Reducing conditions in soil of Gallocanta Lake, NE Spain

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Short title: Reducing conditions in soil
Summary

Saline wetlands have received limited attention only from researchers, and this neglect has often resulted in their degradation, limited conservation, and insufficient information to design conservation and management plans. Gallocanta Lake is a Natural Reserve of international importance for winter birds although soil resources, which support of endemisms and protected habitats, have been recognized more recently. The soil of Gallocanta Lake undergoes strong oscillations of saturation and drainage followed by drying because of irregular rain and variable flooding conditions associated with fluctuations in the level of the lake. This study examined reducing conditions and morphological indicators of reduction of soils around the lake with indicators of reduction in soils (IRIS) tubes, which are coated with iron oxides. We surveyed five sites for between 22 and 34 weeks. The average amount of iron removed from the IRIS tubes during the period studied ranged between 4 and 96%. The intensity of reduction in the soil differs according to subtle topographic differences between sites; it increases with the decrease in elevation. The large soil salinity (ECe from 18.1 to 182 dS m⁻¹), carbonate-rich composition (from 18.4 to 69.7% CCE) and overall small organic matter content (from 0.4 to 6.2% OM) do not seem to constrain iron mobilization because of the reducing conditions. Differences in iron depletion and patterns on the IRIS tubes show the heterogeneity of soil conditions and the complexity of factors involved in redox processes. Further research is needed to gain knowledge of the redox processes in the context of pedogenesis in semiarid lacustrine environments.

Keywords: hydromorphic soils, indicator of reduction in soils (IRIS) tubes, lacustrine, semiarid, soil micromorphology, soil reduction, soil salinity
Highlights:
- How intermittently exposed soils are expressing the redox conditions?
- Current reducing conditions are evidenced in a fluctuating saline lake by IRIS tubes
- Soil reduction occurs in alkaline soils with intermittent waterlogging
- IRIS tubes are suitable field indicators of soil reducing conditions heterogeneity in saline lakes

Introduction

Most recent studies of water levels of the Gallocanta Lake have focused on the effects of climatic and hydrological changes (Comín et al., 1983; Rodó et al., 2002). Few studies have focused on morphological changes in saline soil of shallow fluctuating lakes, where pedogenesis is strongly related to the water level of the lake. The intermittent desiccation of Gallocanta lake, especially during the last few decades because of the decrease of rainfall (Luna et al., 2016), has favoured the succession of subaqueous and oxidizing conditions in the soil that leads to variable saturation. Redoximorphic features in Gallocanta Lake have been described recently in lakebed sediments and soil, and also in the peripheral agricultural soil (Castañeda et al., 2015).

Reducing soil conditions related to anaerobic conditions have agronomic, ecologic and environmental significance, and their importance to wetland functions is widely recognized (Craft, 2001). The reducing conditions in soil are of interest for delineating wetland soil or to confirm the hydric conditions of soil for regulatory purposes (Rabenhorst, 2008). The occurrence of redoximorphic features is a key in many international soil classification systems to infer reducing conditions in soil (reviewed by Dorau & Mansfeldt, 2015). A field method for identifying reducing conditions in soil
based on the indicator of reduction in soils (IRIS) tubes was developed by Jenkinson & Franzmeier (2006), adapted by Rabenhorst & Burch (2006) and evaluated in floodplain areas by Castenson & Rabenhorst (2006). This field method has been approved by the National Technical Committee for Hydric Soils (NTCHS) as a standard method and field indicator of reduced soil conditions in the USA (Rabenhorst, 2012) in wetland delineations. The IRIS tubes have been used for to document reducing conditions in wetland soil (Rabenhorst, 2008; Dorau & Mansfeldt, 2015; Dorau et al., 2016) and, less frequently, in agricultural soil (Costantini et al., 2009).

Redox reactions affect pedogenetic processes and reflect hydrological functioning in the landscape. Even if landscape position is a consistent indicator of hydric soil in wetlands, wetland soil in semiarid regions is problematic and has been studied much less than those of humid regions. Semiarid wetlands undergo strong fluctuations of the water table because of the irregular rain and are frequently saline (3–50 g l⁻¹) or hypersaline (> 50 g l⁻¹) (Williams, 2002; Castañeda & Herrero, 2008). The dearth of inventories of saline wetlands, and maps of soil and vegetation, hampers the understanding of their ecological functions and hydric behavior. The limited amount of available information results in little regulatory recognition and in wetland degradation (Williams, 2002; Castañeda & Herrero, 2008). There has been little research on the processes of oxidation and reduction in the soil of saline wetlands although the factors that control the interactive effects of salinity and oxidation and reduction of iron under laboratory (Cameron et al., 1984; King & Garey, 1999) or field (Snyder et al., 2004) conditions have been published.

Relict redoximorphic features may be preserved in soil that was previously saturated and reduced. Moreover, the development of redox features is only indirectly related to how long soil has been saturated. Therefore, in the absence of site-specific
data on water table levels in Gallocanta Lake, we required a method that reflects the current reducing conditions in the soil. Our aims were to identify the reducing conditions of soil that are currently subjected to intermittent flooding in Gallocanta Lake, to relate the degree of reduction to soil characteristics and to test the applicability of IRIS tubes as a strategy for recognizing hydric soil in such semiarid conditions.

**Study area**

Gallocanta Lake, NE Spain, is the largest and best preserved saline lake in Western Europe. It has been included in the Ramsar list since 1994 and is protected under the European Union (EU) Birds and Habitats Directives. The lake is in a Quaternary depression at the bottom of a karst polje within the Iberian Range at 1000 m a.s.l. (Figure 1). The underlying Triassic lutites and interbedded evaporites contribute both to the high salinity of the lake, which is characterized by alternating wet and dry periods, and also to the subsequent variation in soil salinity (Castañeda *et al.*, 2015) and water chemistry (Comín *et al.*, 1983).

The climate is dry semiarid with very irregular rainfall. The mean annual precipitation for the last 70 years is 488 mm yr$^{-1}$; it ranges from 761 mm (in 1959) to 232 mm (in 2001). Mean temperature is 11.4 °C for the period 1969–2015, with 111 frost days per year. The mean annual water deficit is 605 mm (García-Vera & Martínez-Cob, 2004) which is exacerbated by the frequent winds. The soil temperature regime is mesic, and the soil moisture regime is generally aquic at the lake shore and xeric in agricultural areas (Soil Survey Staff, 2014).

Water level fluctuation has received much attention, mainly because it can be used to identify Quaternary climatic and environmental changes (Schütt, 1998). As compiled by Luna *et al.* (2016), the highest water level was registered in 1974 at 2.84-m depth,
whereas during periods of low rainfall, which have been common in the last few decades, all of the free water of the lake has evaporated.

Methodology

Selection of sites

We designed a purposive sampling scheme to detect redox conditions around the lake. We selected sites that flood intermittently based on a review of historical aerial photographs and Landsat images, geomorphic and pedological evidence (Castañeda et al., 2015), and our field work that extended from 2009 to the present. Our selection criteria required that the sites be undisturbed and accessible. At the time of the survey most sites were dry. Historic photographs and satellite images provide a glimpse of the conditions of the sites through time. The study sites were in different geomorphic units which include lacustrine terraces, lake bed and silt–sand barriers (Figure 1 and Table 1).

Installation and retrieval of the IRIS tubes

The IRIS tubes used to document the development of reducing conditions in soil are coated with an iron oxide suspension and the coating is dried afterwards (Castenson & Rabenhorst, 2006; Jenkinson & Franzmeier, 2006). Under water saturated, anaerobic and chemically reduced conditions, this coating is reduced by heterotrophic microbes and then solubilized and stripped from the tubes.

Five or three IRIS tubes have been used as replicates (Rabenhorst, 2008; Dorau et al. 2016, respectively) to account for soil heterogeneity. Sets of five IRIS tubes 60-cm long with the lower 50 cm coated were installed at each site (Figure 1) between April and July 2014. Five tubes were arranged in a cluster pattern within a one square metre area following the procedure of Rabenhorst (2008). The tubes were inserted into auger
holes made in the soil with a 22-mm push probe. Instead of the four-week period used for basic monitoring with IRIS tubes (Rabenhorst, 2008), we left the tubes in place for between 22 and 34 weeks (Table 1). The removal of iron oxide was monitored every four weeks. This was done by examining the central tube (carefully removed and gently reinserted to avoid abrasion) of all sets for visual evidence of removal of the iron oxide coating. We retrieved the tubes in January 2015, except the set at site 5, which was retrieved in March when the surface water evaporated and the site was easily reached. Each tube was washed gently in the field with tap water to remove any soil that adhered, and then the tube was photographed three times with the tube rotated 120° between each. Photography was done in the field to record the black mottles of iron monosulphide (FeS) coating (Rabenhorst et al., 2010; Dorau et al., 2016) which are metastable minerals under aerated conditions.

The tubes were also photographed systematically in the laboratory under vertical view with a fixed field of vision. The three photos of each tube were cropped and combined into a single digital image of the whole surface of the tube, and their cylindrical shape was projected into an equivalent plane. Black mottles on the IRIS tubes were quantified from the field photographs. The removal of iron oxide coating (Rabenhorst & Burch, 2006) was quantified for each binary image that was converted digitally. For each IRIS tube, the area of maximum removal of the iron oxide coating was calculated within the upper 30 cm of the tube, for a zone of 15 cm (Rabenhorst, 2008).

Laboratory analysis

The soil was sampled by auger (7 cm in diameter), except at sites 4 and 5 whose profiles were sampled and described in pits following Schoeneberger et al. (2012). Soil
samples were air-dried at room temperature before placing in an oven at \( \leq 40 \, ^\circ C \), and sieved through a 2-mm mesh. Soil salinity was measured as the electrical conductivity of the 1:5 soil:water extract (EC1:5) and the saturated paste extract (ECE). Electrical conductivities were expressed in dS m\(^{-1}\) at 25 °C. Calcium carbonate equivalent (CCE) was determined by the Bernard calcimeter method based on the reaction with HCl, gypsum content was quantified by thermogravimetric analysis (Artieda et al., 2006) and organic matter (OM) was quantified by chromic-acid digestion (Heanes, 1984) and a UV/V UNICAM 8625 (Unicam Instruments Ltd., Cambridge, UK) spectrophotometer.

Particle-size distribution was assessed by laser diffraction (Malvern MASTERSIZER 2000, Malver, UK). The pH and EC of groundwater samples were measured with a pH electrode and a conductivity cell (Orion 9157BNMD and Orion 013605MD, respectively, Thermo Fisher Scientific Inc., Beverly, US) and major ions were determined by ion chromatography (Metrohm 861 Advanced compact IC, Metrohm AG, Herisau, Switzerland).

Surface soil samples (0–10 cm) at sites 4 and 5 that appeared black and smelled of sulphur were incubated in the laboratory under aerobic conditions for 18 weeks, and pH was measured weekly following the method of Creeper et al. (2012) and Grealish et al. (2010). Undisturbed blocks of soil from selected horizons were impregnated with a cold-setting polyester resin, and thin sections (135 mm × 58 mm and 58 mm × 42 mm) were prepared by the method of Guilloré (1985) and described under polarizing microscope following Stoops (2003).

Results

Rainfall data during the survey
Based on annual rainfall and following the criteria of the Soil Survey Staff (2014), the year 2014 and years immediately preceding it would be considered to be ‘normal’ precipitation years. The rainfall registered in 2014 at the lake border in Picos weather station (Figure 1) was 377 mm, 23% less than the long-term mean of 488 mm. The meteorological conditions during the study were characterized by a dry spring, with only 53.7 mm of rain from March to May. The autumn was more humid than spring, with 110 mm of rain from September to November. Observations of the depth of the water table indicated that it dropped during spring and summer of 2014, and it did not return to within 50 cm of the soil surface. The low spring rainfall together with the dryness (low level) of the lake caused a delay in the extraction of the tubes until after the autumn.

**Main soil features**

The soil is strongly saline (Table 2), with an ECe up to four times the salinity of the ocean water (182 dS m⁻¹), and has a large CCE content that ranges from 18 to 70%. Soil pH is mostly in the range between 7.6 and 8.6 and is probably dominated by of the large CCE content. There is little organic matter in the soil of the lake fringes, < 2%, whereas it reaches 6.2 and 5.8%, at the lake bottom (site 5) and where there are saline grasses (site 1), respectively. The particle-size distribution indicates that soil texture is essentially clay loam and sand content decreases with depth. Occasionally, gravels accumulate in surface and subsurface horizons in areas where fluvial water enters the lacustrine system (site 3).

The available descriptions of soil morphology in the area (Castañeda et al., 2015; Luna et al., 2016) indicate waterlogging or restricted drainage, with Gypsic Aquisalids at the lake bottom (Figure 2), Typic Aquisalids at the shoreline and Typic Calcixerpts...
in slightly elevated areas (Table 1). The soil at the lowest topographic positions (sites 4 and 5) is a hydric soil that conforms to the field indicator requirements established by USDA–NRCS (2010). At site 4, two horizons (Ag and 2Cg1) have a field indicator F3, ‘depleted matrix’ (USDA–NRCS, 2010), with a grey matrix colour (2.5Y and chroma ≤ 2), and common redox mottles (7.5YR and 10YR, Table 2). At site 5, the profile has a gleyed and an iron-depleted matrix with bluish, low chroma matrix colours (10B and 2.5GY and chroma < 2, Table 2), consistent with the field indicator F2, ‘gleyed matrix’ (USDA–NRCS, 2010). Redox depletions (5Y and 10B) are abundant and are mainly associated with the occurrence of gypsum layers.

Micromorphic pedofeatures related to redox processes in soil on the lake floor include impregnated redoximorphic features such as banded iron and manganese oxide hypocoatings. Coatings adjacent to voids occur in the soil of the surface horizon (Ayzg horizon) where the abundance of biological remains favours the formation of a channel to lenticular soil microstructure (Figure 2c). Accumulation of iron sulphides as framboïds, frequently clustered (Figure 2d), are common in subsurface horizons (Cyg3 horizon) with a massive to vughy microstructure and micritic cristallitic b-fabric as defined by Stoops (2003).

**Groundwater characteristics**

On the dates that the IRIS tubes were installed, observed water table depth ranged from –10 cm (site 1) to –100 cm (site 5) (Table 1). Free surface water occurred intermittently at all sites during the study period. Groundwater is non-saline in the marsh (saline grasses) and reed bed areas, sites 1 and 3. The current lake bed (sites 4 and 5) and the SE terrace (site 2), show similar groundwater characteristics, with a pH of between 6.7 and 7.1 and high salinity (although with a two-fold difference in EC among the
unvegetated lakebed sites) with increased $\text{Mg}^{2+}$ and $\text{SO}_4^{2-}$ concentrations (Table 1). Nitrates are more abundant in saline groundwater, in particular at sites 2 and 4. The bicarbonate content is somewhat variable, with a 2- to 3-fold range between the maximum (854 mg l$^{-1}$) at site 2 and the minimum (366 mg l$^{-1}$) at site 1.

Iron oxide removal from the IRIS tubes

The percentage area with depleted iron in a 15-cm zone within the upper 30 cm of the tube for all five sites varies from 0.5 to 95.1%. It is also very variable between the five tubes at a single site (Figure 3 and Table 3). The greatest variation in iron oxide removal occurred at site 4 (standard deviation, SD, 39.7%), at the southern margin of the lake (Figure 1 and Table 3). Variability at the other sites was more modest (SDs from 2.9% to 11.5%). The zones of the tubes where the iron oxide coating was chemically reduced and removed were almost lacking iron oxide in some cases, whereas in others these zones retained a thin coating of iron oxide that contrasted distinctly from the original reddish brown colour (Figure 3). Occasionally, zones depleted of iron occurred above the zero level line, i.e. the mark on the tube that corresponded to 0 cm or ground-level.

The patterns of iron oxide removal included: (i) spots, corresponding to reducing conditions at microsites, (ii) area of continuous removal, corresponding to the reducing conditions in a whole horizon, 3) doughnut-shaped depletion patterns (Jenkinson & Franzmeier, 2006) similar to that formed by bacterial cultures and (iv) linear depletion patterns (Figure 3) often observed in areas with increased organic matter and microbial activity (Vepraskas & Faulkner, 2001) related to the occurrence of roots as a source of organic matter (Jenkinson & Franzmeier, 2006) because of the activity of phytosiderospheres (Dorau et al., 2016).
The soil in sites 3 and 5 (Figure 4) can be classed as a hydric soil based on the degree of reduction, Technical Standard (NTCHS). A minimum of three out of five IRIS tubes have >30% of their coating removed in a zone 15-cm long starting within 15 cm of the soil surface (Table 3). The rate of reduction, determined as the percentage of iron oxide depleted per month on the surface of the tube, ranges from 0.4 at site 1 (Ojos, Figure 1) to 12% at the neighbouring site 3 (Reguera).

Iron monosulphides can form as black mottles on IRIS tubes by the rapid chemical reaction of soluble sulphide with the iron oxide coatings (Rabenhorst et al., 2010). The black FeS mottles were especially intense at sites 2 and 5, with a mean of 1.4 and 5%, respectively (Table 3). Speciation of aqueous sulphide is pH dependent, and the alkaline pH of the calcareous soil (Table 2) suggests that the pore water sulphide is primarily present as hydrogen sulphide (HS⁻) (Garrels & Christ, 1965). Maximum percentage of black mottles per tube occurs at site 5, with a 12.2% cover of the whole tube (Table 3) and 19.2% of the upper 30 cm of the tube. It is likely that these represent minimum sulphide values for the tubes from site 5, because the black sulphide initially forms as a coating over the iron oxide coating (which strongly adheres to the tubing). However, if all of the iron oxide on the tube becomes converted to the black FeS (from large sulphide concentrations or over long periods of time), the FeS (without an undercoating of iron oxide) does not adhere to the tube and leaving the white tube exposed. Some parts of the white areas at the bottom of the tubes from site 5 appear like this (mostly dark grey and white with little or no iron oxide), Figure 3.

Discussion

The wet saline soil of the Gallocanta saline lake, which is subjected to intermittent flooding, shows evidence of the mobilization of iron and manganese oxides in exposed
soil (Figure 2a) or even temporarily at the soil surface (Figure 2b). In spite of the subtle
topography of the area (from 0.3 to 2.2 m of height difference among sites) the
elevation appears to condition the degree of reduction expressed in the iron oxide
removal from the IRIS tubes. The average percentage of iron oxide removed from 15
cm generally increases from 3% to 81% as the elevation decreases even if the
groundwater depth when the tubes were installed increases (Table 1). The site 3 is an
exception, with 0.6 m of relative elevation increase and an average iron oxide removal
of 81% to 95%, probably due to the surface water inflow from the Reguera intermittent
stream into the lake, producing longer periods of soil saturation in this mouth zone. The
neighboring sites 1 and 3 represent the minimum and maximum intensity of iron
depletion, respectively. Both sites have saline soil and fresh groundwater (Table 1) and
their level of soil OM does not seem to condition the removal of iron from the IRIS
tubes. A high percentage of iron oxide coating removal also occurs at the soil of site 5,
which has a high OM content (up to 6.2%) and gypsum (21% as mean) and where NO₃⁻
is completely removed from groundwater (Table 1) by reduction to N₂.

The vertical distribution of iron depleted zones along the tubes are not uniform
(Figure 3) and shows a great variety of patterns similar to that described by Jenkinson &
Franzmeier (2006) in very different types of soils from a diversity of locations. Even in
a single depleted area of the tubes Dorau et al. (2016) recognize gradients of reducing
soil conditions.

The redox micromorphic pedofeatures show a redox gradient with soil depth,
which accords with the overall pattern of iron oxide removal shown by field
photographs of the IRIS tubes. The iron and manganese oxides in the surface horizon
(Figure 2c) indicate alternating reducing–oxidizing conditions, which are favoured by
the abundant coarse material and the more aerated soil microstructure. In contrast, iron
sulphides only accumulate at depth (Figure 2d), which indicate that reducing conditions 
predominate because of the finer microstructure that controls soil porosity. Iron 
hypocoatings can be produced after several days of water saturation, whereas the 
formation of iron sulphides (pyrite) indicates very wet and reducing conditions from 
several months of water saturation (Lindbo et al., 2010).

Contemporary or relict micromorphological features may occur in the same 
horizon (Lindbo et al., 2010), but because of tubes had been installed for several months 
we recorded features that are actively forming. Based on the redox sequence 
(Ponnamperuma, 1972) and their corresponding $E_{H}$ values summarized by Dorau & 
Mansfeldt (2015), all the sites studied have at least moderate reducing soil conditions 
because exhibit iron oxide removal which indicates $E_{H}$ ranges from 100 to $-100$ mV. 
Sulphate reduction and FeS deposition > 0.2% at sites 2, 3 and 5 indicate that these sites 
have strongly reducing soil conditions with $E_{H}$ values $<-100$ mV, especially site 5, 
which is at the lowest landscape position where iron sulphide deposits were maximum. 
According to the categories proposed by Bartlett & James (1995), soil at sites 2, 3 and 5 
has a sulphidic redox status.

In contrast with other carbonate-rich environments (Stiles et al., 2010) and 
laboratory observations (Couto et al., 1985), in Gallocanta Lake the expression of redox 
features is not inhibited by the buffering capacity associated with the high content of 
CCE (47% as mean). Additionally, in contrast observations in other soils (Craft, 2001) 
the availability of $NO_{3}^{-}$ in groundwater does not appear to hamper iron reduction and 
mobilization in these soils. It is likely, however, that these components may reduce the 
rate of development and expression of redox features.

Although we observed minor reduction of iron oxide coatings after four weeks at 
the lake floor (site 5), generally the time needed for tubes to show evidence of soil
reducing conditions among all sites surrounding Gallocanta Lake was 27 weeks on average (Table 1), which was very long when compared with the time (days to weeks) required in non-carbonatic environments (Jenkinson & Franzmaier, 2006; Dorau et al., 2016) or in controlled experiments (Rabenhorst et al., 2008; Dorau & Mansfeldt, 2015).

The effect of carbonate content was observed during soil incubation, where, despite the presence of oxidizable sulphide, the decrease in pH (down to 7.3 during the first two weeks before rising to slightly alkaline values, 7.8) was inhibited in those soils which had 17.4% and 37.6% of CCE (Table 2), similar to reports by Couto et al. (1985) under controlled conditions. However, the seasonal inundation observed in Gallocanta Lake suggests the occurrence of intermittent water saturation of soil, which is probably the main reason of the low reduction rate found at our soil. Additionally, the delay in reduction timeframes may also be affected by the high carbonate content. As already demonstrated by Dorau & Mansfeldt (2015), the use of Mn-oxide coated tubes may improve the IRIS method by the preferential reductive dissolution of manganese over iron oxides, thus reducing the time of monitoring and enhancing the differences in intensity of reduction between sites.

There is no clear relationship between soil or groundwater composition (and salinity) and the degree of iron removal from IRIS tubes, despite an eight-fold range in ECe (Table 2) and a 50-fold difference in groundwater salinity (Table 1). The bacterial iron oxidation is completely inhibited with 3% (wt/vol) of NaCl ($\cong$ 40 dS m$^{-1}$) under laboratory conditions (Cameron et al., 1984) whereas in the soil studied it occurs at much higher salinity (Table 1) indicating the complexity of natural conditions. This issue would require a fully experimental approach, i.e. controlled conditions only achievable in laboratory or microcosm experiments. This is beyond the scope of this paper.
The iron oxide coating removal is expected to occur mainly when the water table is high. Although continuous water table data are not available for the IRIS sites during the period of study, one can reasonably assume that the occurrence of shallow water table caused the development of anaerobic conditions and the reduction of iron oxide from the IRIS tubes at sites 3 and 5, and probably at site 4. As introduced by Dorau et al. (2016), the monitoring of water tables in parallel to that of iron removal from IRIS tubes would produce more meaningful data for normalizing the iron removal per unit of time (day or week) when water tables are near (within 30 cm of) the soil surface. However, the intensity and duration of reducing soil conditions should be considered as conditioned by multiple factors, and not only by the water table depth or other single soil parameter. The organic matter type and content, pH, soil temperature, and microbial community can vary between sites, making difficult to predict or normalize iron removal, even within a wetland.

Conclusions

This study demonstrates that IRIS tubes are of value to document the development of reducing conditions in saline and carbonate-rich wet soil from research at Gallocanta Lake where the water level fluctuates seasonally and annually. The identification of current reduction in the soil of different geomorphic and edaphic units around the lake confirms that previously observed macro and micromorphological redoximorphic features are probably developing at present in spite of the intermittent dryness of the lake. The alkaline conditions with waterlogging grant novelty to our work.

The differences in magnitude of iron oxide depletion from the IRIS tubes between sites show little association with soil composition or salinity, but seem to be related mainly to subtle differences in topography that control when the soil becomes saturated.
and reducing conditions persist. Interpretation of the processes and factors responsible for the differences in the amount and patterns of iron depletion from the IRIS tubes between sites remain unsolved. This critical limitation of our field approach also poses a subject for future research which should be complemented with laboratory or microcosm experiments.

Acknowledgements

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References


Figure captions

**Figure 1** Colour-shaded LiDAR-derived digital elevation model of Gallocanta Lake with major contour lines and locations of the IRIS tubes.

**Figure 2** Evidence of iron and manganese mobilisation in Gallocanta Lake: (a) in recently exposed soil at site 4, (b) at the soil surface in nearby areas subjected to intermittent flooding. Thin sections show redox micromorphic pedofeatures associated with voids (v), (c) manganese oxide (Mn) and iron-manganese oxide (Fe/Mn) impregnated hypocoatings observed with plane polarized light, Ayzg and (d) framboidal iron sulphide (FeS) coating observed with oblique incident light, 2Cyg3.

**Figure 3** Photographs taken in the field of five replicate IRIS tubes from each site when they were extracted at the completion of the study.

**Figure 4** Photographs of IRIS tubes taken in the laboratory which show the upper 30 cm of the tubes. Black areas correspond to the iron oxide coating removed and red boxes indicate the 15-cm section of the 30-cm tube with maximum removal of iron oxide coating.
<table>
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<th>Site</th>
<th>Reference name</th>
<th>Elevation / m a.s.l.</th>
<th>Geomorphic unit</th>
<th>Soil classification</th>
<th>Landcover</th>
<th>Total number of weeks</th>
<th>Groundwater depth /cm</th>
<th>pH</th>
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<sup>a</sup>USDA Soil Taxonomy (Soil Survey Staff, 2014). ND= not determined.
<sup>b</sup>World Reference Base (IUSS Working Group WRB, 2015).
<sup>c</sup>Electrical conductivity.
<sup>d</sup>n.d. = not detected.
| Depth /cm | Horizon | Munsell colour (Moist) | Mottles | pH 1:2.5 | pH paste | EC1:5<sup>a</sup> | ECe<sup>b</sup> | CCE<sup>c</sup> | Gypsum | OM<sup>d</sup> | Gravels | Sand | Silt | Clay | USDA textural class |
|----------|---------|------------------------|---------|---------|----------|-------------|-------------|--------------|---------|---------|---------|------|-----|-----|--------------|------------------|
| Site 1 (GA54), auger hole |
| 0–25 | 7.6 | 1.2 | 21.3 | 49.9 | 3.7 | 5.8 | 0.6 | 37.8 | 42.2 | 20.0 | Loam |
| 25–50 | 7.9 | 0.6 | 19.1 | 49.9 | 2.9 | 3.8 | 0.9 | 26.0 | 44.5 | 29.4 |
| Site 2 (GA48), auger hole |
| 0–25 | 8.3 | 0.8 | 18.9 | 31.7 | < 2.0 | 0.4 | 2.6 | 35.4 | 41.6 | 23.0 | Clay loam |
| 25–50 | 8.1 | 0.8 | 19.9 | 31.7 | < 2.0 | 0.4 | 2.6 | 35.4 | 41.6 | 23.0 |
| Site 3 (GA53), auger hole |
| 0–25 | 7.9 | 0.7 | 19.3 | 45.4 | < 2.0 | 0.4 | 30.6 | 53.3 | 15.0 | 31.6 | Sandy clay loam |
| 25–50 | 8.0 | 0.6 | 19.1 | 45.1 | < 2.0 | 0.4 | 23.5 | 34.7 | 29.8 | 35.5 | Clay loam |
| Site 4 (Pedon GA30) |
| 0–10 | Ag | 2.5Y 6/2 | 7.5YR 6/6 | 8.3 | 9.4 | 67.7 | 37.6 | 4.4 | 0.8 | 0.8 | 61.2 | 18.5 | 20.4 | Sandy clay loam |
| 10–25 | 2Cg1 | 2.5Y 6.5/1.5 | 10YR 6/6 | 8.1 | 8.3 | 39.3 | 58.7 | 3.8 | 0.5 | 14.1 | 49.0 | 36.9 | Silty clay loam |
| 25–50 | 2Cg2 | 2.5Y 7/1.5 | 69.7 | 2.2 | 0.5 | 23.6 | 33.3 | 43.1 | Clay |
| Site 5 (Pedon GA28) |
| 0–6/10 | Ayzz | 10B 2.5/1 | 79.8 | 15.5 | 4.7 | Loamy sand |
| 6/10–14/16 | Cyg1 | 10B 2.5/1–5Y 6/1 | 8.5 | 36.2 | 146 | 29.3 | 14.5 | 6.2 | 62.4 | 25.1 | 12.4 | Sandy loam |
| 14/16–24 | Cyg2 | 10B 5.5/1 | 10B 5.5/2 | 8.6 | 23.7 | 104 | 36.6 | 17.0 | 3.9 | 44.0 | 31.6 | 24.4 | Loam |
| 24–42 | 2Cyg3 | 2.5GY 6/1 | 10B 4.5/1 | 8.2 | 23.2 | 100 | 28.0 | 28.6 | 3.4 | 44.8 | 26.4 | 28.8 | Clay loam |
| 42–50 | 2Cyg4 | 7.5GY 6/1 | 52.0 | 5.7 | 1.2 | 0.8 | 15.0 | 40.2 | 44.7 | Silty clay |

<sup>a</sup>Electrical conductivity of the soil:water 1:5 extract.
<sup>b</sup>Electrical conductivity of the saturation extract; ECe for sites 1 to 4 was estimated by regression between EC1:5 and ECe of samples from GA28 and GA30 (Castañeda et al., 2015).
<sup>c</sup>Calcium carbonate equivalent.
<sup>d</sup>Organic matter.
Table 3 Percentage of iron oxide depleted from a 15-cm zone of the IRIS tubes within the upper 30 cm of the soil surface (the main zone of interest when considering hydric soil issues) and percentage of black FeS mottles deposited on the tube

<table>
<thead>
<tr>
<th>Iron oxide removal on a 15-cm zone</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
<th>Site 4</th>
<th>Site 5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number of IRIS tubes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>With $\geq 30%$ iron oxide coating removal</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>Surface removal / %</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>3.0</td>
<td>12.3</td>
<td>80.8</td>
<td>33.9</td>
<td>70.4</td>
</tr>
<tr>
<td>Median</td>
<td>1.5</td>
<td>8.2</td>
<td>75.8</td>
<td>8.9</td>
<td>69.6</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>2.9</td>
<td>11.5</td>
<td>8.8</td>
<td>39.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Maximum</td>
<td>7.1</td>
<td>30.4</td>
<td>95.1</td>
<td>86.8</td>
<td>80.9</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.5</td>
<td>1.0</td>
<td>74.1</td>
<td>2.1</td>
<td>61.5</td>
</tr>
<tr>
<td>Range</td>
<td>6.6</td>
<td>29.4</td>
<td>21.0</td>
<td>84.7</td>
<td>19.4</td>
</tr>
<tr>
<td>Monthly rate</td>
<td>0.4</td>
<td>1.3</td>
<td>12.0</td>
<td>3.9</td>
<td>6.9</td>
</tr>
<tr>
<td><strong>Percentage of black FeS mottles$^a$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>0.4</td>
<td>2.6</td>
<td>1.8</td>
<td>0.1</td>
<td>5.4</td>
</tr>
<tr>
<td>T2</td>
<td>0.4</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
</tr>
<tr>
<td>T3</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>12.2</td>
</tr>
<tr>
<td>T4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>2.3</td>
</tr>
<tr>
<td>T5</td>
<td>0.2</td>
<td>3.6</td>
<td>0.1</td>
<td>0.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Mean(SD)</td>
<td>0.2(0.1)</td>
<td>1.4(1.7)</td>
<td>0.4(0.8)</td>
<td>0.1(0.1)</td>
<td>5.0(4.5)</td>
</tr>
</tbody>
</table>

$^a$FeS mottles that occurred along the full 50-cm length of the IRIS tubes at the time they were extracted from the field; T, tube; SD, standard deviation.