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Quantification and spatial distribution of nutrients in the unsaturated zone of the Tablas de Daimiel National Park

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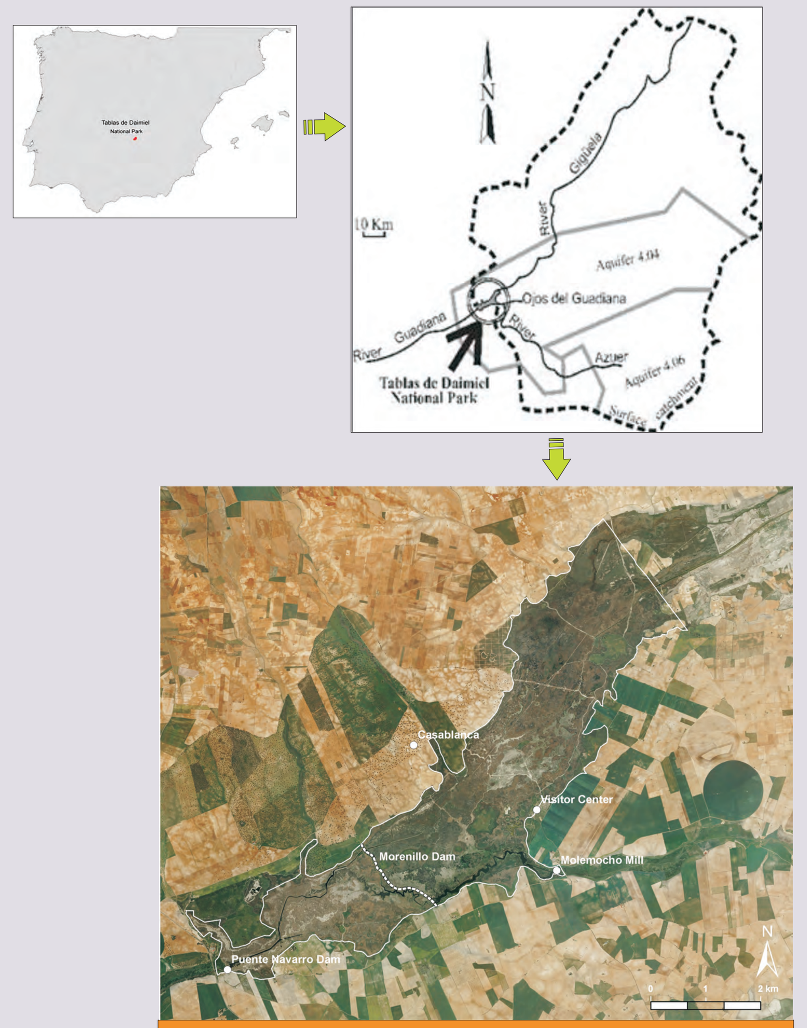


Figure 1. Location of the Tablas de Daimiel National Park (TDNP) within the High Guadiana Basin and the West La Mancha aquifer.

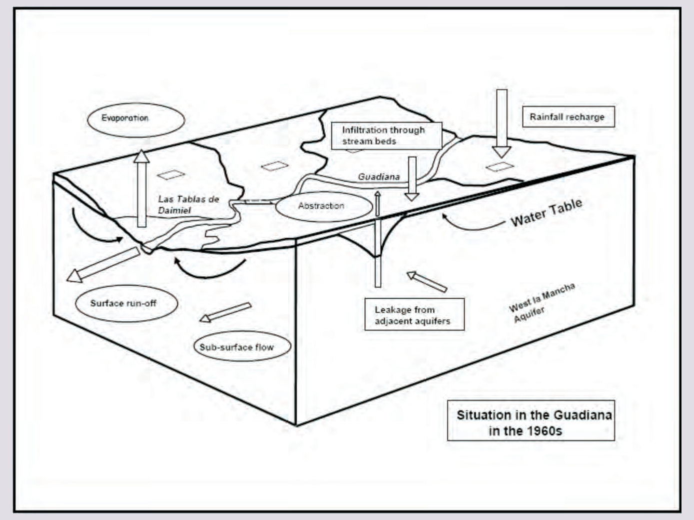
Introduction

The Tablas de Daimiel National Park (TDNP) used to be a natural wetland area in central Spain with high ecological value as carbon and nutrient sink as well as habitat for different waterfowl and plant communities. It is located at the end of a 15,000 km^2 surface catchment, the High Guadiana Basin, and a 5,000 km^2 groundwater one, the West La Mancha aquifer (Álvarez-Cobelas *et al*., 2000). The flooding of the area was mainly due to the overflowing of two rivers with different water qualities, the seasonal Cigüela, more saline, and the Guadiana, bringing fresh carbonatic groundwater.

Primarly due to intensive exploitation of the aquifer for irrigation purposes during the 1970s and 1980s, the hydraulic gradient inverted from upward to downward so groundwater discharge into the wetland stopped and the TDNP became a recharge area where incoming waters tend to infiltrate rapidly (Moreno *et al*., 2007). The progressive drying up of the wetland brought ecological impacts such as decrease in species diversity and changes in composition (ie. substitution of cut-sedge communities for reed, Álvarez-Cobelas *et al*., 2001)

Objective

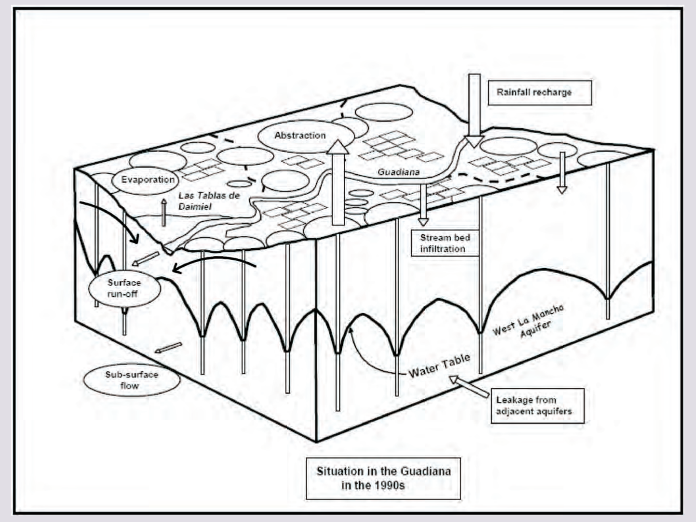
Characterization and quantification of labile nutrients stored in the unsaturated zone at the TDNP, which are readily available to be exported to the saturated zone, in order to assess potential impacts on groundwater quality and other natural ecosystems downward the watershed.



40-50 YEARS AGO

GROUNDWATER EXTRACTION
DRAINAGE
CHANNELIZATION OF RIVER BEDS
POLLUTION

HYDRAULIC GRADIENT INVERSION



TODAY

The recent evolution of the TDNP has favoured the progressive development of a permanent unsaturated zone consisting on different soil functional types regarding their physico-chemical properties for water and solute storage and transmission. These types are based on four soil materials:

Peat: organic matter accumulation under anoxic conditions.

Clay: from both geological and fluvial origin.

Charophyte layers: carbonated sediments biologically produced.

Silt: fluvial sediments in river and channel beds.

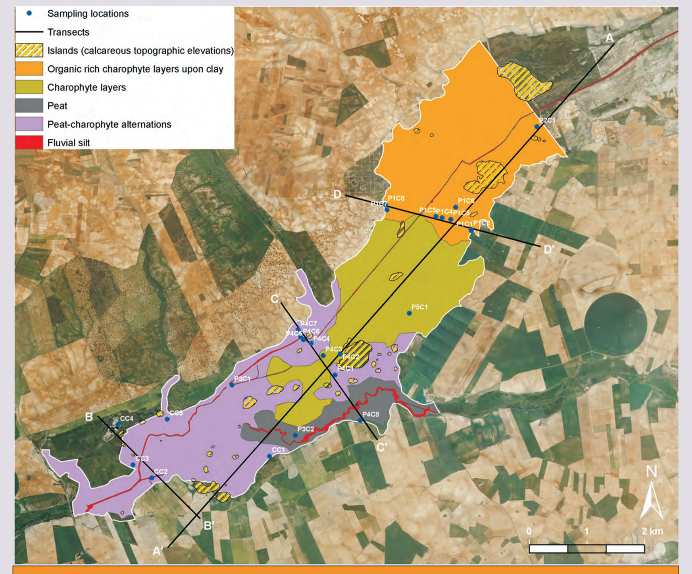


Figure 2. Distribution of soil sampling sites along different transects and map of soil functinal types within the TDNP.

Soil sampling and analysis

- July 2006 (dry soil conditions)
- 25 sampling locations following transects regarding soil type, microtopographic variation and accessibility.
- In each location representative samples were taken manually to a maximum depth of 120 cm at 20 cm intervals and kept in plastic bags (n=121)
- Laboratory analysis (ISRIC, 2002):
  - pH at 1:2.5 ratio for both soil:distilled water and soil:KCl solutions
  - Electrical conductivity (EC) in 1:5 soil:distilled water extract
  - Soluble ions in 1:5 soil:distilled water extract: pH, Na^+, K^+ (atomic emission spectrophotometry), Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, SiO_2 (absortion spectrophotometry by autoanalyser), B (ICP/AES)
  - Organic matter (OM): (Walkley-Black method)
  - Total N (organic and ammonia): Kjeldahl method
  - Available P: Olsen method
  - Carbonates (as $CaCO_3$): acid neutralization and titration with NaOH

Figure 3. Example of soil sample with an alternation of peat and charophyte layers from the field campaing in July 2006.

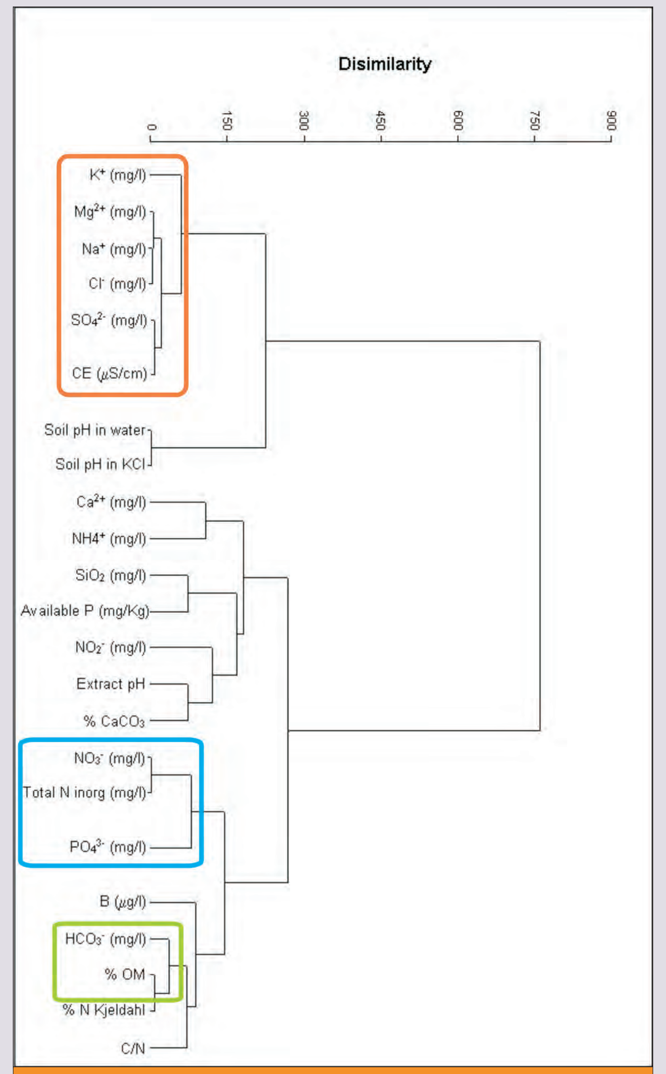


Figure 4. Cluster analysis and grouping for all soil chemical variables.

SOLUBLE NUTRIENTS

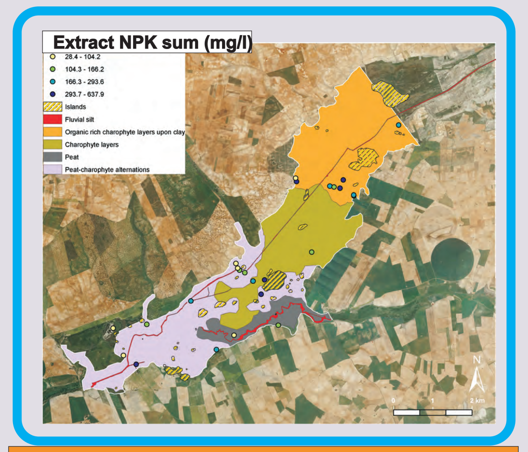


Figure 6. Spatial distribution for median values of the sum of nutrients in the aqueous extracts (NO_3^-, K^+ and PO_4^{3-})

UNEXPECTED CONNECTIONS

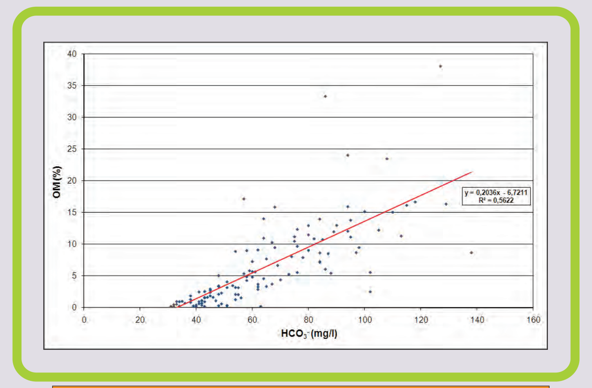


Figure 7. Linear regression between organic matter content and HCO_3^- concentration.

Grouping of soil chemical variables through cluster analysis shows:

Major soluble anions and cations: lithological effect and salinization process towards the northern and western soils of the TDNP, rich in clay and evaporitic sediments, with high EC values and an increase in Mg^{2+} and Cl^- against Ca^{2+} and SO_4^{2-}.

Soluble nutrients: tend to accumulate in central and NE areas of the Park, where organic rich charophyte layers dominate.

Unexpected relationships: related to the actual dynamics of the system, such as the increase of HCO_3^- with the OM content, possibly due to the dissolution in soil water of the CO_2 produced by microbial degradation of OM

SALINIZATION PROCESS

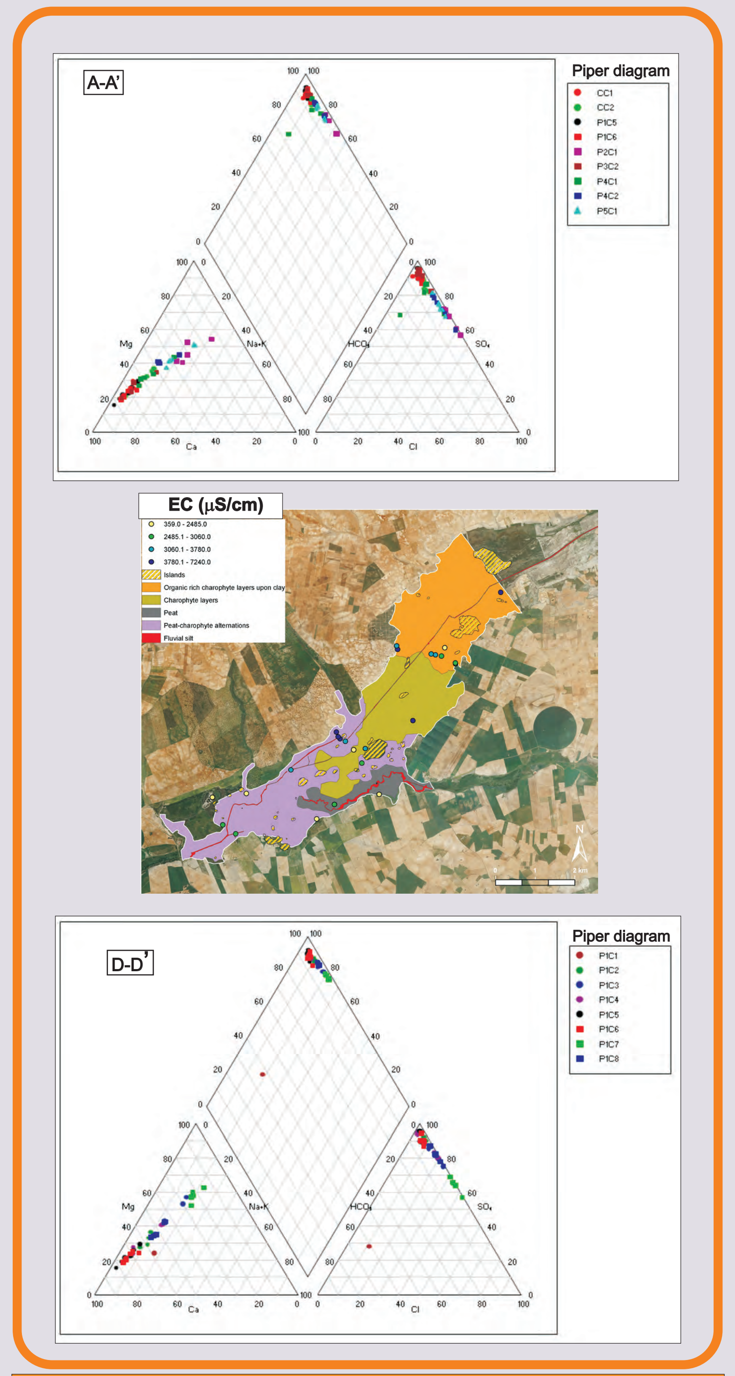


Figure 5. Piper diagrams for anions and cations from the aqueous extracts of samples collected on transects A-A' and D-D', and map of spatial distribution for median values of electrical conductivity (EC) in depth in each soil profile.

Results

OM and, therefore, **total organic N** accumulate in central and southern parts, in peaty, charophytic and silty areas, where also reed communities are widely present acting as nutrient source. **Available P** also accumulates in these areas and it seems to be specially related to silty fluvial beds (Table 1). However, centralization of values hides the actual high amounts of available P that is present in surface layers, as can be seen in the box-plots of distribution in depth. In general, nutrient (except for NH_4^+) concentrations are higher in the first 20-40 cm of the soil profile, where oxidation of OM takes place, being the levels of **NO_3^-**, **OM** (at all depths), **total N** and **available P** particularly elevated. The **C/N** ratio ranges between 6 and 12 indicating a slight mineralization trend. **pH** both in the extract and in the soil-water solution is quite homogeneous and neutral through the profile, probably due to the important amounts of $CaCO_3$ observed data not shown). Dispersion is high because of the variability and heterogeneity in soil properties.

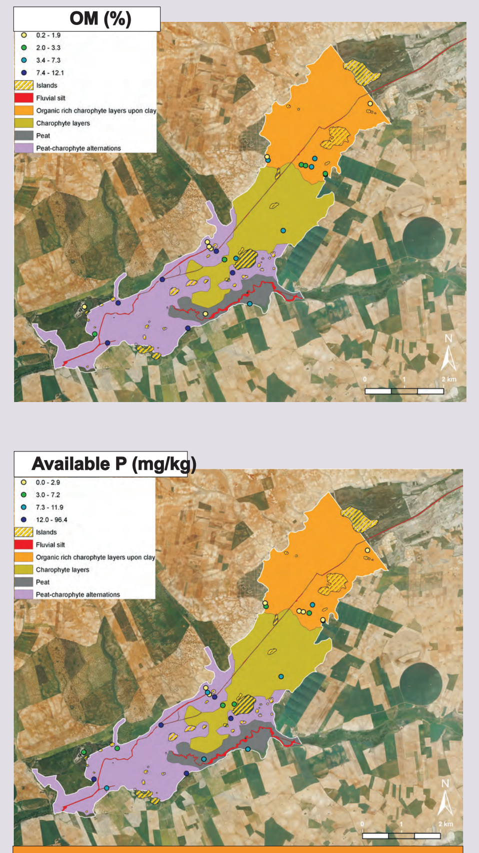


Figure 8. Spatial distribution for median contents of organic matter (OM) and available phosphorus (P) in depth.

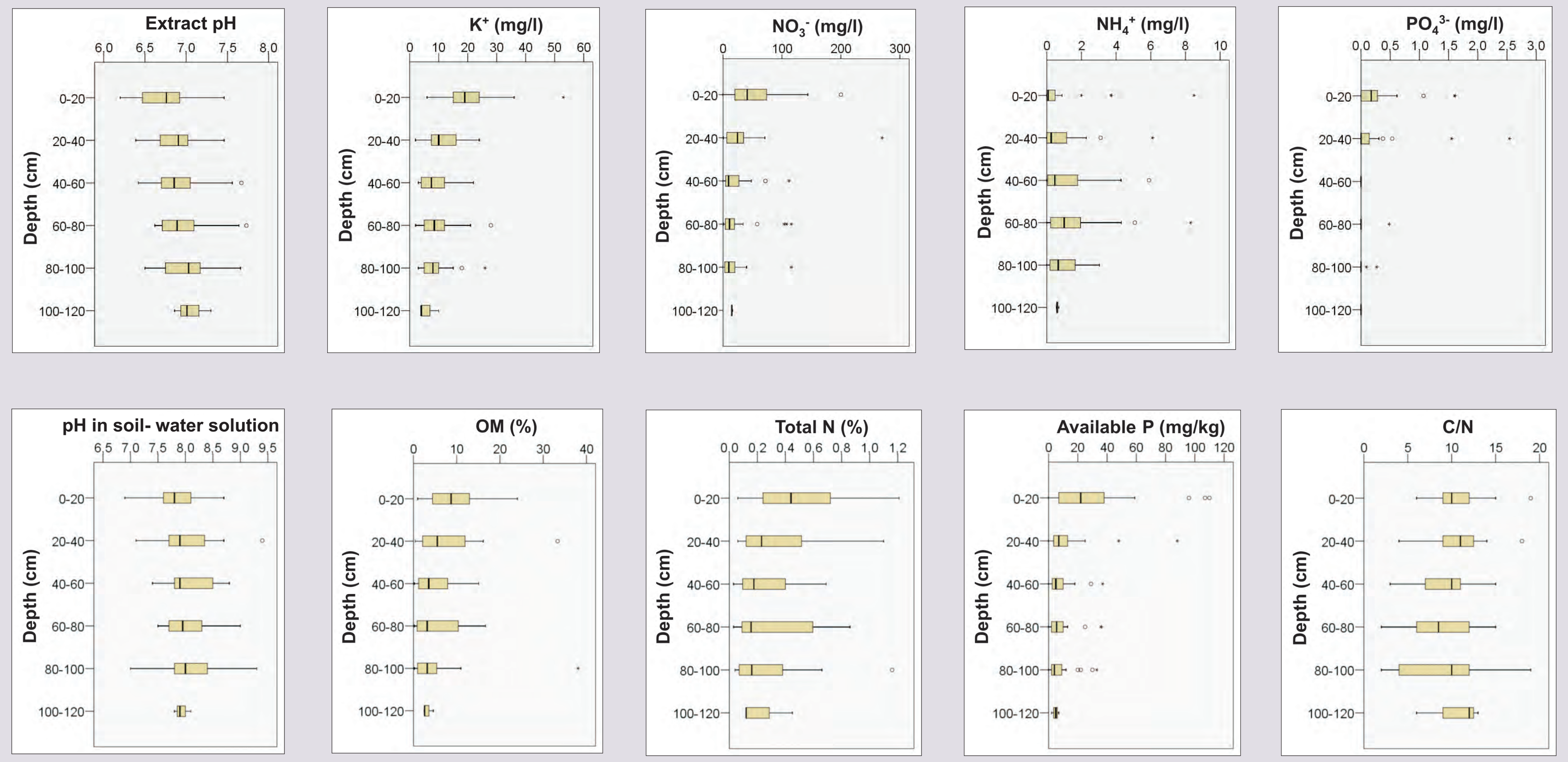


Figure 9. Box plots showing the distribution in depth of pH and concentration of labile nutrients from the aqueous extracts of the samples (top), and distribution in depth of pH, organic matter (OM) content and concentration of nutrients in the soil matrix (bottom)

		EC (µS/cm)			K^+ (mg/l)			NH_4^+ (mg/l)			NO_3^- (mg/l)			PO_4^{3-} (mg/l)			B (µg/l)			OM (%)			Total N (%)			P (mg/kg)		
Location	Soil type	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD	Me	X_M	SD
P2C1	Clay	5970	6926	2984.2	21.0	26.2	15.1	0.3	0.6	0.8	18.0	31.4	32.3	0	0.1	0.1	0	0.0	0.0	1.0	1.7	1.7	0.1	0.1	0.1	2.0	2.8	2.7
P1C5	Organic rich charophyte	2650	2597	399.9	4.5	4.8	2.8	3.3	3.6	3.6	71.0	74.0	56.1	0	0.5	0.8	0	84.2	133.8	7.1	9.7	7.6	0.4	0.4	0.3	7.2	7.2	3.1
P4C3	Charophyte	2330	2211	275.8	7.0	8.2	3.8	1.7	1.3	0.8	17.0	25.4	21.7	0	0.0	0.1	0	49.2	110.0	3.3	4.2	2.2	0.2	0.2	0.1	6.5	8.2	3.3
P4C8	Peat	2230	2026	694.9	3.0	9.0	9.5	0.1	0.1	0.2	8.0	14.4	11.8	0	0.3	0.5	0	119.2	169.8	5.8	8.8	5.9	0.4	0.5	0.3	8.8	13.2	9.1
P3C1	Fluvial silt	3430	3694	744.3	17.0	20.4	8.9	1.8	1.8	1.8	7.0	13.6	11.1	0	0.0	0.1	332	334.0	74.9	9.7	10.3	1.3	0.5	0.4	0.1	37.1	60.4	34.8

Table 1. Central and dispersion values for the concentration of nutrients in the aqueous extracts and in the soil matrix of 5 sampling locations representative of each soil material (Me: median; X_M: mean; SD: standard deviation)

Conclusions

Chemical composition and high electrical conductivity values in the aqueous extracts reflect the predominant litological characteristics and the ongoing salinization process in the northwestern clay rich areas.

High labile nutrient concentrations within the first 40 cm of soil profiles suggest an active process of leaching and accumulation of nutrients. These nutrients are stored in surface areas of organic rich charophyte layers and that they mainly come from reed decomposition. They also accumulate in silts filling natural and anthropic fluvial channel beds and other points related to the surface drainage network

Organic matter content is very high both in surface layers and deeper down the profiles. Therefore, there is a risk of nutrient mobilization towards the saturated zone, given that the water table is quite shallow in some areas (< 1m) This process would also be favoured by the infiltration of poor quality waters (Koerselman *et al*., 1993) such as the treated sweage waters from a close town, which are added to the Cigüela channel just 6 km upstream from the TDNP north limit, or the saline ones coming from groundwater recirculation, which are directly poured to the Park to keep a minimum flooded surface.

References

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Aknowledegments

The present study is part of the CICYT project referenced as CGL2005-06458-C02-01 under the following title: "The influence of climate and human activities on the degradation of protected wetlands (Tablas de Daimiel National Park)" We want to thank TDNP managers and keepers for their support and colaboration and also the Edaphology Department from the Complutense University of Madrid where some of the laboratory analysis were carried out.