 1985).~~

Rock~~-~~-forming minerals were analyzed ~~on a~~ by X-Ray diffraction (Bruker D8 Advance~~, X-ray diffractometer (XRD, Cu-Kα anode~~, 40 kV, 40 mA, Bruker AXS Inc., USA) ~~and~~ and Fourier transform infrared spectroscopy (FTIR; Nicolet iS10; Thermo Fisher Scientific; USA)~~. on pressed powder samples with a Thermo Fisher Scientific Nicolet iS10 device (wavenumber 4000 to 400 cm^{-1}, Thermo Fisher Scientific, USA).~~

3.6 Grain size analysis of soils

Grain size analysis of all major soil groups (144 duplicates) were carried out on filtered (< 125 µm), decarbonized (HCl) and organic-free (H_2O_2) samples (Laser Particle Sizer, Analysette 22, Fritsch, Germany).

~~The two-dimensional correlation of geophysical and geological well logs was carried out with well management software GeoDIN V.8 (Fugro Consult GmbH, Germany). The scope of the correlation was to figure out lateral continuity of flow domains separated by aquitards for achieving information about potential modes of bedding-parallel, intrastratal and cross-formational fluid flow.~~

3.7 Geospatial analysis and ~~re~~construction of preferential groundwater recharge areas

Maps of soil groups and geology, were created and jointly analyzed with aerial imagery and a digital elevation model (DEM, 2 m resolution) using ArcGIS 10.3 (ESRI Inc., USA). ~~For the assessment of the major recharge areas, overlays of the~~

~~compiled geological and soil maps with land use maps interpreted from field observations and aerial imagery, as well as a digital elevation model (DEM) with 2 m resolution were prepared using ArcGIS 10.3 (ESRI Inc., USA).~~ The primary data sets were interpreted in terms of land use types, surface morphology and drainage patterns with special focus on karst phenomena like caprock sinkholes, which are ~~discussed~~ considered~~in the literature~~ as preferential input ~~features~~ structuresfor ~~surface/rain water~~funneled infiltration (Nennstiel, 1933; Mempel, 1939; Hecht, 2003). ~~Owing to the local geology with geological strata inclined at an angle steeper than the hillslope, the area, position and land use types in the aquifer recharge zones can be reconstructed and preferential infiltration/recharge areas can be identified for each fractured limestone interval (potential aquifer).~~ The two-dimensional correlation of geophysical and geological well logs was carried out with well management software GeoDIN V.8 (Fugro Consult GmbH, Germany) by graphical correlation of prominent high gamma-ray peaks and stratigraphic marker beds (grainstones/rudstones). ~~The scope of the correlation was to figure out lateral continuity of flow domains separated by aquitards for achieving information about potential modes of bedding-parallel, intrastratal and cross-formational fluid flow~~. The spatial correlation of marlstones presumes that basin-center marlstones are laterally more continuous than shallow water limestones (Aigner, 1985). According to published examples for multi-storey subsurface architecture (Haag and Kaupenjohann, 2001; Heinz and Aigner, 2003; Klimchouk, 2005; Sharp, 2007), we use the term "aquifer storey" to emphasize our conceptualization of the fine-stratified setting by arbitrary definition of intervals that are dominated by fractured limestone beds and confined at the top and base by unfractured or low permeable beds, the latter with an effective minimum thickness of 80 cm. The degree of aggregation is a compromise between increased detailedness to account for different hydrogeochemical patterns and the necessary well yield for recovering water samples.

3.8 Soil group map

The soil group map was constructed from ddifferent geospatial data sources including (1) land management map (interpreted from satellite images and field observations), (2) outcrop areas of surface geology (mapping data) and the (3) DEM2. After conversion into raster data, a (4) slope gradient map and a (5) topographical position index (TPI; Weiss, 2001) map with an empirically chosen radius parameter of 75 meters were calculated using the “Slope”-function of the ArcMap toolbox. The slope position/relief position (i.e. shoulder, midslope) was calculated using the “Relief Analysis”-tool of ArcGIS (Deumlich et al., 2010). It considers slope gradient, relative elevation and profile curvature (concave/convex) by using the slope gradient (4) and the TPI-raster (5). The spatial distribution of soil groups was calculated with a query function, which considers land management, slope position and slope gradient for the following substrata: “carbonate soil series”, “mixed carbonate-siliceous soil series”, “claystone series” and “loess loam series”.

3.9 Groundwater recharge potential map

For the determination of preferential zones for infiltration/recharge, we calculated qualitative maps of the recharge potential (compare to Muir and Johnson 1979; Shaban et al., 2006; Deepa et al., 2016) in ArcGIS 10.3 by a weighted linear combination of surface/subsurface properties that influence water infiltration and percolation. The input raster datasets and the respective weight factors were chosen based on expert knowledge and the best fit to measured soil hydraulic conductivities: aquifer storey overburden thickness (40 %), type of bedrock (limestone-dominated vs. marlstone-dominated strata; 15 %), soil classes (15 %), fracture/karst zones (10 %); vegetation and type of land management (10 %), soil thickness (5 %) and slope angle classes (5 %).

~~3~~ 4 Results

4.1 Surface characteristics of Hainich CZE

~~34~~.1.1 ~~Landscape morphology, hydrography and land use~~Relief and surface water network ~~in~~ the groundwater catchment

~~The study area covers altitude regions between 170 and 494 masl with an average slope of 35 m/km. The relief forms a stepless, gently inclined plane and is cut by more than ten straight, parallel and roughly equidistant SW-NE oriented oblique valleys with steeper upper slope angles in headwater areas. Karst phenomena like sinkholes (each of up to 80 m in diameter) are concentrated in a NW-SE oriented lineament at the middle Hainich hillslope (at about 355 masl). Sinkholes occur on local ridges and not in valleys. A second and parallel lineament of shallow elongated (uvala-like) karst depressions with a horizontal extent of up to 400 m crosses the lower Hainich hillslope (at about 270 masl).~~The study area ranges from the Hainich ridge ~~low mountain range is the (~~topographic water divide) ~~with eastward discharge~~ towards the Unstrut ~~River~~ valley and ~~westward towards the Werra River~~ covers altitude regions between 170 and 494 masl with an average slope of 35 m/km. ~~Only~~ Two orders of relief types are here distinguished: the first order (regional) relief grades from the culmination of the Hainich low mountain range towards the low-angle midslope (<5°) and footslope. The second order (local) relief is formed by a bundle of ten straight, parallel and roughly equidistant, parallel, SW-NE oriented transverse valleys with slopes >5°. Second order relief elements are also the two NW-SE oriented lineaments of more than eighty caprock sinkholes (which are passive karst phenomena) with up to 80 m in diameter. Caprock sinkholes are mostly exhibited on local ridges. A second and parallel lineament of three shallow elongated (uvala-like) karst depressions with a horizontal extent of up to 400 m crosses the lower Hainich hillslope (Fig. 2 A). A~~a~~ few small contact springs occur in the study area~~, most of them coupled to boundaries between geological formations~~. Larger springs ~~(for instance the springs coupled to the Küllstedter fault zone; Fig. 1)~~ occur at the lower eastern slopes of the Hainich ridge, tracing regional fault/fracture zones. Headwater areas of creeks, small rivers, ~~oblique~~ transvere valleys and even agricultural drainage ditches are mostly dry. During our monitoring period (November 2013 to May 2016) ~~surface water~~stream runoff typically occurred from December to March.

~~3~~4.2 ~~1~~.2 Land management and~~Land use~~ history of land management

Major types of land ~~use types~~ management are agriculture (crop, pasture) and forest (unmanaged and managed deciduous forest). Forests are to a large extent within the unmanaged Hainich National Park that occupies summit to midslope positions. Extensive forest management has been the dominant type of land ~~use~~ management during all time periods even with no deforestation during the medieval ages (Otto, 2000). Mode of forest operation shifted from random selection of wood via coppice use (since the 15th century) and planter forestry (since the 20th century) to unmanaged woodland with the foundation of the Hainich National Park ~~(www.nationalpark-hainich.de)~~ in December 1997 (Otto, 2000; Röhling and Safar, 2004). Parts of the study area (12 %), which are actually unmanaged grassland/scrubland areas within the Hainich National Park, had been formerly used as a military training area since 1964, particularly for tank trainings from 1980 until 1990 (Otto, 2000; Poser, 2004). Cultivated grasslands outside the Hainich National Park, which are used both as meadows and pastures, cover parts of the midslope and locally some cleared glades at the shoulder as well as riparian areas of small rivers. Cropland (locally used for wheat, corn and canola production) covers mainly the midslopes and footslopes (Fig. 2 A). Agricultural plots are typically large due to organization by GDR´s agricultural production cooperatives (from 1945 to 1990). These plots are now (since 1990) managed by privately owned agricultural cooperatives.~~As we assume that the land use affects severely the properties of soil and the quality of the groundwater, we aimed for a thorough reconstruction of the land use history of the presumed rural region. We found that extensive forest use has been the dominant land use in all time periods with even no deforestation during the medieval ages (Otto, 2000). Mode of forest operation shifted from random selection of wood via coppice use (since the 15th century) and planter forestry (since the 20th century) to unmanaged woodland with the foundation of the Hainich National Park (www.nationalpark-hainich.de) in December 1997 (Otto, 2000; Röhling and Safar, 2004). Parts of the Hainich National Park, which are now unmanaged grassland/scrubland areas, had been formerly used as a military training area since 1964, particularly for tank trainings from 1980 until 1990 (Otto, 2000; Poser, 2004). Crop and pasture agriculture of the lower Hainich hillslope had been organized by agricultural production cooperatives in the former GDR time (from 1945 to 1990) and are now (since 1990) managed by privately owned famer's~~

~~cooperatives.~~

~~34~~.3 ~~2~~ ~~Soil series and surface geology~~Soils in the groundwater catchment

4.2.1 Soil distribution and soil development

~~The landscape of the Hainch low mountain range has been developed within the Triassic formations of the Upper Muschelkalk and Lower Keuper. (Fig. 2). As the geological strata in the study region dip NE in the direction of, but steeper than the angle of surface relief, outcrops of lower/older stratigraphic units are located at the upper slope positions only. To this end, all formations outcrop in distinct zones along the eastern slope of the Hainich ridge (Fig. 2). In addition to the general NE inclination, the upper slope includes a NW-SE oriented normal fault with offsets of about 10 m. Parallel, fault bound troughs are also found near this fault. Near-surface karstification is observed for limestones outcropping at the upper hillslope. The Triassic rocks are covered by young loess loam in sheltered, concave depressions of the east-exposed slopes. Alluvial soils and colluvium fill the valley bottoms. Both sediments are absent at the upper slope and increase in both thickness (max. 3.5 m) and areal cover from the middle to the lower slope.~~

Soils cover the entire landscape with major soil series developed from carbonate rocks ("carbonate soil series"~~;~~: Rendzic Leptosols to Chromic Cambisols), siliceous rocks ("siliceous soil series"~~;~~: Luvisols, Stagnosols) or alluvial sediments (WRB and German soil groups: Table 1). Culmination areas and adjacent shoulder positions are covered with Cambisols. Small plateaus and spurs between transverse valleys in shoulder positions exhibit Chromic Cambisols which grade into Cambic Regosols on the shoulder and Calcaric Regosols on the midslope. Chromic Cambisols are also found in local depressions and old caprock sinkholes. Rendzic Leptosols occur in form of narrow patches in western crestal areas (close to well H11). Luvisols are coupled to the spatial distribution of loess loam in the central and eastern midslope/footslope areas. In case of a very thin loess loam cover, soils are developed as Pelosol-Cambisol and Cambisol. Fluvial soils cover the central parts of headwater areas and the complete valley floor in the lower parts (in the northeast) of the study area. Colluvisols occur at the margins of local valley flanks in the shoulder and midslope area (Fig. 2 B)~~Cambisols are found at the upper and middle slope, Luvisols at the middle and lower slope (both of them mostly used as cropland/pasture) and Stagnosols are restricted to the lower slope. Chromic Cambisols are found in local depressions and old sinkholes~~. Typical sequences of two ~~layer~~ superimposed soils ~~profiles, developed from two different substrates, are~~comprise (I) Chromic Cambisols (paleosols) developed from marlstones and (II) Luvisols developed from loess loam (with windblown loess sedimentation after the formation of soil (I)~~overlying (II) Chromic Cambisols developed from marlstones~~ (Fier, 2012). Average soil thicknesses are 21 cm (for Rendzic Leptosols), 32 cm (Rendzic Leptosol-Cambisol transitions), 66 cm (Cambisols), 54 cm (Chromic Cambisols), 71 cm (Luvisols), 132 (Fluvisols), 91 cm (Stagnosols) and 78 cm (Colluvisols). Subsoils show higher average clay and fine silt content compared to the topsoils of the same soil group (Fig. 3).

4.2.2 Soil hydraulic properties

Average (Median) soil hydraulic conductivities (Ks) of the five major soil groups infer, that Rendzic Leptsols and Chromic Cambisols (2.5 to 5* 10^{-5} m/s) form the most conductive soil cover in the study area, followed by Cambisols, Luvisols (1.3 to 1.5* 10^{-4} m/s) and Stagnosols (about 6* 10^{-7} m/s; Table 1, Fig. 3 and 8). Topsoils of Chromic Cambisols are considerably more conductive than those in Rendzic Leptosols and Luvisols. Generally subsoils are less conductive than topsoils of the same location. Soil hydraulic conductivities (Ks) are essentially uncorrelated with the soil texture (i.e. correlation Ks vs. Median grain size: Spearman r^2 = + 0.17). Soil thickness is uncorrelated to the slope gradient (r^2 = -0,24 and barely better if slope positions are correlated individually).

4.2.3 Geological outcrop zones

The landscape of the Hainch low mountain range has been developed within the Triassic formations of the Upper

Muschelkalk and Lower Keuper. All formations outcrop in distinct zones along the eastern slope with dip angles steeper than the slope: from 5 ° (footslope) to 8 ° (shoulder position); and lower/older strata outcrop in higher relief positions (Fig. 2 A). A NW-SE oriented normal fault is located close to the Hainich summit with offsets of about 10 m (Fig. 2A). Fault-bound troughs (up to 700 m long and 150 m wide) are also found parallel to this fault. The Triassic rocks are covered by young loess loam in sheltered, concave depressions of the east-exposed slopes. Alluvial soils and colluvia fill the valley bottoms with increasing thickness (maximum 3.5 m) and areal cover from the midslope to the footslope (Fig. 2A).

4.3 Subsurface properties of Hainich CZE

~~3~~4.~~4~~ 3.1 ~~Lithology,~~ Lithostratigraphy and ~~host~~ bedrock mineralogy ~~and lithostratigraphic framework~~

~~The succession of the strata outcropping within the study area comprises Middle Triassic sedimentary rocks of the Middle and Upper Muschelkalk subgroup as well as the Lower Keuper subgroup. According to the German stratigraphy, the Middle Muschelkalk is separated into the Karlstadt, Heilbronn, and Diemel formations, the Upper Muschelkalk comprises the Trochitenkalk, Meissner, and Warburg formations and the Lower Keuper is synonymously used for the Erfurt formation (Deutsche Stratigraphische Kommission, 2002). The Upper Muschelkalk subgroup, which hosts the target aquifers of the Hainich CZE, is organized by bio- and lithostratigraphic marker beds (Ockert and Rein 2000; Kostic and Aigner, 2004).~~ The stratigraphic succession is characterized by thin-bedded carbonate-siliciclastic alternations of which only the limestone beds are fractured and therefore represent potential aquifers.~~The Triassic strata is bounded by an erosional unconformity on top, which is overlain by aeolian loess loam developed from loess deposits of the last glacial period (Weichsel glacial in Germany; Greitzke and Fiedler, 1996) and alluvial/colluvial sediments of Holocene age (Rau and Unger, 1997).~~ The Diemel formation (mmDO) comprises thin (1-3 cm) yellowish dolomitic marlstones, fine crystalline dolomite and rarely cavernous dolomites without any fossils, gypsum or salt. The 7 m thick Trochitenkalk formation (moTK) with thick (5-30 cm), gray, coarse bioclastic limestones (mainly rudstones with the rock~~-~~forming fossil *Encrinus liliformis*) forms a carbonate-rock~~karst~~-fracture aquifer ~~classifiable as(~~-intrastratal karst ~~(~~according to Ford and Williams, 2007). Large scale (meter-scale) and consistent fractures, a high fracture index and dissolution-enlarged fractures and vugs (cf Lucia, 1983), as well as karst breccia and conduits at the base of the formation are common features. The fractures found in rock cores are mainly developed as stratabound (Odling et al., 1999) fractures that are restricted to the limestone beds, as common in limestone-marlstone alternations (Meier et al., 2015). All fractures and pores are stained with red brownish (~~Munsell~~ 10R6/6) coatings. Karst features in the Trochitenkalk formation occur from the near surface down to 90 m depth. Rock mineralogy is dominated by calcite and very low contents of dolomite with trace~~s~~ amounts of quartz, muscovite, chlorite and Na/K-feldspar. Based on a consistent (moTK) formation thickness, bed thickness and limestone types (cf Dunham, 1962) in all wells, lateral facies changes within the Trochitenkalk formation are negligible.

The 34.6 m thick Meissner formation (moM) consists of 5 m thick basal marlstones with three discrete bioclastic limestone beds (Kalkbank α/β/γ), overlain by 29 m of alternating thin (2-5 cm) limestones (mudstones to grainstones) and marlstones. These are covered by a thick (> 60 cm) bioclastic, regional biostratigraphic marker horizon, the Cycloidesbank, which is a known regional aquifer (Grumbt et al. 1997; Hecht, 2003) of minor importance. Limestones in the Meissner formation are fracture aquifers and ~~the mineralogical compositions~~their rock matrices are predominantly composed of calcite and ~~subordinate~~ trace amounts of dolomite, ~~and traces of~~ quartz, illite and feldspar. The overlying 16 m thick Warburg formation (moW) with predominantly marlstones (mineralogically: calcite, dolomite, quartz) and the 35 m thick Erfurt formation (kuE) with dolomite rocks (dolomite, calcite and quartz), siltstones, silty sandstones and claystones (illite, muscovite, chlorite and gypsum), ~~are~~ represent both unfractured aquitards (Hoppe, 1952; Hecht, 2003) and form the low permeable top-seal strata of the Upper Muschelkalk aquifer ~~assemblages~~ storeys at the ~~lower slope~~footslope positions (Table 2). The Triassic strata are bounded by an erosional unconformity on top, which is overlain by aeolian loess loam developed from loess deposits of the

last glacial period (Weichsel glacial in Germany; Greitzke and Fiedler, 1996) and alluvial/colluvial sediments of Holocene age (Rau and Unger, 1997).

~~3.4.5~~ 3.2 ~~Aquifer stratigraphy and h~~Hydrostratigraph~~ic~~y ~~standard section~~

The correlation of sedimentological core logs and geophysical borehole logs infers that a multilayer hydrostratigraphy is applicable and all aquifers and aquitards are presumably continuous (and with similar thickness and limestone type) on the scale of the research transect (Fig. 4). In the Upper Muschelkalk strata (Trochitenkalk formation (moTK) and Meissner formation (moM)), ~~that represent the target formation of this study,~~ the alternat~~ied~~ed bedding of ~~ng~~ limestone~~s and~~, marlstones and claystones ~~beds~~ result in permeable fracture aquifers (dense matrix, varying fracturing) and low permeable marlstones (dense matrix, unfractured). Ten aquifer storeys are newly defined for the Hainich CZE. Of these, the Trochitenkalk formation contains one aquifer storey (moTK-1) and the Meissner formation contains nine aquifer storeys (moM-1 to moM-9; Table 2). ~~In~~All ~~the lower slope~~footslope ~~both aquifer assemblages are overlain by low to~~aquifer storeys are overlain by impermeable cap rocks of the Warburg formation (Upper Muschelkalk) and the Erfurt formation (Lower Keuper). Flow paths are predominantly fractures and matrix porosity is lower than 5 % in all stratigraphic intervals. ~~create numerous aquifer and aquitard layers. Of these, the Trochitenkalk formation (moTK; referred to as HTL = Hainich transect lower aquifer assemblage by Küsel et al., 2016) is the most productive regional aquifer assemblage in current use (Hecht, 2003). It~~ Although it is of karst-fracture type with partially solution-enlarged fractures, the karstification and the development of conduits is limited and concentrated at the formation´s very base. ~~without prominent marlstone interlayers and is sealed at the base~~ Below moTK-1, the~~by~~ impermeable dolomitic marlstones of the Diemel Formation (mmDO) form a hydraulic basis seal. We observed an intact and unweathered base seal in all wells that were drilled to the base of the moTK-1. The ~~second major aquifer assemblage is the~~ Meissner formation (moM~~; referred to by Küsel et al. (2016) as HTU = Hainich transect upper aquifer assemblage~~) ~~that~~ contains limestone-fracture aquifers which are interbedded ~~with~~ marlstone-aquitards on the decimeter to meter scale ~~(Table 2)~~. Limestones of this formation are almost exclusively fracture aquifers with very little matrix porosity, concentrated at certain thickly bedded limestone marker beds. ~~According to published examples for multi-storey subsurface architecture (Haag and Kaupenjohann, 2001; Heinz and Aigner, 2003; Klimchouk, 2005; Sharp, 2007), we use the term "aquifer storey" to emphasize our conceptualization of the fine-stratified setting by arbitrary definition of intervals that are dominated by fractured limestone beds and confined at the top and base by present, unfractured or low-permeable beds, the latter with a minimum thickness of 80 cm.~~

~~Based on the lithological core description, the lower aquifer assemblage (HTL) represents one aquifer storey termed moTK-1, and the upper assemblage (HTU) is organized into nine aquifer storeys (moM-1 to moM-9; Table 2), sandwiched between less permeable units. The correlation of sedimentological core logs and geophysical borehole logs infers, that the subsurface is stratified and all aquifers and aquitards are presumably continuous on the scale of the research transect (5.4 km). In the case of all aquifer storeys flow conditions are confined, preferential groundwater recharge takes place in the upper slope positions (outcrop zones) and regional discharge is towards the NE, due to lithology and orientation of the strata.~~~~Based on the lithological core description, the lower aquifer assemblage (HTL) represents one aquifer storey termed moTK-1, and the upper assemblage (HTU) is organized into nine aquifer storeys (moM-1 to moM-9; Table 2), sandwiched between less permeable units.~~~~Due to their different lithological and bedding properties, the two aquifer assemblages HTL and HTU show significantly different aquifer characteristics: The HTL-assemblage, characterized by thick limestone packages without considerable aquitard interlayers, tends to have strong karstification features, broad fractures as well as shallow soils in the recharge area. By contrast, the HTU-assemblage with its finely alternating aquifer-aquitard stratification exhibits a lesser intensity of karstification, fine fissures as flow paths and it recharges in mid-slope areas with thicker soils that partially inhibit rain water infiltration at lower slope areas. In the lower slope both aquifer assemblages are overlain by low to impermeable cap rocks of the Warburg formation (Upper Muschelkalk) and the Erfurt formation (Lower Keuper)~~

4.3.3 Land use types and soils within the outcrop zones of aquifer storeys

The outcrop zones of the two lowermost aquifer storeys (moTK-1, moM-1) are predominantly covered by forest, whereas the outcrop zones of stratigraphically higher storeys show mixed types of land management including, forest, cropland and pasture (Fig. 5 A) Within the aquifer outcrop zones, the four major soil groups (Rendzic Leptosol, Leptic Cambisol, Cambisol and Chromic Cambisol) are present in different spatial proportions (Fig. 5 B). Significant proportions of Luvisol cover the outcrop areas of moM-7, moM-9 and moTK-1. Stagnosol and Colluvisol are restricted to the outcrop area of mm, moTK-1 and moM1-4. The grain size classes of subsoils show a slight trend of increasing silt content towards the outcrop zones of stratigraphically higher aquifer storeys (moTK-1 to moM-9). Argillaceous soils occur frequently in moM-4 to moM-6. Pure clay as subsoil category is restricted to moM-2 to moM-7 (Fig. 5 C).

4.4 Groundwater chemistry

~~34.6~~ 4.1 ~~Groundwater chemistry~~Groundwater classification

The groundwater in the carbonate rock landscape is classified as little to strongly mineralized earthalkaline, bicarbonatic type (site H1/2/3/4), and earthalkaline, bicarbonatic-sulfatic type (cf TLUG, 1996) for ~~(~~groundwater of the deep well H51 (~~HTL;~~moTK-1~~Thüringer Landesanstalt für Umwelt, 1996~~). The order of abundance for dissolved ions is: $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and $HCO_3^{-} > SO_4^{2-} > Cl^{-}$ ~~(Fig. 3)~~. According to the groundwater subtypes of Kralik et al. (2005) the moM~~ (HTU)~~ waters (except for well H14) plot in the "dolomite"-field, moTK-1 ~~(HTL)~~-waters (wells H13/21) and water from H14 (moM~~, HTU~~) plot in the "calcite"-field. All other moTK-1 ~~(HTL)~~ wells (H31/41/51) are classified as the mixed subtype ("calcite+dolomite"~~; Fig. 3~~). Two contact springs in the recharge area (~~Hünenteich~~ Grauröder Quelle~~spring~~, Ihlefeldquelle ~~spring~~) and two karst springs in the discharge area (Kainspring, Melchiorbrunnen, coupled to NW-SE oriented fault zones~~: Fig. 1)~~, are classified as carbonate-earth alkaline type, predominantly in contact with calcite in the recharge area and a calcite-dolomite mixing type in the discharge area. Groundwater chemistry in aquifer storeys in deeper stratigraphic positions, exhibit high O_2, SO_4^{2-}, Sr^{2+} and low Mg^{2+}, HCO_3^{-}, Si^{4+}, K^{+}, Na^{+} and NO_3^{-} concentrations. Shallow aquifers storeys are partly anoxic in midslope/footslope positions and deeper aquifer storeys are oxic in all slope positions (Fig. 6). Aquifers in footslope wells show higher concentrations of K^{+}, Mg^{2+}, Si^{4+}, Sr^{2+}, SO_4^{2-} and Cl^{-} compared to the same aquifer in summit positions.

4.4.2 Statistics of hydrogeochemistry and chemical composition of groundwater groups

Hierarchical cluster analysis revealed 5 clusters. Cluster~~Cluster~~ 1 ~~includes~~ comprises the groundwater samples from upper slope moTK-1 ~~(HTL)~~ wells (H13/21) and the moM-1 well H14 ~~(HTU)~~. Cluster 2 encompasses the groundwater samples from moTK-1 wells H31/41 ~~(HTL) as well as~~and also from moM-5/6 well H32 ~~(HTU)~~. Groundwater samples from moTK-1 ~~(HTL)~~ well H51 plot in cluster 3. Cluster 4 includes ~~(HTU)~~ moM-6/7/8 wells H42/43/4~~4~~SB, while cluster 5 consists of two moM-3/4/8 ~~(HTU)~~ wells of the same site (H52/53; Fig. ~~4~~7). Multi-case clustering does not occur. ~~Hierarchical cluster analysis (HCA) reveals no multi-case clustering.~~

As a result of the principal component analysis (PCA) using the complete parameter set (Fig. ~~4a~~7 a), and the parameter set without redox sensitive parameters (Fig. ~~4b~~7 b), data points fall into very similar groupings compared to the HC~~A~~.

According to the PCA of the complete parameter set, the first two components (PC1 plus PC2) explain 54.9 % (variances of PC1: 34.6 % and PC2: 20.4 %), and according to the parameter set without redox sensitive parameters PC1 plus PC2 explain 62.1 % (variances of PC1: 35.4 % and PC2: 26.8 %) of the total variability, respectively. For both PCA, the parameters with the ~~controlling factors~~ highest factor loads ~~for hydrochemical grouping~~ are Si^{4+}, K^{+}, Na^{+}, HCO_3^{-}, Mg^{2+} for PC1 and Sr^{2+}, SO_4^{2-}, EC-25 and Cl^{-} for PC2. ~~In general, average chemical values of all aquifer storeys infer, that groundwater of the~~

~~moTK-1 (HTL) aquifer exhibits generally higher O_2, SO_4^{2-}, Sr^{2+} and lower Mg^{2+}, HCO_3^-, Si^{4+}, K^+, Na^+ and NO_3^- concentrations compared to the HTU (moM formation) aquifer assemblage when sampled at the same locations. Groundwater sampled from the moTK-1 (HTL) aquifer show consistent chemical trends from the recharge to the discharge area: ion sums increase, in particular in the concentrations of K^+, Mg^{2+}, Si^{4+}, Sr^{2+}, SO_4^{2-} and Cl^- (Fig. 5).~~

The average chemical composition of the five groundwater clusters is significantly different with respect to their physico-chemistry and major ion composition. Cluster 1 shows high pH and Eh, as well as high concentrations in dissolved O_2, TOC and Ca^{2+}. High concentrations in HCO_3^-, NO_3^{2-}. TOC, Cl^- and Mg^{2+} are distinctive for Cluster 2, whereas Cluster 3 is characterized by very high SO_4^{2-}, Ca^{2+}, Cl^-, and Sr^{2+} concentrations in combination with high redox potential and moderate K^+ and Na^+ content. Cluster 4 shows very high concentrations in $Fe^{2+/3+}$, $Mn^{2+/4+}$, TOC, Cl^- in combination with very low redox potential and very low dissolved oxygen. The latter is also applied to Cluster 5, that additionally contains high concentrations in K^+, Na^+ and Mg^{2+} (Fig. 8).

4.4.3 Fluctuations of groundwater levels and quality

Groundwater levels are confined in footslope wells. In the wells of site H5, groundwater rises 30 m (H53), 50 m (H52) and 70 m (H51) higher than the base of the screen section. Fluctuations of groundwater levels in our monitoring wells range from 1-3 m in the hilltop recharge area (well site H13) to more than 25 m in the groundwater transit area (well site H5). The groundwater level fluctuations show a strong seasonality with annual highstands (March to April) and lowstands (October to December). Monitoring wells of different sites and screen depths differ in average concentrations of the major solutes. These spatial differences are generally higher than the seasonal fluctuations in the wells. An exception to these conditions are marked seasonal fluctuations of Ca^{2+} (monitoring well H31/41), Cl^- (H52/53), K^+ (H41), Mg^{2+} (H41), Na^+ (H31/41), Si^{4+} (H41) and SO_4^{2-} (H31/41).

4.4.4 Recharge potential map

The recharge potential is here defined as a qualitative measure of the probability for infiltration, percolation and groundwater recharge.The maps (Fig. 8) visualize potential spatial variation in infiltration-recharge, waiving spatiotemporal variable conditions like precipitation characteristics and antecedent soil moisture. The recharge area maps of two selected aquifer storeys (Fig. 8A and 8B) show the largest recharge potential for their outcrop areas on the Hainich hillslope. Increasing overburden thickness is accompanied with a drastic decrease in recharge potential towards the NE. With respect to the relief position, greatest recharge potential is assumed for local valleys and in the extension of sinkhole lineaments, although these areas show increased soil thicknesses. In areas with greater thickness of the overburden strata, valleys are considered as areas of preferential recharge. A slightly higher recharge potential is assumed for pasture and cropland areas compared to forests. The same holds for the flat summit/culmination and upper slope areas while the slopes of transverse valleys show greater surface water runoff.

~~4~~ 5 Discussion

5.1 Hydrostratigraphy~~According to published examples for multi-storey subsurface architecture (Haag and Kaupenjohann, 2001; Heinz and Aigner, 2003; Klimchouk, 2005; Sharp, 2007), we use the term "aquifer storey" to emphasize our conceptualization of the fine-stratified setting by arbitrary definition of intervals that are dominated by fractured limestone beds and confined at the top and base by present, unfractured or low permeable beds, the latter with a minimum thickness of 80 cm.~~

~~Due to their different lithological and bedding properties, the two aquifer assemblages HTL and HTU show significantly different aquifer characteristics: The HTL assemblage, characterized by thick limestone packages without considerable aquitard interlayers, tends to have strong karstification features, broad fractures as well as shallow soils in the recharge area.~~

~~By contrast, the HTU assemblage with its finely alternating aquifer-aquitard stratification exhibits a lesser intensity of karstification, fine fissures as flow paths and it recharges in mid slope areas with thicker soils that partially inhibit rain water infiltration at lower slope areas. In the lower slope both aquifer assemblages are overlain by low to impermeable cap rocks of the Warburg formation (Upper Muschelkalk) and the Erfurt formation (Lower Keuper).~~**~~4.2 Flow path continuity and aquifer grouping inferred from geology and hydrochemistry~~** ~~Although we identify two major aquifer assemblages, t~~

5.1.1 Aquifer structure evaluated by lithology

~~he chemistry of the groundwaters fall into five distinct clusters.~~ The lithologically defined aquifer-aquitard succession in combination with the increase in karstification towards the base, and the preferential presence of groundwater at the base of limestone packages point to confined aquifers with stratigraphic flow control (Klimchouk and Ford, 2000; Goldscheider and Drew, 2007). ~~Furthermore,~~As hydraulic heads and chemical groundwater compositions of different aquifers at the same sites [H13/14 (cluster 1); H41/42 (cluster 2 and 4); H51/53 (cluster 3 and 5)] are significantly distinct, vertical communication between aquifer storeys is highly reduced. ~~, indicating no vertical connection.~~ Thus we interpret the thin aquifer beds as confined, "sandwich flow type" aquifers (term: White, 1969; Klimchouk, 2005) which are interbedded with confining aquitards. The assumed lateral continuity of aquifers and aquitards results in a "layer-cake" aquifer architecture which has been demonstrated for the Upper Muschelkalk of Central Europe (Aigner, 1982, 1985; Merz, 1987; Simon, 1997; Borkhataria ~~et al.~~ et al., 2005).

Secondary mineralizations, that indicate groundwater flow (for instance Liesegang banding), occur on limestone fracture walls~~s~~. Fracturing of aquifer rocks increases close to the (NE-SW-striking) fault zones (Hoppe, 1962) and karstification follows the network of faults (Goldscheider and Drew, 2007). Red and brown iron and manganese oxides on upper to mid~~dle~~ slope fractures (H1/2/3; cluster 1 and 2) ~~signal~~ indicate temporarily unsaturated conditions, whereas green/gray fracture minerals in the ~~lower slope~~footslope domains (~~HTU,~~ H4/H5, cluster 4/5) point to permanently water-saturated conditions ~~(and likely anoxic conditions, for instance no~~due the lack of oxidized Fe/Mn-minerals~~)~~. Corrosion occurs ~~as~~ in the form of intrastratal karstification, ~~which means~~i.e. one or more layers of soluble strata is covered or sandwiched between insoluble beds (Palmer, 1995). Karstification is consistently high in the thick bedded aquifer storey (moTK-1~~, HTL~~) and less pronounced in ~~thinly~~ thin-bedded aquifer storeys (moM-1/4/5/6~~; HTU~~; Fig. ~~6~~4) as the bed thickness controls continuity, spacing and width of joints (Goldscheider & Drew, 2007). In general, the lithological definition of hydrostratigraphy allows a structuring with a high spatial resolution.

5.1.2 Evaluation of groundwater chemistry

Stratigraphically deep aquifers in summit positions are grouped in Cluster 1 (aquifer storey moTK-1 and moM-1). Cluster 2 (moTK-1 and moM-5+6) encompasses deep and stratigraphically intermediate aquifer storeys in midslope positions and cluster 3 (moTK-1) a deep aquifer storey in the footslope position. Shallow aquifer storeys (moM-6//7/8) in midslope position within a local valley are grouped in cluster 4 and intermediately deep aquifer storeys (moM-3/4/8) are grouped in cluster 5. According to this grouping, the slope position and the depth below surface is important, likewise to the depth level within the hydrostratigraphy (= the aquifer storey).

Principal component analysis (PCA) using the complete parameter set (a) ~~does not simply reflect aquifer stratigraphy, as~~infers, that ~~each~~ aquifer ~~assemblage~~ storey contains more than one type of groundwater chemistry (Fig. ~~6~~7). By contrast, the PCA (b) carried out with the limited parameter set (without redox-related parameters) shows a clear separation of ~~HTL~~ moTK-1 and ~~HTU~~ moM-1-9 aquifer ~~assemblages~~ storeys (except cluster 2). ~~The comparison of groundwater samples, that fall in the individual clusters, with the control factors derived from the PCA (using parameter set a), depends on aquifer rock type, slope position, land use and soil group in the recharge area as well as with the proximity to karstification zones results in the following interpretation of the clusters:~~

According to the PCA, cluster 1 encompasses high factor charges in pH, Eh, O_2, NO_3^- and low factor charges in Mg^{2+}, Na^+,

K^+, Si^{4+}. The same is less markedly applied for cluster 2 whereas factor charges in cluster 5 point in opposite directions. We explain this linear trend of cluster grouping as a consequence of a trend of the chemical evolution from summit wells (cluster 1) with small recharge areas and shallow aquifers towards midslope (cluster 2) and footslope (cluster 5) passages with thicker overburden strata The latter are affected by minor surface influences and longer groundwater travel times/residence times within the bedrock. Data points of different aquifer storeys are grouped (but within the clusters), and slope position and aquifer depths seem to be more important for groundwater chemistry than the position in hydrostratigraphy, here. Apart from this trend, cluster 3 which is limited to the deepest well (in footslope position) exhibits high factor charges in Ca^{2+}, SO_4^{2-}, EC, Sr^{2+} and low charges in Ba^{2+}, HCO_3^-, $Fe^{3/4+}$, $Mn^{2/4+}$, whereas cluster 4 (limited to shallow wells in midslope position) shows opposite factor charges for these parameters. In general, clusters are grouped in a line of chemical development and by oxic/anoxic conditions and different mineralizations depending on the position in aquifer stratigraphy.

5.1.3 Modes of groundwater flow

Within the aquifer-aquitard-sandwich, fast conduit groundwater flow, which is typical for karstified carbonate rocks (Wong et al., 2012), likely takes place in the moTK-1 and partially in the moM-1 aquifer storeys, whereas slow diffusion in slightly fractured, thin aquifers beds is anticipated in the moM-2 to moM-9 aquifer storeys. Confined diffuse flow is considered laminar and takes place in interparticle pores and fractures of dense limestones with low primary porosity (Smart and Hobbs, 1986). This results in the well oxygenated moTK-1 and moM-1 groundwaters and a significant oxygen consumption/deficiency (coupled to the mobility of Fe^{2+} and Mn^{2+}-ions and the low mobility of NO_3^- and SO_4^- ions) in the moM-2 to 9 groundwater, resulting in completely different milieu conditions for the biogeochemical processes and for the life in the subsurface as well.

5.2 Surface-subsurface connectivity

~~**4.1 Groundwater recharge**~~Potential zones for interactions between surface and subsurface waters are the outcrop areas of the aquifers, incised valleys (cutting into the stratigraphic succession), springs and surface karst phenomena. Nearby faults and valleys, an increased number of additional non-stratabound, connected fractures that provide pathways for pronounced and preferential fluid flow (Meier et al., 2015) are likely.

5.2.1 Preferential r~~R~~echarge areas

As a typical feature of aquifer-aquitard alternations in a tilted hillslope setting, p~~P~~referential recharge ~~areas for the aquifer storeys match with the~~ takes place at the aquifer outcrop zones (Andreu et al., 2011; Fig. 2 A). Based on the tectonically tilted and subsequently exhumed hillslope, the main aquifer recharge area is situated in the upper hillslope/summit area, which is covered by forest with very low anthropogenic impact. A predictable geological structure allows a general tracking of flow paths from the recharge to the discharge area. ~~It is reasonable to infer that catchment sizes, travel distances and residence times are generally larger for lower slope wells (site H4/5) compared to upper slope wells (site H1/2). Valley incision forces partial exfiltration of moM 3 to 9 groundwaters via contact springs and thus reduces the effective catchment size of these aquifers storeys. Additional concentrated~~ The second route for preferential ~~infiltration~~ recharge ~~takes place in~~is related to the lines of caprock sinkhole~~s~~ lineaments, which can be tracked over more than four kilometers in the mid~~dle~~ slope between transect locations H2/3 and H4. The origin of these sinkholes does not lie in the karstification of the Upper Muschelkalk strata itself, as the combination of aquifer fracture networks (tight conduits) and stabilizing, insoluble aquitard beds do not cause sufficient mass deficits that will allow hanging wall collapses. Here, caprock sinkholes are related to mass deficits by subrosion in the underlying evaporite rocks with gypsum and halite (Mempel, 1939; Malcher, 2014). As caprock sinkholes are arranged in lineaments (Fig. 2 A) parallel to regionally known fault orientations, it is very likely that they are coupled to the penetration of surface/subsurface water at fracture zones (compare to: Smart and Hobbs, 1986; Worthington,

1999; Klimchouk, 2005), that promote preferential recharge (Smart and Hobbs, 1986; Suschka, 2007). Although dissolution of soluble rocks is limited within the target aquifers of this study, it is reasonable, that collapse structures are accompanied by enhanced rock fracturing and permeability. ~~Lineaments of sinkholes likely represent fracture zones (Smart and Hobbs, 1986; Worthington, 1999; Klimchouk, 2005) and are here related to the fault-related penetration of surface water and the subsequent subrosion of Middle Muschelkalk evaporites like salt and gypsum (Mempel, 1939; Malcher, 2014).~~

5.2.2 Influences of soils in the recharge area ~~Soil distribution and soil development~~

The spatial distribution of the soil groups reflect the outcrop zones of limestones/marlstones (Greitzke and Fiedler, 1996; Brandtner, 1997; Rau and Unger, 1997) and the succession of aquifer storeys in the summit/shoulder area of the hillslope which exhibits little quarternary rocks coverage and thin soils (Rendzic Leptosol, Chromic Cambisol) with favorable infiltration properties in the aquifer outcrop areas of moTK-1 and moM-1/6/8. Thicker relictic Chromic Cambisols which are formed by intensive decarbonatization (Rau and Unger, 1997; AG Boden, 2005) are restricted to accumulations in former depressions (i.e. caprock sinkholes) on shoulder regions of the hillslope (moTK-1 and moM-1 outcrops). ~~Chromic Cambisols are relict soils in Germany (AG Boden, 2005) and represent the final stage of decarbonatization (Rau and Unger, 1997).~~ Besides these depressions, Chromic Cambisols with low hydraulic conductivities are typically the subsoil layer of sequences with two layer superimposed soils, resulting in lateral soil interflow (Ali et al., 2011) as it is observed in the shoulder and midslope region during the measurement of soil hydraulic conductivities. Soils on unfractured marlstone/claystone aquitards are typically Calcaric Regosols and Stagnosols with low hydraulic conductivities of both, soils and parent rocks. According to our dataset, soil thickness is primarily controlled by the slope gradient of transverse valleys with increasing soil thickness and water storage options towards the center of valleys. As a result of the increasing coverage of parent rocks by loess loam from the regional midslope to the footslope, (related to solifluction of windblown dust; Kleber, 1991; Bullmann, 2010), loess loam becomes the dominating soil substratum in the outcrop areas of aquifer storeys moM 7-8-9. In this area, Luvisols cover local ridges and Luvisol-Stagnosol-transitions (related to the continuous vertical clay relocation (Rau and Unger, 1997) cover local valleys, whereas older caprock sinkholes are either filled by colluvisols or with loess loam, leading to either poor or very good infiltration/recharge properties. In the same context, Bachmair et al. (2009) considers the role of micro-depressions in soils as one of the major factors for preferential recharge.

Although median grain size, grain size sorting and the standard devitation of grain size fractions is comparable in all soils, “carbonate series soils” (Rendzic Leptosol and Chromic Cambisol) offer higher hydraulic conductivities than “siliceous series soils” (Cambisol, Luvisol, Stagnosol) by one order of magnitude. Soil hydraulic conductivities (Ks) are uncorrelated to soil texture properties. For this reason a linear transfer function (Ks vs. median grain size or grain size category) for extending the 16 Ks measurements to the 271 mapped soil profiles was not possible with the actual dataset. A low correlation between Ks and texture is related to strong influences of soil structure and aggregation (Totsche et al., 2017) rather than texture on Ks. Structural parameters are for instance the content and proportion of macro and microaggregates, a hierarchical aggregate system, the presence and frequency of secondary pores and anthropogenic changes like former plough traces or traces of forestry machines. Bachmair et al. (2009) for instance identify tillage-related macropores as a main factor for deep infiltration into cropland soils, whereas surface littler layers inhibit infiltration in forest soils. Moreover preferential infiltration through biomacropores (i.e. earthworm borrows, root channels), that bypass the soil matrix are of great significance in aggregated and argillaceous soils with low matrix conductivity for the infiltration during heavy rain events (Deurer et al., 2003; Weiler and Naef, 2003; Blouin et al., 2013). Klaus et al.,(2013) identify vertical macropores of anecic earthworms as a major flow control in a hillslope tile drain system. Wienhöfer and Zehe (2014) additionally consider loose, litter-rich topsoils, lateral preferential pathways, preferential pathways at the soil-bedrock surface and bedrock topography. ~~Soil groups reflect geology and slope position: in the upper slope position and on steep slopes, the soil groups (Rendzic Leptosols, Calcaric Regosols and Chromic Cambisols) are determined by the carbonate rock parent material (Greitzke and~~

Fiedler, 1996; Brandtner, 1997; Rau and Unger, 1997). Chromic Cambisols are relict soils in Germany (AG Boden, 2005) and represent the final stage of decarbonatization (Rau and Unger, 1997). Soil groups in moderately inclined mid slope and toe slope positions are Luvisols and Stagnosols developed from (solifluction) mixed carbonate (marlstone) and siliceous (loess) material (Kleber, 1991; Bullmann, 2010) by continued clay relocation to the subsoil (Rau and Unger, 1997).

5.2.3 Influences of land management in the recharge area on groundwater quality

The forest areas as a source of groundwater from catchment-near summit/shoulder wells are confirmed by their aquifer outcrop areas (moTK-1, moM-1) within the managed (and partly unmanaged) forest. In contradiction, we detected potentially agriculture-related substances (NO_3^-, K^+, Cl^-) in the wells drilled to all aquifer storeys in midslope location wells (H31/41), although,these groundwater types are recharged mainly within the forest (up to 96.5 % forest). These surface signals are interpreted to be related to the cropland and village areas within the preferential recharge zones with sinkhole lineaments. Anoxic groundwater in aquifers (moM8/9) partially recharged from outcrop areas with agricultural and village land use, are likely attributed to microbial oxygen depletion resulting from the degradation of organic carbon or oxidation of inorganic electron donors. For shallow wells in valleys (H42/43/4S), lateral soil water inflow with high organic/fertilizer load towards the valley is a second option for enhancement of oxygen depletion. Much lower NO_3^-, K^+, Cl^- concentrations in the footslope wells (H52/53) are likely a consequence of the argillaceous caprocks that increase in thickness towards the footslope.

The type of land management influences the infiltration properties (Hohnvehlmann, 1995). For the same soil group, Ks values are higher on cropland in comparison with forest and pasture. Land use related differences are greater for topsoils than for subsoils. Aquifers in (fertilized) agriculturally used catchment areas (for instance aquifer moM 9), are anoxic, probably due to microbial oxygen depletion resulting from the degradation of organic carbon compounds or oxidation of inorganic electron donors. Catchment areas (defined for all individual aquifers) show a predominance of forest land use (44.5 to 96.5 % forest). However we detected potentially agriculture related substances (NO_3^-, K^+, Cl^-) in the wells drilled to all aquifer storeys in middle and lower slope locations (H3/4/5) wells. This points to a influence of surface waters entering the aquifers vertically via fractures or caprock sinkholes.**Infiltration properties of soils and the unsaturated zone**

The thickness, clay content and clay distribution in soils influence the infiltration (Smart and Hobbs, 1986). Overall infiltration properties decrease from the upper slope towards the lower slope with increasing thickness of young cover strata like loess loam (Kleber, 1991; Bullmann, 2010). Infiltration is assumed to be inhibited by thick argillaceous soils in alluvial valleys, uvala like depressions and local toe slope settings, with accumulations of alluvial/colluvial clay (Fig. 2). However, plateau positions (with reduced erosion) at the crest of the Hainich hillslope also show thicker cover strata and thus low infiltration. Fracture and karstification zones like sinkholes or dry valleys (in upper slope positions of the study area) promote the preferential infiltration (Smart and Hobbs, 1986; Suschka, 2007). Two layer soil profiles (Cambisols/Luvisols overlying Chromic Cambisols) inhibit infiltration and promote soil water interflow within the topsoil or at the topsoil subsoil interface.

Rendzic Leptosols of upper slope positions offer better infiltration properties (Hiekel, 2004) than Cambisols, Lithic Udorthents and argillaceous Chromic Cambisols (Brandtner, 1997). Young/initial Luvisols, developed from predominantly silty loess loam show better infiltration properties than mature Luvisols and Stagnosols with layers of subsoil clay. Water of short and heavy rain events preferentially infiltrates through macropores (desiccation cracks and biopores/earthworm burrows), bypassing the soil matrix pores (Luxmoore, 1991; Edwards and Bohlen, 1996).Two layer soil profiles (Cambisols/Luvisols overlying Chromic Cambisols) inhibit infiltration and promote soil water interflow within the topsoil or at the topsoil subsoil interface. Water of short and heavy rain events preferentially infiltrates through macropores (desiccation cracks and biopores/earthworm burrows), bypassing the soil matrix pores (Luxmoore, 1991; Edwards and Bohlen, 1996). Intense surface karstification and fracturing is found in valleys, which represent zones of local geostructural

~~weakness (Klimchouk, 2005) as well as the more regional fracturing found in the upper slope (Mempel, 1939; Hoppe and Seidel, 1974; Jordan and Weder, 1995).~~

~~The land use type also influences the infiltration properties (Hohnvehlmann, 1995), as it is discussed and classified by Dunne and Leopold (1978) for the United States. The soils of the former military (tank) training area very likely inhibit infiltration and favor surface runoff due to compaction. Cropland cultivation modifies soil fabrics, reduces the humic content and increases the soil bulk density. Aquifers in (fertilized) agriculturally used catchment areas (for instance aquifer moM-9), are anoxic, probably due to microbial oxygen depletion resulting from the degradation of organic carbon compounds or oxidation of inorganic electron donors. Catchment areas (defined for all individual aquifers) show a predominance of forest land use (44.5 to 96.5 % forest). However we detected potentially agriculture related substances (NO_3^-, K^+, Cl^-) in the wells drilled to all HTU and HTL aquifer assemblages in middle and lower slope locations (H3/4/5) wells. This points to a significant influence of surface waters entering the aquifers vertically via fractures or sinkholes.~~

5.2.4 Utilization of the recharge potential for interpreting groundwater quality

Due to the recharge potential map (Fig. 8), thick, limestone-dominated aquifer storeys in the deeper sections of the hydrostratigraphy (i.e. moTK-1) are mainly recharged in their outcrop areas and subordinarily in sinkhole lineaments and transverse valleys. Within these areas, Ah-Cv soils (i.e. Rendzic Leptosol) and fractured limestone bedrocks offer the highest recharge potential. A drastic decrease in recharge potential with increasing overburden strata is confirmed by low concentrations in surface-related substances (i.e. NO_3^-.Cl^- , K^+) in well sites H1/2/4/5 for the aquifer storey moTK-1. Increasing concentrations of ions, which are related to the dissolution of the carbonate (aquifer) bedrock (Ca^{2+},Mg^{2+}, HCO_3^- and Sr^{2+}) point to an evolution of groundwater in the direction of discharge (H1 to H5). A moderate to high recharge potential combined with cropland/pasture areas) in the recharge direction of site H3 is reflected by increased concentrations in TOC, NO_3^-.Cl^- , K^+, Na^+ and O_2 (Fig. 6 and 8). Aquifer storeys with thin-bedded limestone-marlstone alternations (i.e. moM-8, Fig. 8) generally show a lower recharge potential in their aquifer outcrop zones, compared to thick, limestone-dominated aquifers (moTK-1), which is related to thicker soils and a high marlstone-limestone ratio. This is reflected in the groundwater quality of moM-8 wells (H42/43/53) with low Eh and low concentrations in O_2, pointing to slow flow velocities and long residence time within the argillaceous soils and marlstone-dominated and thinly fractured bedrocks.

5.2.5 Flow directions

The four modes of presumed groundwater flow are (1) vertical percolation, (2) bedding-parallel flow, (3) descending, cross-formational flow and (4) ascending cross-formational flow. (1) Vertical percolation through the soils and the unsaturated zone takes place in the whole Hainich CZE catchment area, following diffuse/non-point infiltration. As the aquitard interbeds highly reduces vertical flow connections, outcrop zones of the aquifer storeys as well as caprock sinkholes act as important preferential infiltration pathways which are typical for hillslope recharge zones. Since caprock sinkholes remain dry, even directly after precipitation events, high infiltration rates can be assumed for these structures. (2) An undisturbed sequence of aquifers and aquitards with constant bed characteristics, comparable groundwater chemistry within the same aquifer storey and the high pressure heads (well H51/52/53: 70/50/20 m rise within the well pipe) are interpreted to indicate bedding-parallel flow (stratigraphic flow control; Goldscheider, 2005) in the groundwater transit zone. This is supported by the spatial variation of groundwater chemistry within the same aquifer storey (i.e. increase in K^+, Na^+, Mg^{2+} and Si^{4+} within moM-8 from well site H4 to H5), provided a cut-off from surface influences, there. Also the combination of saturated conditions within the shallow storey and temporarily unsaturated conditions within the lower aquifer storey in well site H3 points to highly reduced vertical flow.~~In this study we distinguish between three different modes of subsurface water flow could be distinguished: (1) Vertical and descending water flow (gravitationally driven) takes place in the recharge areas of the aquifers at the crest and upper slope zones of the Hainich hillslope (including sites H1/2, HTL, cluster 1). (2) Bedding-~~

~~parallel, confined groundwater flow (stratigraphic flow control, Goldscheider, 2005) occurs in the tectonically undisturbed zones, with intact aquitard interbeds, between, and downstream the two sinkhole lineaments of caprock sinkholes. Confined flow could explain the long water-rock contact times in cluster 5 (HTU) and also the very low concentrations of NO3 , NO2 and NH4+ (with potential agricultural origin) of cluster 4 (HTU) aquifers, which are sealed at the top.~~ Bedding parallel flow is also supposed for fractures with small fault displacements that do not exceed the thickness of the interbedded aquitard (compare to Goldscheider & Drew, 2007). ~~This situation is probably applied to the straight and equidistant oblique transverse valleys, which are probably fault zones.~~ (3) Zones with enhanced fracture indices (fractures/m drill core) in well sites H3 as well as consistent Fe/Mn-oxide fracture walls in all aquifer storeys of this site points to a quick and cross-formational descending flow of oxygenated groundwater (thus with low Fe/Mn mobility; Hem, 1985) via vertical master joints (term: Dreybrodt, 1988; Ford and Williams, 2007) close to potential fracture zones. This is supported by higher concentrations in Na^+, K^+, NO_3^-, Cl^- and TOC in the deeper site of H3 compared to the shallower well of this site, related to agriculture and fertilizing (Matthess, 1994; Kunkel et al., 2004). Cross-formational descending flow in shattered or fractured rocks is assumed to take place in fracture zones (Worthington, 1999; Goldscheider & Drew, 2007), tracked by lineaments of caprock sinkholes (Mempel, 1939; Hoppe, 1962; Smart and Hobbs, 1986; Jordan and Weder, 1995). (4) Groundwater chemistry of footslope well H51 (screen base at the base of moTK-1 aquifer) bears a combination of highly concentrated in Ca^{2+}, SO_4^{2-}, Sr^{2+}, Cl- (and SO_4^{2-}/HCO_3^--ratios) and low concentrations in K^+, Na^+, NO_3^- concentrations which point to a non-surface import of sulphate (-chloride) groundwater due to dissolution of evaporites (Edmunds and Smedley, 2000). The location of this lowermost aquifer storey directly above dolomite, gypsum and halite beds (Middle Muschelkalk; Jordan and Weder, 1995) points to ascending cross formational groundwater flow (Garleb, 2002; Völker and Völker, 2002). The ascent of groundwater which is well known for artesian settings (Klimchouk, 2005), could be related to hydraulically confined conditions as measured for site H5 and the assessed groundwater flow crossing a sinkhole lineament between well site H4/H5 (Fig. 10). Alternatively, the ascent of Middle Muschelkalk-groundwaters is probably related to a decrease in permeability within the Middle Muschelkalk aquifers, as subrosion of sulfate rocks (succeeding from the summit to the footslope region) has not reached the groundwater transit zone yet, resulting in the presence of low permeable sulfate rocks and an ascent of groundwaters discharging the Middle Muschelkalk (Hoppe and Seidel, 1974; Garleb, 2002).~~(3) Cross-formational flow through open faultsin shattered or fractured rocks is assumed to take place in fracture zones (Worthington, 1999; Goldscheider & Drew, 2007), tracked by lineaments of caprock sinkholes (Mempel, 1939; Hoppe, 1962; Smart and Hobbs, 1986; Jordan and Weder, 1995). Descending flow of surface waters very likely takes place in the middle slope caprock sinkholes with the sites H3/4 downstream (cluster 2, HTL and HTU wells) and ascending groundwater flow is supposed for the lower footslope well H51 (cluster 3 HTU, Fig. 8).~~

~~In the case of all aquifer storeys flow conditions are confined, preferential groundwater recharge takes place in the upper shoulderslope positions (outcrop zones) and regional discharge is towards the NE, due to lithology and orientation of the strata.~~

5.3 Controls on groundwater quality and groundwater provenance

Cluster 1 comprises the shallow to intermediate deep moTK-1 (H13/21) and moM-1 (H14) wells with a base depths of screen sections between 7.0 and 30.5 m. Groundwater chemistry with ~~Cluster 1 (upper slope HTL wells H13/21 and HTU well H14) comprises the moTK-1 aquifer storey in shallow (near surface) positions with recharge areas, exclusively used as forest. Relatively~~ high HCO_3^- and Ca^{2+} as well as low Mg^{2+}, SO_4^{2-}, Na^+, K^+, Si^{4+} concentrations (Fig. 8) correspond with the pure calcite limestone ($CaCO_3$) aquifer lithology. ~~without any gypsum and very thin marlstone (clay mineral) interlayers.~~ Low concentrations in Cl^-, K^+, Na^+, Mg^{2+} are related to parts of the catchment area that is exclusively used as forest and to soils (mainly Rendzic Leptosols) with high hydraulic conductivities and with little clay content, resulting in short residence

times of water in soils. Relatively high concentrations in TOC are interpreted as little organic degradation due to short travel times. Fast infiltration also arises from aquifer outcrop zones in culmination areas, that allows a high ratio of infiltration vs. lateral soil interflow. According to the PCA, Cluster 1-wells could be interpreted as one end member at the beginning of a "groundwater development series". Generally, groundwater compositions in summit-near regions of hillslopes are comparable to the composition of the bedrock. Surface signals (i.e. soil or vegetation-derived organic carbon) can be traced more clearly due to little organic degradation (and low filtering) along the flow path by the soils and bedrock pores/fractures.

Cluster 2 encompasses moderately deep moTK-1 wells (H31/41) and one moM-5/6 well (H32) with base depths of screen sections between 22.0 and 47.5 m. The hydrochemistry with moderate concentrations in Ca^{2+}, Mg^{2+}, SO_4^{2-} and low K^+, Na^+ as well as high Mg/Ca-ratios is not linked to the pure calcite limestones (moTK-1) or the calcite, illite/kaolinite/chlorite mineral composition (moM-5/6) and requires an external source of Mg^{2+}. Nitrate and TOC contents are higher than expected by the forest (moTK-1)/forest-dominated type of land management (moM-5/6) in the aquifer outcrop zones and are likely explained by cropland/pasture in a sinkhole lineament in the recharge zones of sites H3/4. Oxygenated groundwater~~s~~ in both aquifer storeys (thus with low Fe/Mn mobility; Hem, 1985) and a high degree in rock fracturing and fracture mineralization with Fe-/Mn-oxide minerals (aquifer storeys moM-9/8/7 and 6), point to a vertical penetration with near surface groundwater via fracture zones through all aquifer storeys. Enhanced concentrations in Na^+, K^+, NO_3^-, Cl^- and TOC (Fig. 7) are likely related to agriculture and fertilizing (Matthess, 1994; Kunkel et al., 2004) around the sinkhole lineaments. As nitrate, which is generally derived from agricultural fertilizers (Agrawal et al., 1999; Jeong, 2001), is still present in the deep aquifer waters of site H3, vertical bypassing through master joints (term: Dreybrodt, 1988; Ford and Williams, 2007), must be faster than the denitrification process. Quick infiltration is here mostly related to the preferential sinkhole recharge, as the soils (Luvisol/Cambisol, both with low-conductive subsoils and a high degree in lateral soil interflow) in the outcrop zones bear only moderate to poor soil hydraulic conductivities. In general groundwater in the discharge of exceptionally highly conductive preferential recharge spots can reflect surface signals, even in stratified aquifer/aquitard successions. These zones are therefore suggested to be of uppermost importance for groundwater protection. ~~Cluster 2 (HTL in middle slope wells H31/41 and HTU well H32) includes aquifer storeys in shallow and moderate depth with mixed forest and agricultural catchment. The sites H3/4 are located in the discharge of a prominent karstification zone with sinkholes crossing the line of the research well transect. In addition, round and elongated areas on cropland (recognized on aerial images) with increased soil thickness (inferred from soil mapping), point to former/filled sinkholes.~~

Cluster 3 contains groundwater of the deepest moTK-1 well (screen base 88 m) drilled to a cropland plot in the footslope area. As it is discussed in 4.2.5, ascending sulphatic groundwater is likely responsible for the SO_4^{2-} - HCO_3^- type of groundwater. High chloride concentration is interpreted with a long groundwater travel distance. Very weak surface signals (in form of low nitrate and TOC concentrations) attest the inhibition of vertical infiltration by aquitards and a likely result from long groundwater travel distances (high reseidence time) from the forest recharge zone of the moTK-1 aquifer. However, high groundwater oxygen concentration in more than 5 kilometers from the capture zones requires a very quick oxygen supply by more rapid flow events. In general, deeper groundwater in the transit zone may bear surface signals, if flow velocities are great enough for transporting young groundwaters into the subsurface. This is applied for the more karstified aquifer storeys in aquifer/aquitard successions. ~~Cluster 3 (HTL in footslope well H51) encompasses the moTK-1 aquifer storey in depths of greater than 85 meters, with more distant (4-5 km) forest catchment. Very high concentrations of Ca^{2+}, SO_4^{2-}, Sr^{2+}, Cl^- (and SO_4^{2-}/HCO_3^- ratios) that do not reflect the pure limestone ($CaCO_3$) lithology of this aquifer storey, as well as the combination with low K^+, Na^+, NO_3^- concentrations point to a non-surface related source of sulfatic waters. A non-agricultural source of SO_4^{2-} is supported by significantly lower sulfate concentration in the more surface-near wells of (H52/53) of the same site. Increased Cl^- concentrations could be due to dissolution of evaporites (Edmunds and Smedley,~~

2000). The geostructural position in the discharge of a karstification lineament (fracture zone) and the stratigraphic position (of HTL), directly overlying the Middle Muschelkalk subgroup (containing Ca (Sr) sulfate rocks; Jordan and Weder, 1995) point to the import of rising sulfatic Middle Muschelkalk groundwaters (Garleb, 2002; Völker and Völker, 2002). Mixing of Ca-sulfate and Ca-carbonate waters results in an oversaturation and precipitation of calcite and a decrease in alkalinity (Moral et al., 2008), which is supported by a slightly lower pH in well H51. The ascent of confined groundwaters from stratigraphically lower to higher formations, which is well known for artesian settings (Klimchouk, 2005), is assumed to be coupled to a certain threshold value of confinement and hydrostatic pressure, that is probably reached between the well sites H4/5 (cross section in Fig. 8). Alternatively, the ascent of Middle Muschelkalk groundwaters could be promoted by the lateral permeability decrease from the recharge to the discharge area within the Middle Muschelkalk aquifers of the Hainich region. This decrease in permeability is related to a "subrosion front" (probably between site H4/5; Fig. 8), as the dissolution of sulfate rocks is completed (high permeability) in the recharge area whereas impermeable sulfate rocks are still present in the discharge area (Hoppe and Seidel, 1974; Garleb, 2002).

Cluster 4 includes groundwater of the shallow moM-6/7/8 wells H42/43/H4SB with screen depths in 11.5 to 19.0 m. Low-conductive alluvial cover sediments reduce vertical infiltration drastically. High HCO_3^- and low Na^+, K^+, Si^{4+}, Sr^{2+} concentrations as well as the moderately high Mg/Ca ratio in the groundwater reflect the calcite and dolomite aquifer mineralogy. Cluster 4 (HTU in valley position wells H42/43/44) includes aquifer storeys in shallow depth with thick (> 5 m) alluvial (argillaceous) cover sediment in valley position, with mixed forest/agriculture/village catchment. The aquifer lithology (limestones) is reflected by high HCO_3^- groundwater concentrations. Low K^+, Na^+, Si^{4+} point to a small influence from marlstones (clay minerals; Bakalowicz, 1994), and thus the alluvial, argillaceous sealing strata at the top is very likely intact. High $Fe^{(2+ \text{ and } 3+)}$, $Mn^{(2+ \text{ and } 4+)}$ and low SO_4^{2-} concentrations correspond to a low redox potential and the absence of dissolved oxygen, controlling the mobility of these ions (Hem, 1985; Hsu et al., 2010). Although the aquifer catchment of moM-6/7/8 is of mixed forest/agriculture/village type, TOC and NO_3^- concentrations are low, due to the consumption of organic matter and the denitrification under anoxic conditions (Agrawal et al., 1999). Relatively high Cl^-, K^+ concentrations are probably remnants of agriculture/village-related surface signals. The discrepancy of a close distance to the recharge area and the low oxgen content could be explained by low hydraulic subsoil conductivities of moM-7 outcrop area (Luvisols, Stagnosols, Cambisols) and very narrow fractures in the aquifer rocks of moM-8. Generally aquifer confinements in valleys of hillslope aquifers could result in low aquifer quality, directly depending on the fracture sizes and soil hydraulic conductivities. Under the given physico-chemical conditions, the NO_3^- concentration is low due to the denitrification by anaerobic bacteria (Agrawal et al., 1999).

Cluster 5 encompasses groundwater from deep (50.0 - 69.0 m screen depths) aquifers storeys moM-3/4/8 (wells H52/53) Cluster 5 (HTU in footslope wells H52, H53) comprises aquifer storeys which are covered by very thick (> 40 m), low permeable cover strata (Erfurt formation, Warburg formation). and long (flow) distances (> 3 km) to their recharge area. Based on the aquifer lithology, groundwater discharges through interbedded limestones and marlstones. High K^+, Na^+, and Mg^{2+} and Si^{4+} concentrations point correspond to long residence times of groundwater (Bakalowicz, 1994; Khan and Umar, 2010) in marlstone/limestone successions due to the distant (>3 km) recharge zones. If the grouping of groundwater types in the PCA represents a "chemical evolution series", then cluster 5 stands for the most developed /oldest groundwater. In general, caprock-covered footslope aquifers with narrow fractures contain likely more developed groundwaters that mostly reflect subsurface influences and less surface influences (i.e. in comparison with more conductive aquifers of the same well site H5). to long residence times with clay minerals (Bakalowicz, 1994). High silica concentrations are proportional to (long) residence times of groundwater in the subsurface (Khan and Umar, 2010). Low NO_3^- concentrations correspond with low redox potentials due to the denitrification of nitrate (Jang and Liu, 2005).

5.4 Assessment of vulnerability factors

The configuration of the aquifer system in the hillslope setting also controls the groundwater resource vulnerability. With our multi-method investigation of the different subsurface compartments, we also revealed factors of the areas´ intrinsic vulnerability. Characteristics of intrinsic vulnerability are solely controlled by hydrogeological properties of the aquifer and overburden (Vrba and Zoporozec, 1994), and integrate the inaccessibility (i.e. by low-permeable cover strata) of the saturated zone and the attenuation capacity (retention, turnover) of the overburden (Adams and Foster, 1992).

The stacking of aquifers/aquitards, the coverage with caprocks and the lateral continuity of strata reduces the overall dominating disperse infiltration and, thus the intrinsic vulnerability. Threatening of single aquifer storeys or assemblages is predominantly controlled by fractures/faults (valleys) or karst phenomena bypassing the protective cover of soils and unsaturated zones (Fig. 8). A moderate degree of physical filtering by the narrow fractures, which are the predominant flow paths, is assumed. Also the claystone and marlstone interlayers bear a certain filtering of contaminants by sorption. The preferential recharge/outcrop zones of the aquifer storeys are characterized by generally highest vulnerability. However, these zones, located in the summit to upper midslope of low mountain ranges, are mostly covered by forest. Generally, the summit position of outcrop zones of the main aquifer storey (moTK-1) lowers the risk for contamination, paradoxically, due to the thin soils that prevented lasting agricultural use and settlements. Further zones of higher vulnerability are located in the discharge of sinkhole lineaments or fracture zones that bypass surface water or percolates into the aquifers. A mapping and structural investigation of these geostructural links will be recommended for (i.e.) proper dimensioning of drinking water protection zones. In comparison to classical karst sites (i.e. massive carbonates) with pronounced karst phenomena, (Doerfliger et al.,1999, Witowski et al., 2002), our portrayed setting shows an overall low to moderate vulnerability, that is locally elevated by inherent factors (outcrop zones) and inherited features (i.e. karstification of the underlying Middle Muschelkalk subgroup).

~~4.3 Controls for variations in karstification~~

~~Karstification and carbonate dissolution is mainly controlled by CO_2 exchange, and thus related to the concentration of dissolved CO_2 in the groundwater (Zötl, 1974; Powell, 1977; Dreybroth, 1981; Hoffer-French and Herman, 1989) as it is exemplified below:~~

~~Calcite dissolution: $CaCO_3 + CO_2 + H_2O \leftrightarrows Ca^{2+} + 2\ HCO_3^-$~~

~~Dolomite dissolution: $CaMg(CO_3)_2 + 2\ CO_2 + 2\ H_2O \leftrightarrows Ca^{2+} + Mg^{2+} + 4\ HCO_3^-$~~

~~The production of metabolic carbon dioxide within the soils is discussed as a major driving force for the karstification in the near surface carbonate rocks (Krämer, 1988; Ford and Williams, 2007), for instance in epikarst settings (Pan and Cao, 1999). With increasing distance from soil related CO_2 sources, the corrosion and the width of fractures and conduits decrease (Ford and Williams, 2007; Williams, 2008). The dissolution of calcite is a relatively fast reaction (Plummer et al., 1979). Kinetic calculations of Dreybroth (1981) infer that $CaCO_3$ saturation within karst groundwater in general is reached after a few meters. To this end, the hydrological system in karst groundwaters theoretically grades from wholly karstic to non-karstic (Ford and Williams, 2007) with 50-80 % of carbonate dissolution occurring in the uppermost 10 meters of the subsurface in unconfined settings (Smith and Atkinson, 1976). This contradicts the observed karst features and high CO_2 concentrations in our wells 4 to 5 kilometers away from the groundwater catchment.~~

~~One aspect for subsurface carbonate dissolution is the continued release of carbon dioxide by microbes living in the groundwater and rocks far away from the groundwater catchment (Lian et al., 2011). According to Gabrovšek et al. (2000), evenly distributed microorganisms deliver constant production rates of carbon dioxide, as long as organic matter and oxygen is available. In addition, microbes produce organic acids during fermentation under lowered oxygen concentrations that~~

~~occur in a deprotonated form under pH neutral conditions (for instance acetate or proprionate) or enzymes (carbonic anhydrases) that both enhance limestone weathering (Lian et al., 2011). In addition to organic acids and alcohols released during fermentation, high amounts of carbon dioxide are released. Also other anaerobic processes using Fe(III) or sulfate as terminal electron acceptor produce carbon dioxide which can be applied to the anoxic aquifer storey moM-8 (HTU, cluster 4). Alternatively, karstification may be to a large extent triggered and maintained to the provision of strongly undersaturated (mean ion sums: 123 mg/l for forest, 65 mg/l for grassland) and weakly acidic (pH: 5.9 for forest, 6.0 for grassland), precipitation-fed seepage of CO_2-containing water via fracture zones and lines of sinkholes. Such deep penetration of surface waters is supported by the presence of agriculture-born substances in the deep aquifer storey moTK-1 (HTL) of the well sites H4/5. As the groundwater compositions of all aquifer storeys are chemically different, mixing corrosion (Bögli, 1964; Wigley and Plummer, 1976) is also possible, for instance through the cross-formational mixing of HCO_3^--groundwater with rising groundwater from the Middle Muschelkalk via fracture zones. Mixing corrosion is based on the mixing of two CO_2-HCO_3^--waters with different chemical composition and both saturated in carbon dioxide (Palmer, 1995). However, more recent studies (Gabrovšek and Dreybrodt, 2000) show, that the dissolution kinetics of carbonate minerals strongly affect the intensity of karstification. In addition to the chemical aspects, turbulent flow in conduits, which is rather normal for karst aquifers (White, 1969), could enhance pre-existing fractures and conduits mechanically (Howard and Groves, 1995).~~

~~5~~ 6 Conclusions

We applied a multi-method approach for a detailed investigation of Critical Zone functioning and reconstruction of groundwater quality in the hitherto scarcely described setting of thin-bedded alternating carbonate-/siliciclastic rocks in a hillslope terrain. For the Hainich Critical Zone Exploratory that offers unique access to a multi-storey groundwater system in the common and widely distributed geological setting, we found the following factor manifestations of local geology, relief, soils and land use for recharge and chemical evolution of groundwater:~~We investigated the origin of groundwater found in aquifers of the western peripheral bulge of the Thuringian Basin developed in carbonate rocks, with the goal of understanding the potential links between geology, topography, soils, land use, water recharge and chemical evolution.~~

- Low-permeable marlstone beds within a marine succession of high lateral continuity represent a number of aquitards that cause a multi-storey hydrostratigraphy of the Upper Muschelkalk formations.
- As a multi-storey hydrostratigraphy exhibits limited vertical percolation, the outcrop zones of dipping aquifer storeys become very important as preferential surface-recharge areas for inputs of matter and energy.
- Diffuse fracture flow dominates over karst/conduit flow in the mixed/multi-layered lithology. Subsurface water flow predominantly takes place in bedding-plane parallel mode / in stratabound fractures of the limestone beds and it is trackable from the recharge areas along the storeys.
- From summit to footslope positions, travel distances and presumably groundwater ages generally increase. For the individual storeys however, travel distances to monitoring wells decrease in the downslope direction, whereas their groundwater ages very likely increase due to lower fracturing and higher retention. In the same direction, surface controls (i.e. nutrient input) decrease and subsurface controls (water-rock-interaction) increase.
- Compared to more vulnerable settings (i.e. massive carbonate karst, open karst), the mixed carbonate-siliciclastic alternations exhibit moderate intrinsic vulnerability. This is due to lateral continuity of low permeable interbeds, soil covers and caprocks, of which the latter successively increase in thickness towards the footslope. Areas downstream the caprock sinkhole lineaments (and likely transverse valleys) are likely more threatened by anthropogenic (mostly agricultural) input.
- The quality of groundwater resources with peripheral hillslope recharge benefits from extensive land management or, ideally (managed/unmanaged) forest coverage and reveals the importance of recharge area protection.

~~Due to lithological differences between HTL (moTK-1) and HTU (moM-1 to 9), the limestone-dominated, highly karstified lower aquifer assemblage (HTL) is significantly more vulnerable with regard to anthropogenic influence and pollution.Pedological/geological data infers that soil-borne particulate (for instance soil microorganisms) and dissolved substances with sizes up to tens of microns could be transported to and between the partially disjoint aquifers levels. This applies especially for Rendzic Leptosols on limestones (with earthworm borrows) and for highly permeable silt-dominated Luvisols, developed from loess, that directly cover fractured limestones.Within the aquifer-aquitard-sandwich, fast conduit groundwater flow takes place in the karstified and fractured moTK-1 (HTL) and the moM-1 (HTU) aquifer storeys, whereas slow diffusion in slightly fractured, thin aquifers beds is anticipated in the moM-2 to moM-9 (HTU) aquifer storeys. This results in oxygenated moTK-1 and moM-1 groundwaters and a significant oxygen consumption/deficiency (coupled to the mobility of Fe^{2+} and Mn^{2+} ions and the low mobility of NO_3^- and SO_4^- ions) in the moM-2 to 9 waters, resulting in completely different milieu conditions for geochemical processes and supposedly also for the life in the subsurface.~~

In general, for mixed carbonate-/siliciclastic rock alternations that are prone to develop multilayered aquifer systems, both the aquifer configuration (spatial arrangement of strata, hillside cutting, outcrop positions) and the related geostructural links (preferential recharge areas, karst phenomena) are major controls of impacting surface and subsurface factors. For the studied type of thin-bedded carbonate aquifer setting, we were able to demonstrate, that a comprehensive investigation of aquifer connectivity in the transit/discharge area as well as soil cover and land use in the recharge area is mandatory and must be rated indispensable for a thorough understanding of the state and evolution of groundwater quality. Linking groundwater hydrochemistry mostly to surface factors such as land use would result in a contradiction, as groundwater chemistry does not reflect the type of land use in immediate proximity to the wells. Furthermore, footslope wells´ hydrochemistry is strongly impacted by aquifer stratigraphy, karst phenomena input and the cross-formational ascent of sulphatic groundwater that could not be evaluated without spatial lithostratigraphical data. A geostructural investigation and mapping is essential for the localization of aquifer outcrop areas and the assumption of stratigraphy-controlled flow directions. In case the soils group and the type of land use would have been neglected, discrimination between influences by natural and anthropogenic controls would have been ambiguous. If the dataset included hydrochemistry and multivariate statistics only, the interpretation of this dataset would have been ambiguous, as different chemical surface/subsurface sources result in similar hydrochemical compositions.

Recent studies of the CRC AquaDiva focus on signal transformations of surface signals. This is for instance applied to surface-sourced organic matter and microorganisms (Küsel et al., 2016, Schwab et al., 2017, Lazar et al., 2017) to further investigate subsurface connectivity, surface-subsurface interactions and functions of microbial life in groundwater environments. Further CZ exploration should also aim the investigation of deeper strata connection by regional groundwater flow, hydraulic properties and proportions of unsaturated zones and matter processing within.~~Based on the mapping of the outcrops of aquifer storeys and infiltration pathways in near surface fractures and karst, we found that potential rain water infiltration times for the target aquifers are short, hydraulic conductivities are assumed to be high and the retention potential for airborne or soil-borne solutes is relatively low, but higher than for unconfined karst/settings. This results in a lower groundwater vulnerability, than recorded for unconfined karst/carbonate settings (Doerfliger et al., 1999; Witowski et al., 2002) that do not show a stratified aquifer/aquitard subsurface. Due to lithological differences between HTL (moTK-1) and HTU (moM-1 to 9), the limestone-dominated, highly karstified lower aquifer assemblage (HTL) is significantly more vulnerable with regard to anthropogenic influence and pollution.~~

~~Pedological/geological data infers that soil-borne particulate (for instance soil microorganisms) and dissolved substances with sizes up to tens of microns could be transported to and between the partially disjoint aquifers levels. This applies especially for Rendzic Leptosols on limestones (with earthworm borrows) and for highly permeable silt-dominated Luvisols, developed from loess, that directly cover fractured limestones. The geological sandwich structure enforces confined groundwater flow conditions. Within the aquifer-aquitard-sandwich, fast conduit groundwater flow takes place in the~~

~~karstified and fractured moTK-1 (HTL) and the moM-1 (HTU) aquifer storeys, whereas slow diffusion in slightly fractured, thin aquifers beds is anticipated in the moM-2 to moM-9 (HTU) aquifer storeys. This results in oxygenated moTK-1 and moM-1 groundwaters and a significant oxygen consumption/deficiency (coupled to the mobility of Fe^{2+} and Mn^{2+} ions and the low mobility of NO_3^- and SO_4^- ions) in the moM-2 to 9 waters, resulting in completely different milieu conditions for geochemical processes and supposedly also for the life in the subsurface.~~

Data availability

Plot data will be deposited on the BExIS2 (http://bexis2.uni-jena.de) data portal of the CRC AquaDiva (https://aquadiva-pub1.inf-bb.uni-jena.de). Access to the AquaDiva data portal for review purposes is granted. Hydrochemical data will not be shared publically at this point of time, as this paper represents the first of a series of three related papers, using similar data sets for different aims. For instance the prepared time series analysis as well as flow and transport models will rely on the same data sets.

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Author contribution

BK and RL contributed equally to this article. RL and BK organized and conducted the geological mapping, soil mapping, as well as the analysis and correlation of drill cores and geophysical logs. RL organized and partly conducted the groundwater monitoring and obtained authorization from authorities and landowners/companies. PS carried out parts of the soil mapping/description and hydrochemical analyses and carried out the descriptive and multivariate statistics. KUT, SET and KK provided editorial comments on the manuscript. KUT designed and coordinated the project and supervised the field work, data analysis, data presentation and manuscript preparation. KK, KUT and SET are speakers of the CRC AquaDiva.

Competing interests

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Tables

Table 1 Soil groups (WRB, 2003 and AG Boden, 2005), soil texture and soil hydraulic properties ~~and soil properties~~

WRB soil group	**Rendzic Leptosols, Calcaric Regosols**	**Chromic Cambisols**	**Cambisols**	**Luvisols**	**Stagnosols**	**Fluvic Cambisol**
German soil group	Rendzina, Pararendzina	Terra fusca	Braunerde	Parabraunerde	Pseudogley	Vega
Substratum	Limestone, marlstone	limestone	marlstone, loess loam	loess loam, marlstone	loess loam, marlstone	alluvial silt+clay
Thickness	5-35 cm	85-100 cm	35-80 cm	50-100 cm	80-190 cm	up to 3.3 m
Soil category ~~(grain size)~~	medium silty clay	slightly silty clay	medium silty clay	slightly clayey silt	medium silty clay	strongly silty clay
Median grain size (µm)	12.6 ± 3.6	13.3 ± 4.9	13.2 ± 3.6	17.3 ± 4.2		17.8 ± 5.0
% Clay + Fine silt	34.0 ± 7.8	33.9 ± 9.7	32.3 ± 7.0	27.0 ± 9.4		25.6 ± 9.1
Water storage capacity	low	high	high	medium	very high	very high
Roots	< 35 cm	30-60 cm	20-80 cm	20-180 cm	30-80 cm	15-40 cm
Cracks and borrows	earthworm borrows down to the host rock	earthworm borrows down to the host rock	frequent	deep borrows (voles, worms)	limited to shallow soil horizons	limited to shallow soil horizons
Decarbonatization	no	complete	almost complete	complete	incomplete	no
Typical color (subsoil)	yellowish gray 10YR3/2	dark yellowish gray 7,5YR4/3	brownish gray 10YR5/6	yellowish gray 10YR4/6	greenish gray 2,5Y4/2	yellowish gray 10YR4/3
Hydromorphic attributes	no	oxidative	oxidative	oxidative	oxidative + reductive motteling	oxidative + reductive motteling
Soil water	> 200 cm	rarely and > 80 cm	rarely and > 100 cm	rarely and > 100 cm	commonly in 1-2 m	very common > 40-60 cm
Morphologic position	middle slope + all steep local slopes	culmination + -local plateaus	culmination to middle slope	lower slope, (middle slope)	lower slope, valley	valley center
Land use	forest + military training area	forest + some grassland	cropland, grassland, forest	cropland, grassland, uncommon-ly forest	grassland, uncommon-ly forrest	grassland
Anthropogenic changes	compacted (tanks), drained	uncommon	ploughed, compacted	ploughed, compacted	drained	drained
Hydraulic conductivity Ks [m/s] (Median, ± SD)	$5.2*10^{-5}$ ± $4.9*10^{-5}$	$2.5*10^{-5}$ ± $1.2*10^{-5}$	1.5*10-^{4} ± $5.2*10^{-5}$	$1.2*10^{-4}$ ± $1.2*10^{-4}$	$6.5*10^{-7}$	not measured

Table 2 Hydrostratigraphic standard section: relative positions of aquifer storeys (this study) in comparison with a published classification (Küsel et al., 2016) in the context of the the German stratigraphy and time scale.

Time scale (DSK, 2002; Gradstein et al., 2003) [Ma]	**Level above base of moTK** [m]	**German strati-graphy** (DSK, 2002)	**Regional stratigraphy** (Central Germany. Seidel, 2003)	**Aquifer assem-blages** (Küsel et al., 2016)		**Aquifer storeys** (this study) X aquifer - aquitard	**Level above base of moTK** [m]	**Ground-water well** (screen section)
0.01...0			soils alluvial sediments (qhf)					
0.1…0.01 232.5...0.1			loess (qwLo)	erosional unconformity				
235.0... 232.5	61.3… >90.0	Erfurt formation (kuE)	Graue Mergel (kuGM)		-			
			Sandstein-komplex1 (kuS1)		X	**kuS1-2**	74.5…76.5	
					X	**kuS1-1**	68.0…70.0	
			Grenzschichten (kuGR)		-			
	43.4… 61.3	Warburg formation (moW)	Glasplatten (moCGP)		-			
			Glaukonitbank (moCG)		X	**moW-1**	53.0…54.0	
			Zinkblendebank		-			
			Fischschuppen-schichten (moCFU)		- X			
			Cycloidesbank (moCC)		X	**moM-9**	42.0…45.0	
238.5... 235.0	8.7… 43.4	Meissner formation (moM)	Discites-schichten (moCD)	**HTU** (Hainich transect upper aquifer assem-blage)	X	**moM-8**	38.0…40.5	H42, H43, H53
					-			
					X	**moM-7**	34.0…36.0	H4SB
					-			
					X	**moM-6**	31.0…33.7	H32, H4SB
					-			
					X	**moM-5**	27.0…29.0	H32
					-			
					X	**moM-4**	22.9…24.5	H52
					-			
					X	**moM-3**	18.9…21.8	H52
			Gervilleien-schichten (moCGV)		-			
					X	**moM-2**	15.2…18.3	H23
					-			
					X	**moM-1**	8.0…13.2	H14
					-			
>238.5	0.0… 8.7	Trochiten-kalk formation (moTK)	Trochitenkalk (moT)	**HTL** (lower aquifer assem-blage)	X	**moTK-1**	0.0…6.6	H11, H12, H13, H21, H22, H31, H41, H51

Figures

Fig. 1. Location of the Hainich CZE (a + b): Prominent karst springs in the Hainich CZE are coupled to NE-SW oriented fault zones (b; modified from Mempel, 1939 and Jordan and Weder, 1995). (c): Geological setting of the eastern Hainich hillslope with monitoring wells of the research transect, accessing Upper Muschelkalk target formations (mo); Data sources: DEM ©GeoBasisDE/TLVermGeo, Gen.-Nr.: 7/2016.

Fig. 2. (A): Types of land management, outcrop zones of aquifer storeys, sinkhole lineaments, potential fracture zones and measurement points for soil hydraulic conductivities. Aquifer storeys which are lower in stratigraphy outcrop in higher positions on the Hainich hillslope. The AquaDiva well transect H1 to H5 (also shown) covers hillslope regions from the summit (H1) to the footslope (H5). (B) Conceptional soil map showing calculated soil groups and mapped calibration data points. Signatures of the mapped soil profiles represent the grain size class (soil category) of the topsoil. Interpolated isolines of mapped soil thickness show increasing thickness towards the NE and towards the transverse valleys.

Fig. 3. Physical properties of topsoil/subsoils and parent rocks of the four major soil groups. (A): Median frequencies of the fine grain size fractions (clay + fine silt) showing increasing proportions towards the bedrock, respectively. (B): Median soil hydraulic conductivities of soil groups showing higher median soil hydraulic conductivity in the "carbonate series soils" compared to the "siliceous series soils" and general decreases in hydraulic conductivity towards the subsoil. The error bars describe the root of the estimation variance of the average.

Fig. 4. Graphical correlation of marlstone/claystone intervals in gamma-ray logs, biostratigraphic limestone marker beds (grainstones/rudstones) and the degree of karstification (red bars and red scale bar below: solution-enlarged bedding planes to karst breccia). The geological aquifer correlation is cross-checked with the hierarchical clustering of hydrochemical parameters.

Fig. 5. Surface and subsurface properties of the aquifer outcrop zones (moTK-1 to moM-9) on the Hainich hillslope. Area sizes are related to the 29 km^2 area of this study. (A): Absolute abundances of land management types in the preferential recharge areas of the aquifer storeys. The two basal aquifer storeys are characterized by the largest aquifer outcrop areas and the highest amounts of forest within these areas. Agricultural land management increases towards the higher aquifer storeys (moM-2 to moM-9). (B): Relative abundances of soil groups within the aquifer outcrop zones showing high diversitiy in all aquifer outcrop zones depending on slope positions and quarternary loess loam/alluvial clay coverage, (C): Grain size groups of the topsoils and subsoils in the aquifer outcrop zones.

Fig. 6. Stratigraphic succession of the Upper Muschelkalk with stratigraphic marker beds (left), a gamma-ray log, aquifer assemblages HTL/HTU, aquifer storeys moTK-1 to moM-9 and the average chemical compositions of monitored groundwater (left: ions of carbonate/sulphate minerals; middle: redox-sensitive ions; right: ions which are potentially related to the type of land management). The color code of hierarchical clusters is identical to Fig. 4.

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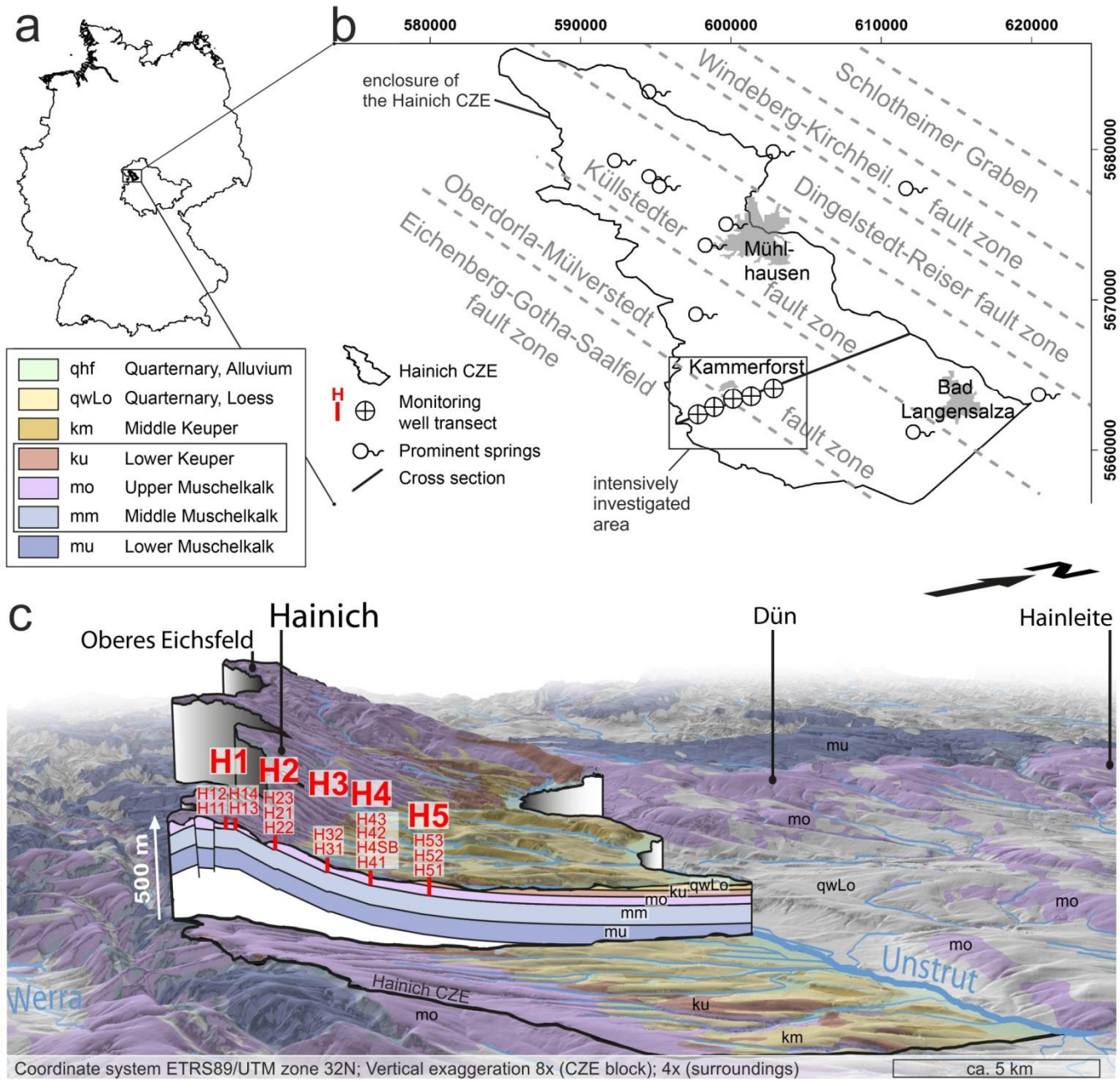
Fig. 1



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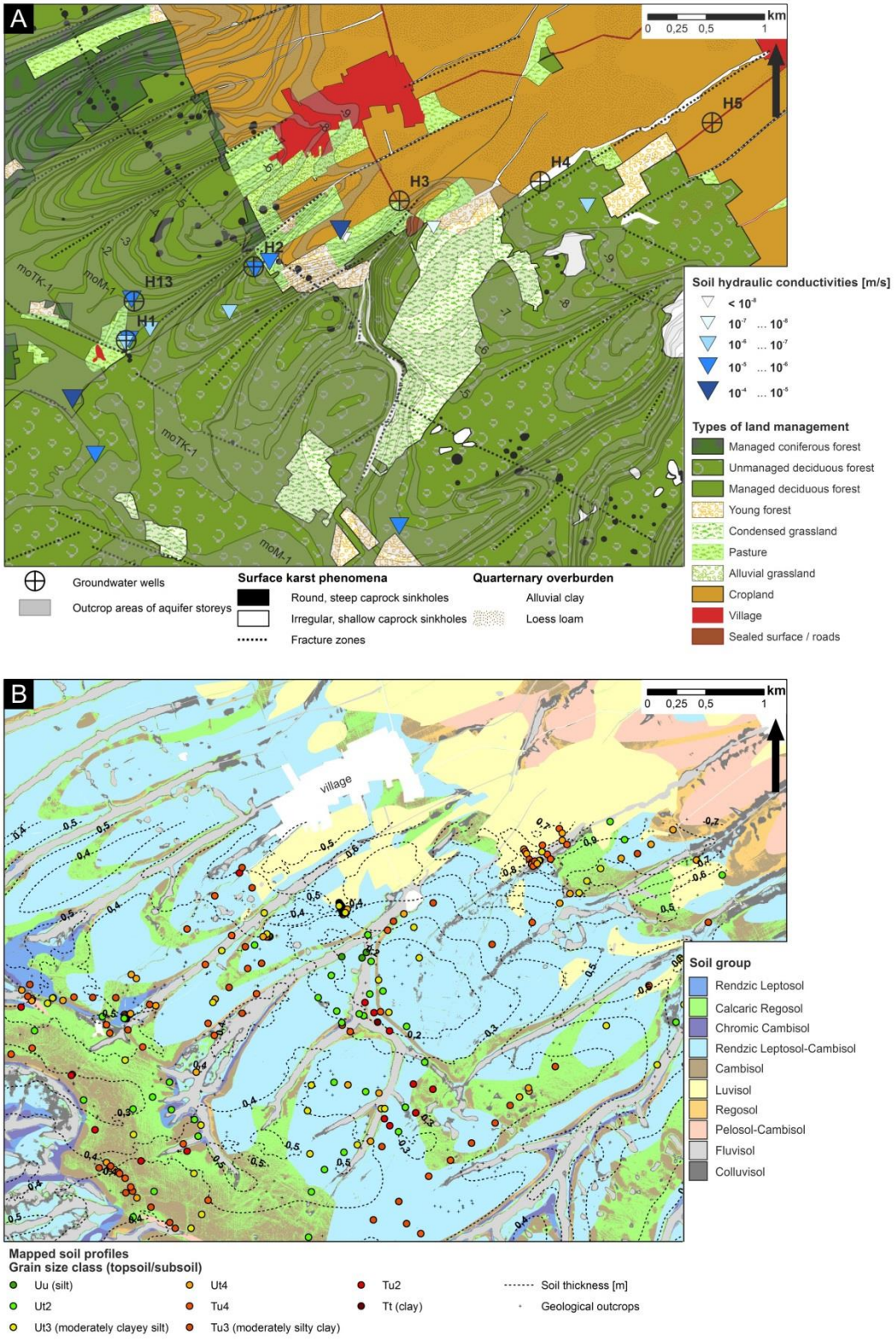

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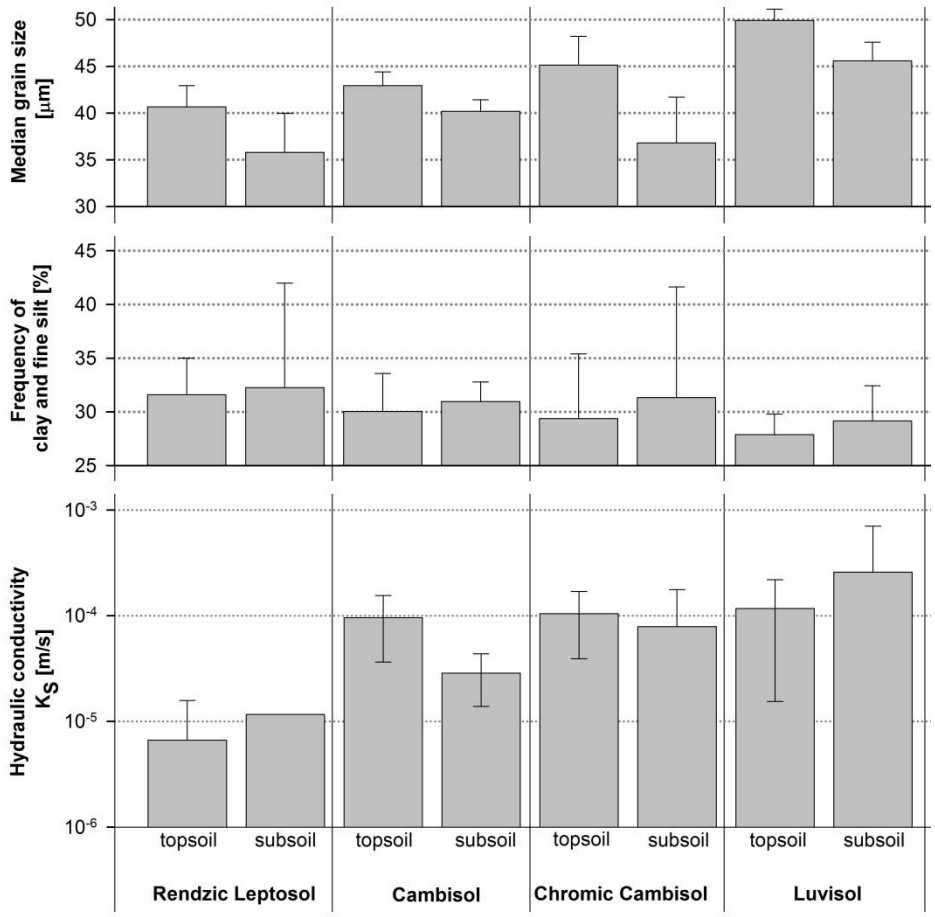

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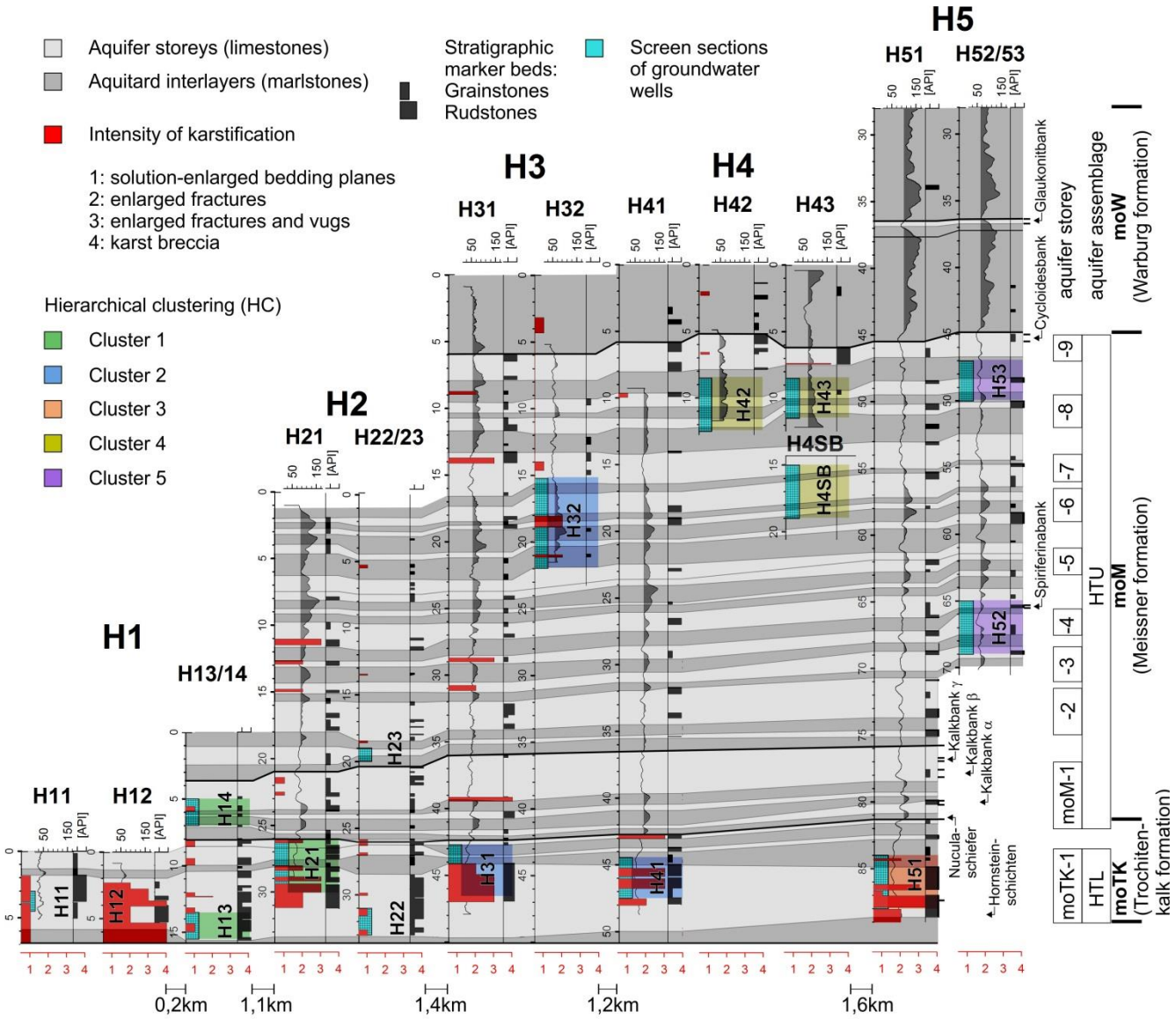

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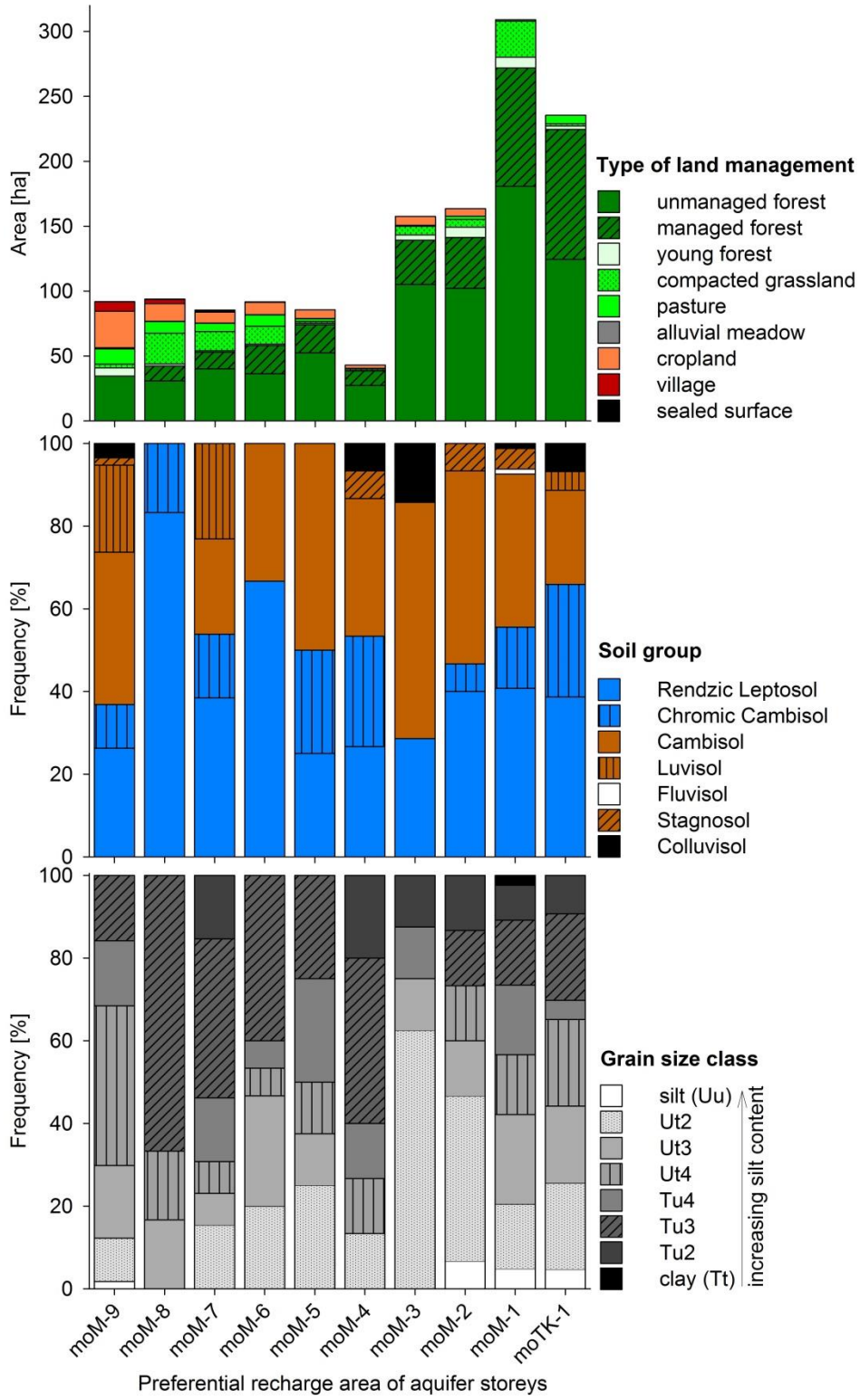

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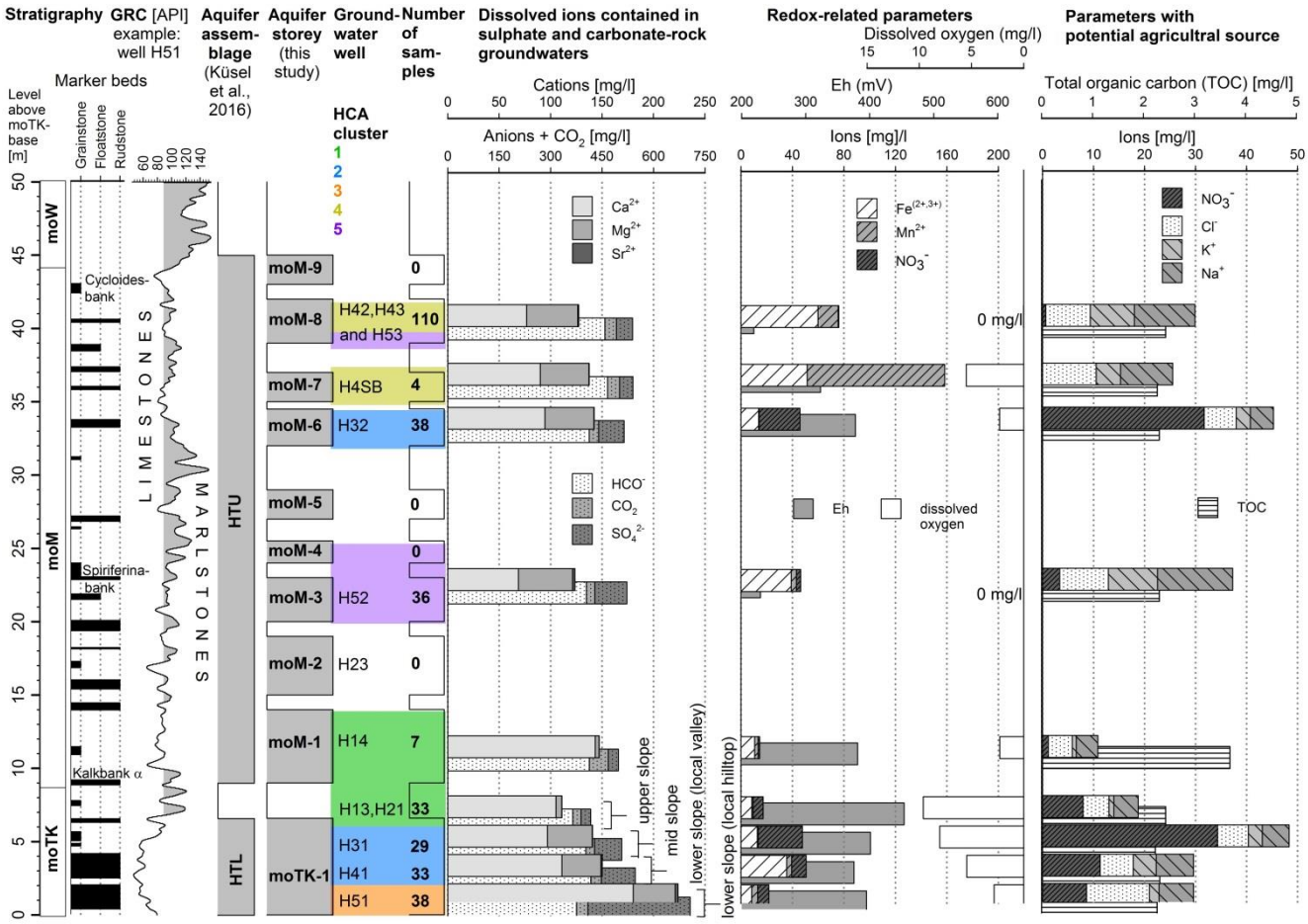

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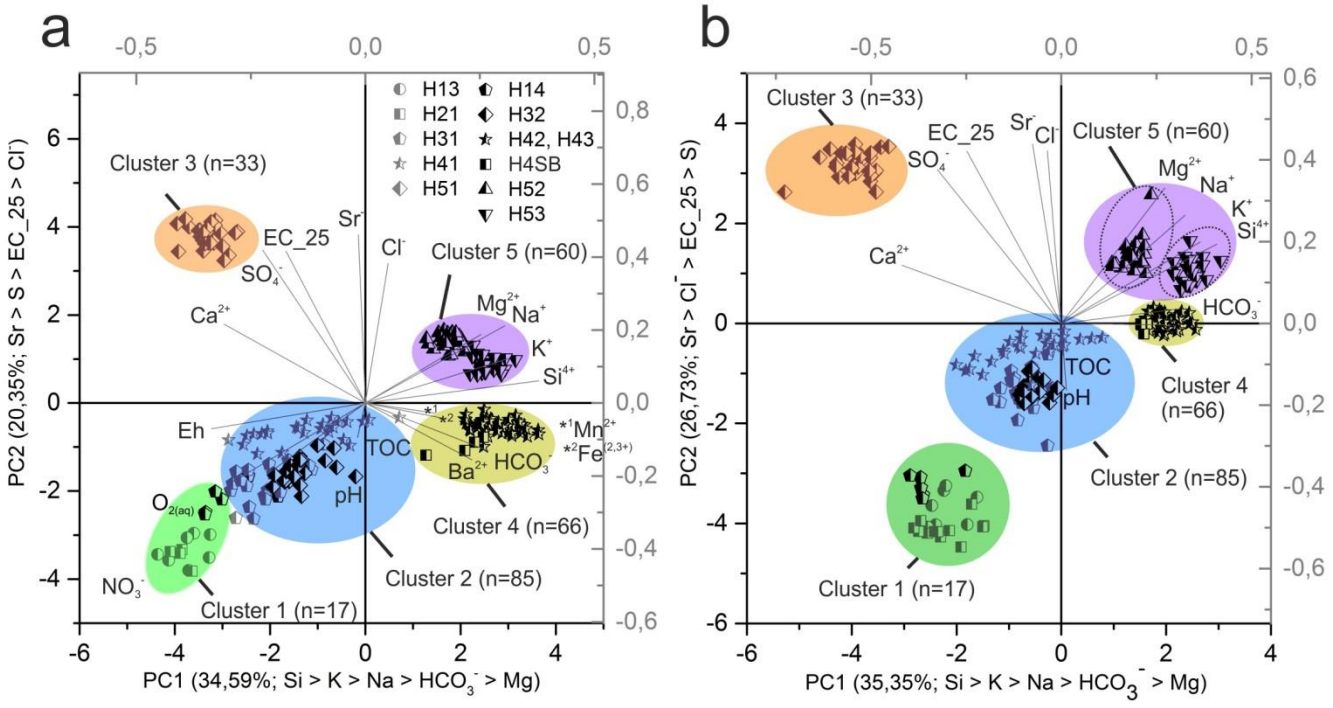

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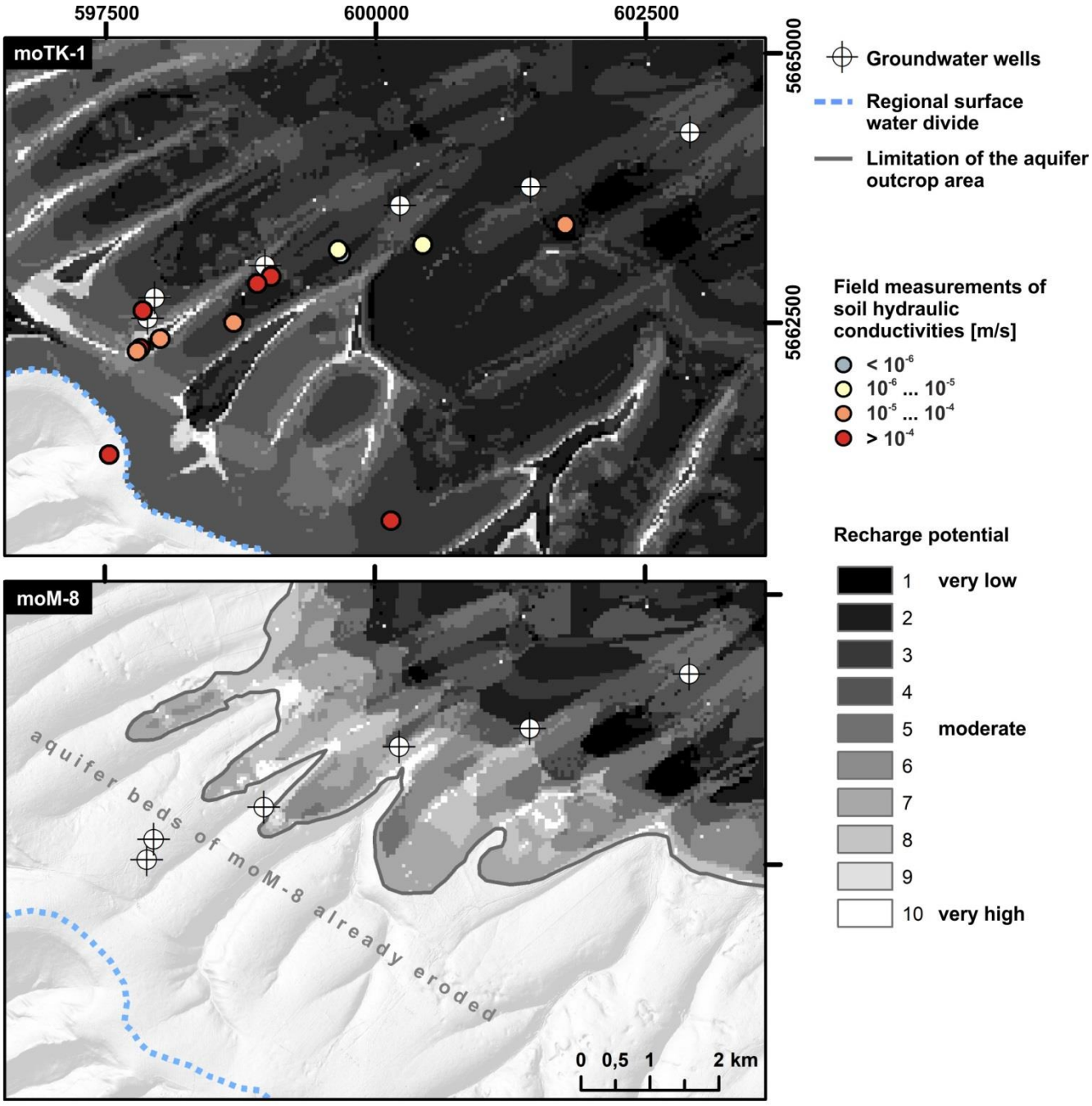

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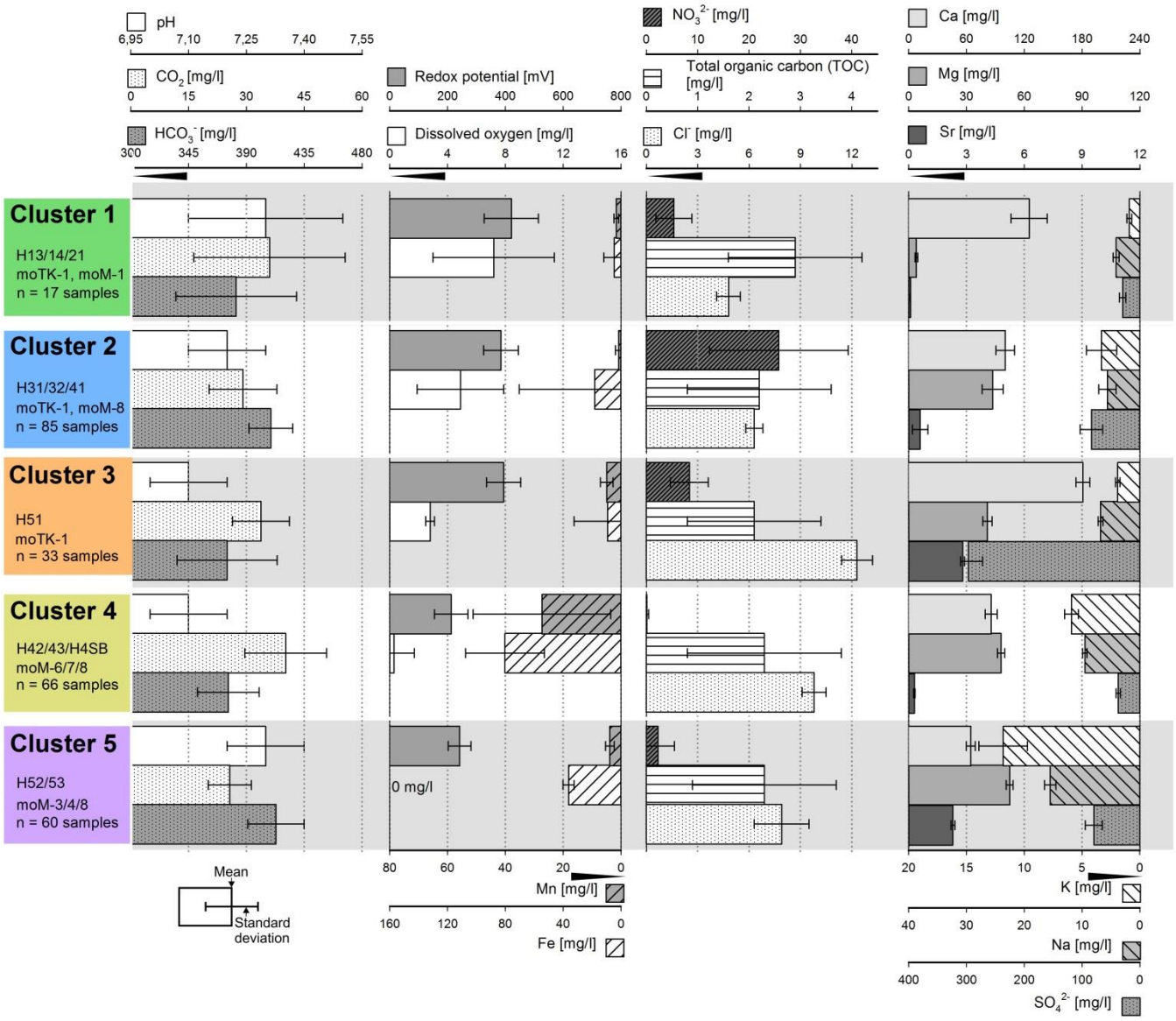

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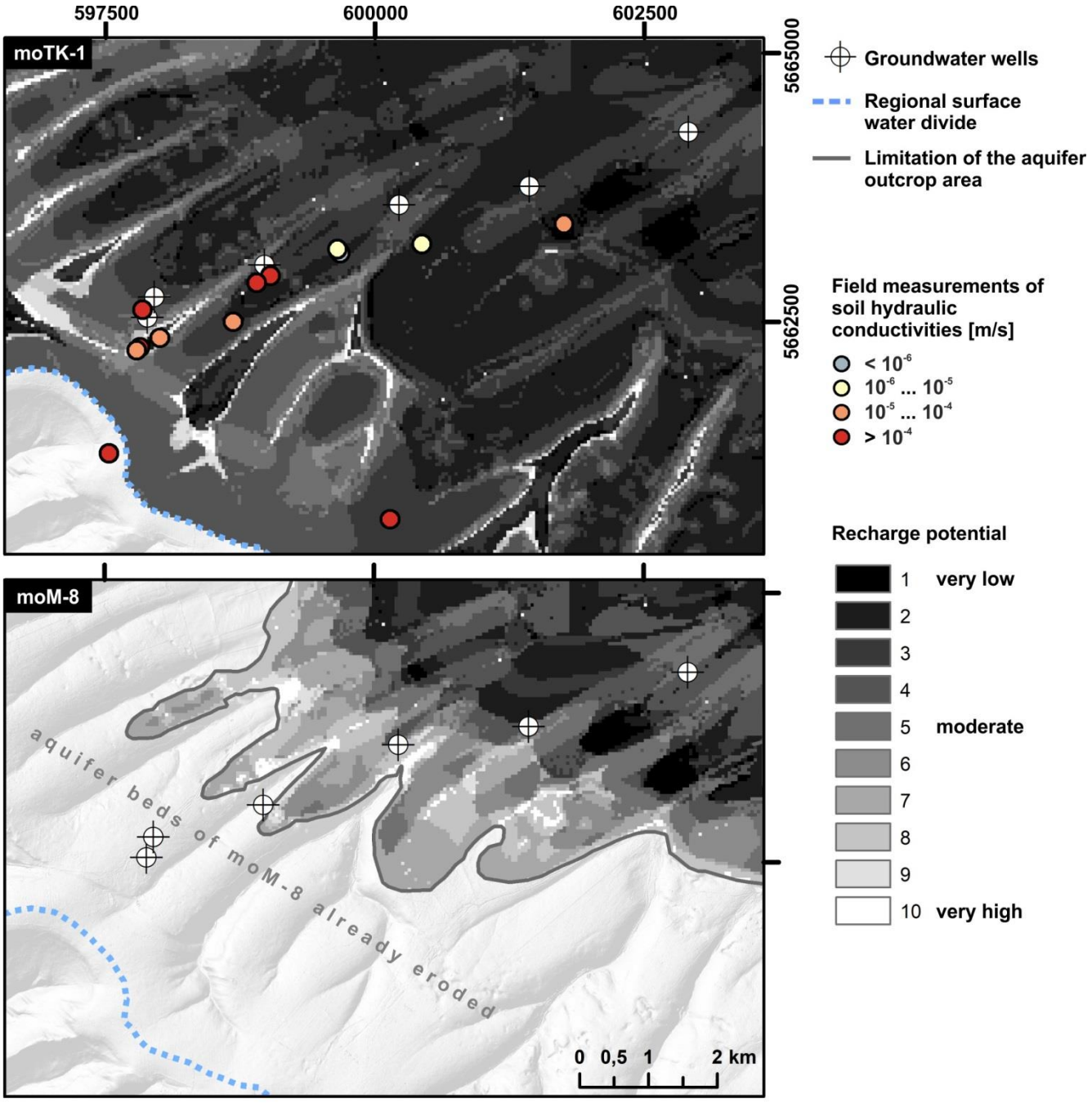
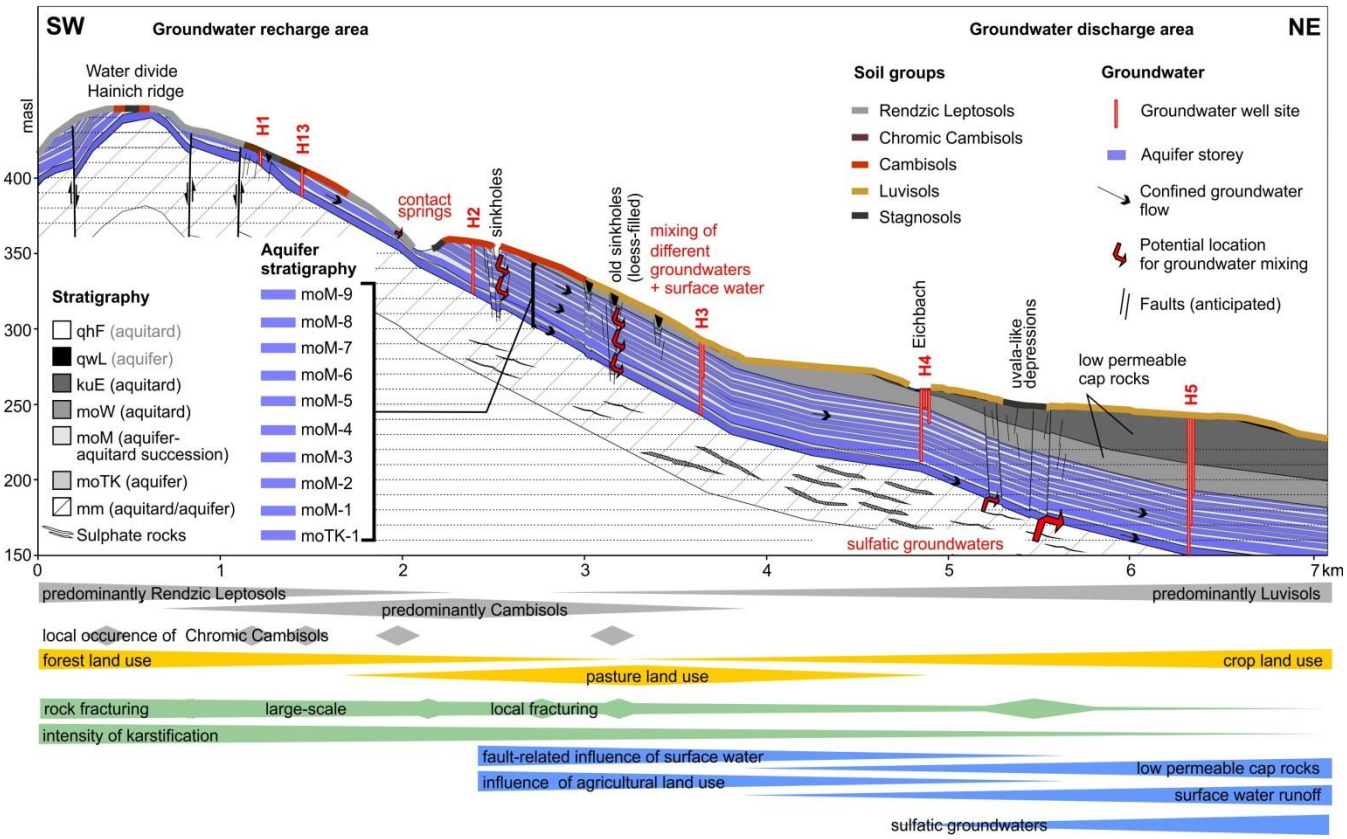

597500
600000
602500
5665000
5662500
moTK-1
moM-8
aquifer beds of moM-8 already eroded
0 0,5 1 2 km
Groundwater wells
Regional surface water divide
Limitation of the aquifer outcrop area
Field measurements of soil hydraulic conductivities [m/s]
< 10-6
10-6 ... 10-5
10-5 ... 10-4
> 10-4
Recharge potential
1 very low
2
3
4
5 moderate
6
7
8
9
10 very high

;

Fig. 10



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