

The effect of varying pH of the rhizosphere on the sorption of pharmaceutically active compounds

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Introduction

Constantly changing environmental parameters like pH, and temperature can be affecting the sorption mechanisms of various pharmaceutically active compounds (PhACs) in soils.

Low molecular-weight organic acids (LMWOAs) are generated at the interface of the rhizoplane and rhizosphere during the vegetation period and it can significantly modify the adsorption and desorption mechanism of the PhACs

The main focus: How do the LMWOAs (citric and oxalic acids), and the non-organic compounds affect the adsorption and desorption interactions of PhACs?

Materials and methods

The experiments were carried out in calcareous arenosol (WRB2014).

Samples were taken from three different depth levels (0-20 cm, 20-40 cm, 40-60 cm).

The pH has been adjusted with non-organic compounds (NaOH, HCl), and with LMWOAs (oxalic acid, citric acid).

Tested PhACs:

17 α -ethynylestradiol (EE2), carbamazepine (CBZ), diclofenac-Na (DIC).

Batch experiments:

Adsorbent: solution ratio: 1:12

Adsorption experiment period: 24 hours at room temperature (20 °C) in an incubator (dark)

UHPLC- FLD/PDA detector

Principle component Analysis (PCA)

Langmuir isotherm (1)

Freundlich isotherm (2)

Dubinin-Raduskevich isotherm (3,4,5)

$$q_e = Q_{max} \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

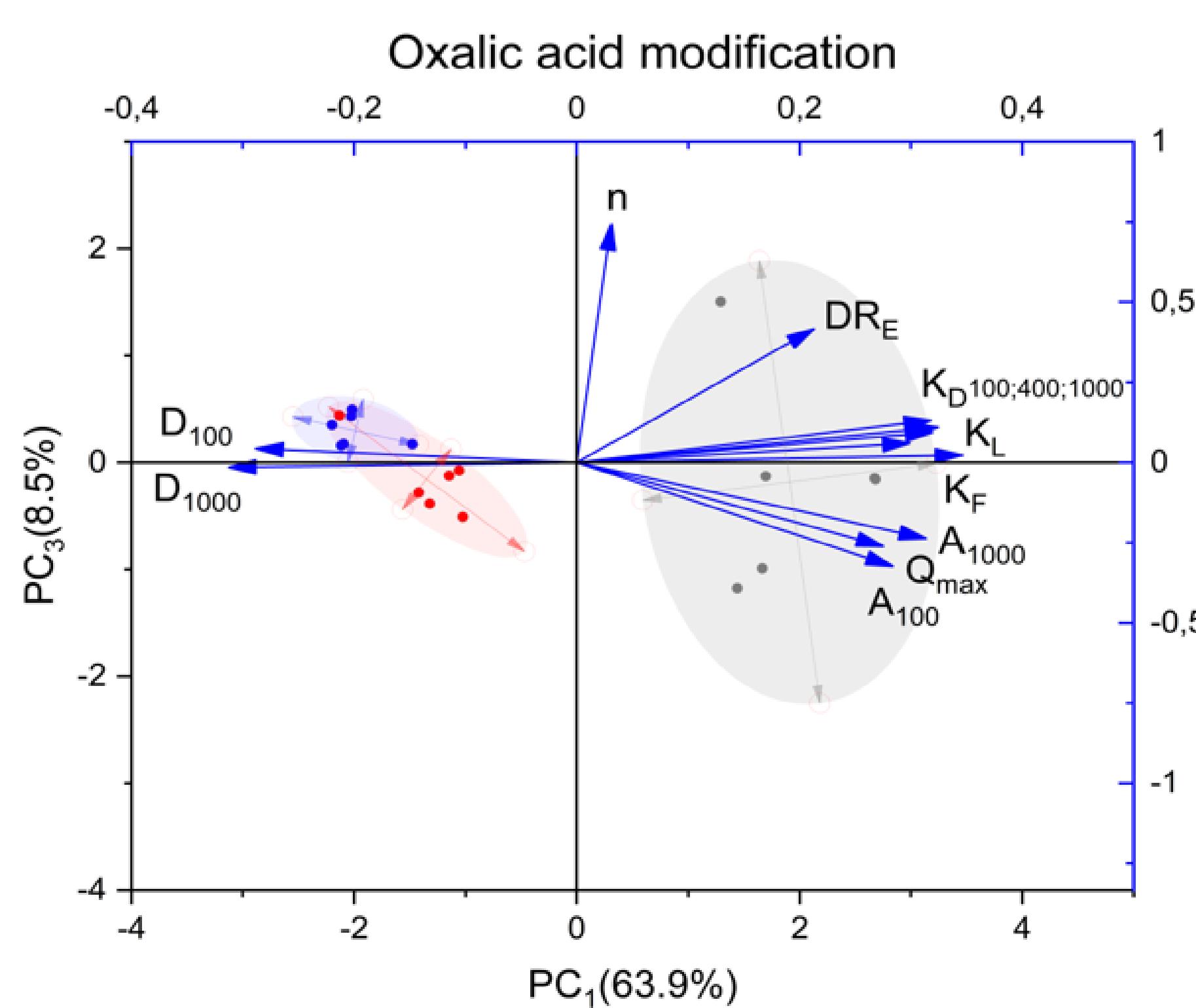
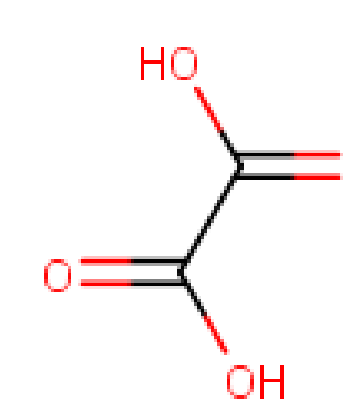
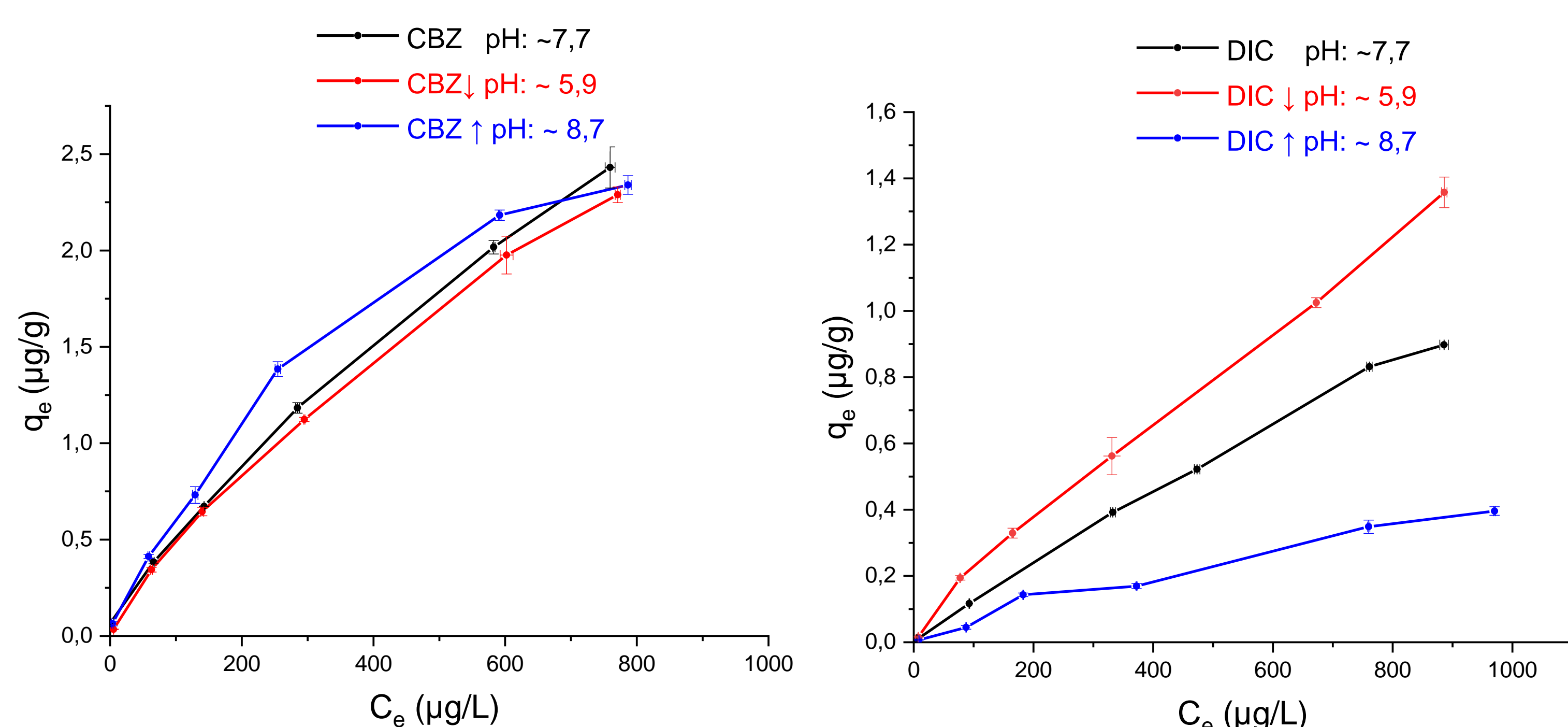
$$q_e = q_m e^{-\beta \varepsilon^2} \quad (3)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4)$$

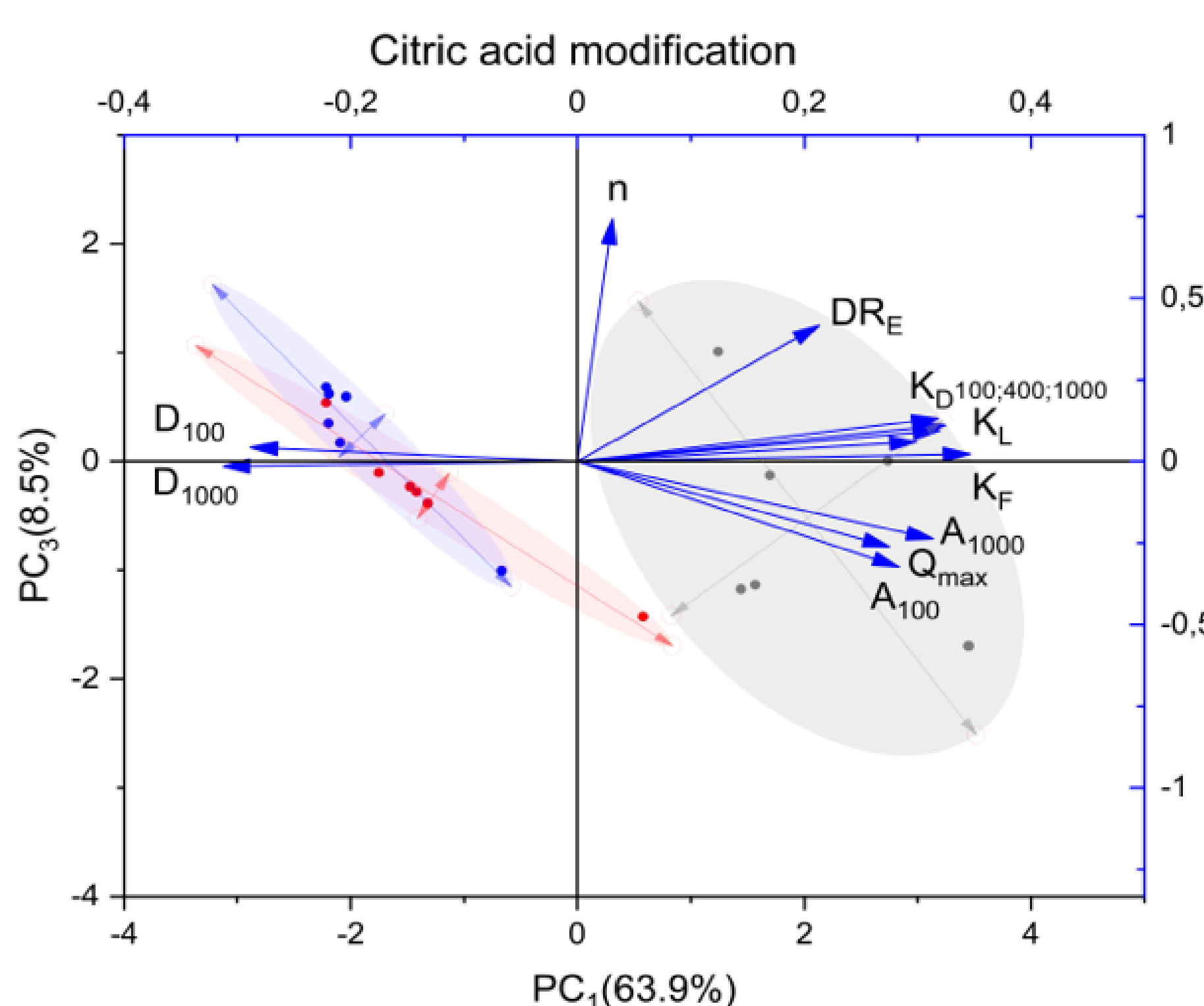
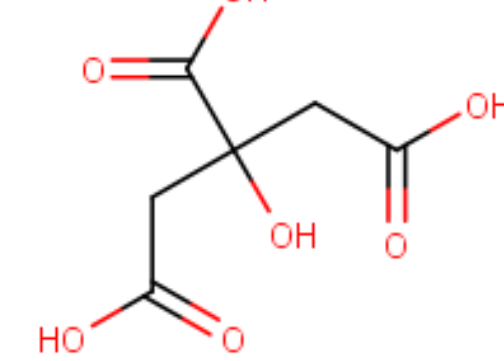
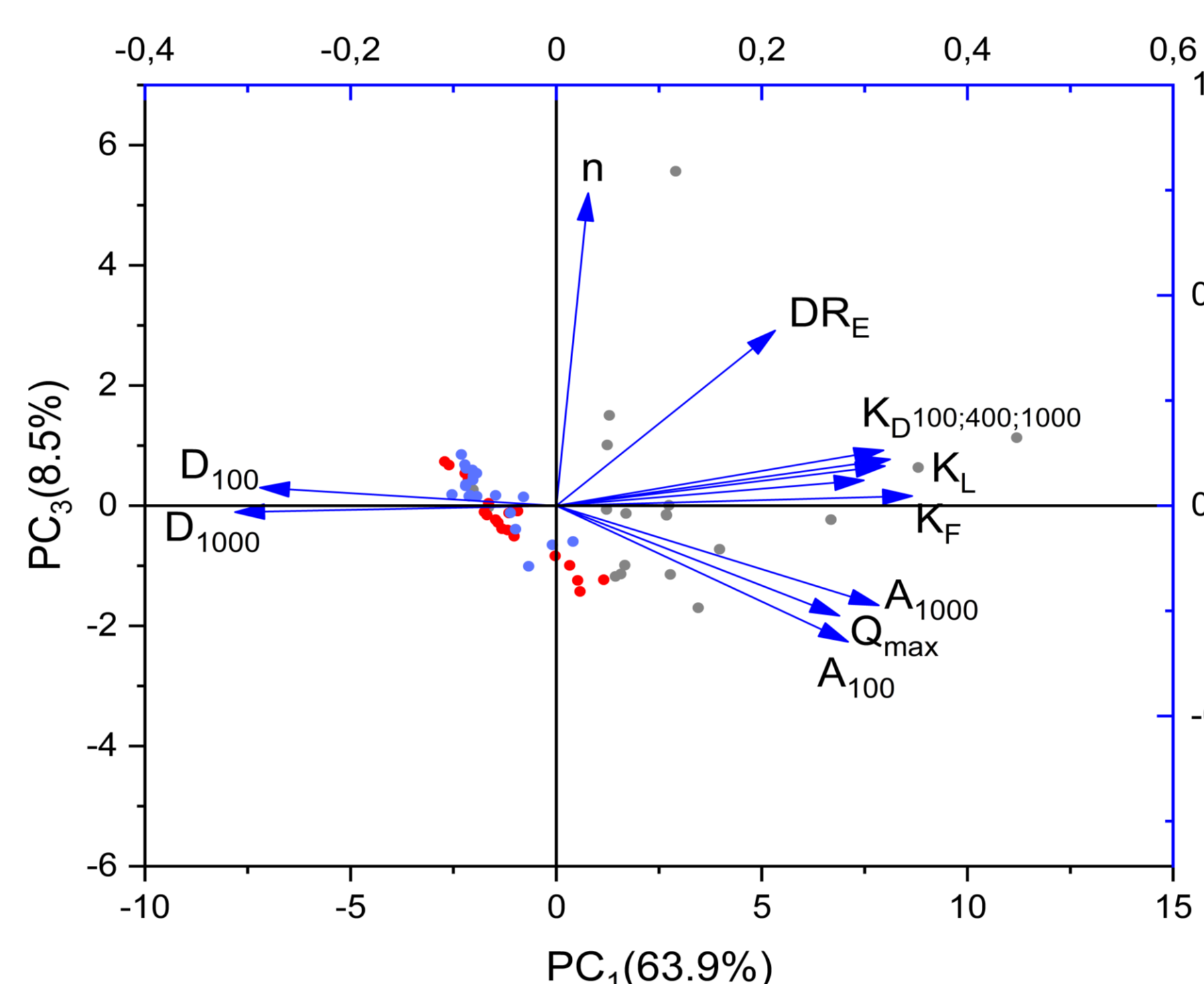
$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

Results

pH modified with NaOH and HCl



Principal component analysis of the sorption parameters of PhACs in the presence of LMWOAs



K_L : Langmuir adsorption coefficient, K_F : Freundlich adsorption coefficient, Q_{max} : maximum adsorption capacity, DR_E : Dubinin-Raduskevich adsorption energy, $K_{D,100;400;1000}$: partition coefficients, $A_{100;1000}$: adsorption amounts of PhACs, $D_{100;1000}$: the rate of desorption.

Discussion

- In the presence of NaOH and HCl, the adsorption of dissociated DIC was significantly affected by pH changes, whereas the adsorption of non-dissociated CBZ was not influenced considerably by acidification and alkalization.
- Based on the PKa values DIC is dissociated into an ionic form at environmental pH values, while the non-dissociated EE2 and CBZ have got a neutral form, which is why the PhACs were being adsorbed onto the soil particles with different sorption mechanisms.
- The PCA results suggest that the co-presence of LMWOAs and PhACs in the sorption system has a synergistic effect on CBZ and DIC. As the concentration of LMWOAs increases, the adsorbed amount of CBZ and DIC increases, indicating that more adsorption sites are available.
- Because of the high adsorption energy there is no difference in EE2 values in the competitive system regardless of the amount of acid added.

Conclusion

- LMWOAs rich in -OH and -COOH functional groups can not only modify the sorption processes of PhACs, but can also adsorb onto soil particles, providing extra adsorption sites.
- These organic pollutants could potentially be present -become available during nutrient uptake- at the boundary between the rhizoplane and the rhizosphere, and this phenomenon that could pose a significant risk to agricultural production.

References

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