

Epoxiconazole and tebuconazole in biochar amended soils: Degradation and bioaccumulation in earthworms

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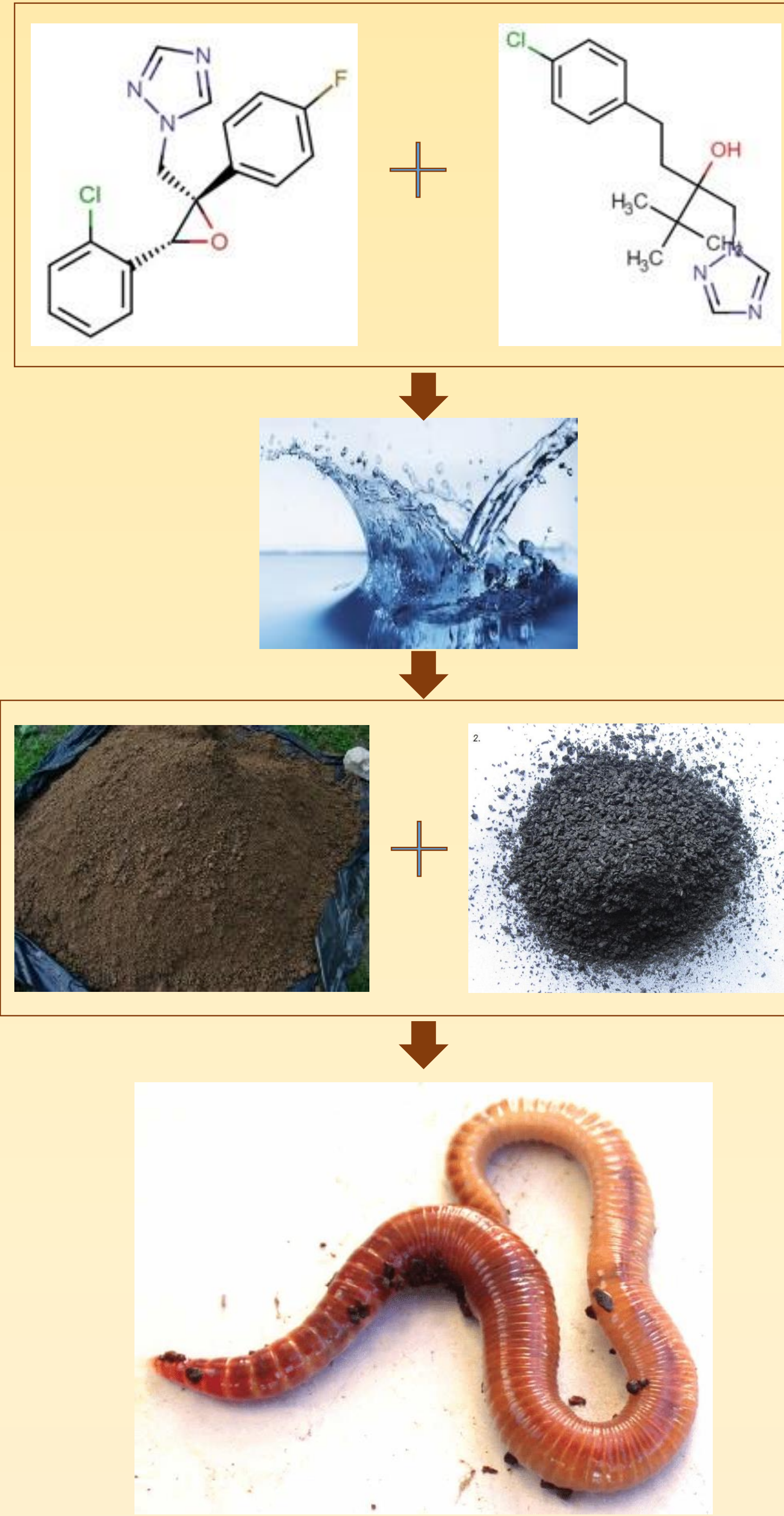


Introduction and objectives

- Our study explores the fate (degradation) and bioaccumulation (in the *Eisenia andrei* earthworm) of two model conazole fungicides, epoxiconazole (EPC) and tebuconazole (TBC), in two soils amended with three biochars (BCs) at two levels.
- The soils and BCs used were selected from previous experiments as maximally contrasting by means of their sorption of the fungicides and their properties.
- We aimed to investigate the effects of contrasting soil and BC properties, different BC doses in soil-BC mixtures, and different compounds on the degradation and bioaccumulation.

Materials and methods

- Combinations of two soils (low - L and high - H sorbing soils) and three BCs (low - L, moderate - M, high - H sorbing BCs) gave in total 14 combinations L, LL02, LL2, LM02, LM2, LH02, LH2, H, HL02, HL2, HM02, HM2, HH02, HH2.
- Final soil concentrations were 1 and 10 mg/kg<sub>soil-dw</sub> of EPC and TBC, respectively.
- The soil-BC variants (170 g at 50 % WHC) were weighed into 500 ml jars and amended with eight adult earthworms.
- No food was added to the jars.
- The experiments were conducted in an environment-controlled greenhouse with a temperature setting of 15 °C overnight (21-05 h) and 21 °C over the day (10-16 h), and light period of 16:8 with the light intensity of 95-115 mmol m<sup>2</sup>/s.
- After 0.5, 1, 2, 4, 7, 14, 21 days after the introduction of the earthworms into the jars, sampling was performed in triplicate.
- After the sampling, earthworms from the vessels were cleaned with distilled water, dried with tissue, weighed and placed in a Petri dish for one day to empty their guts.
- On the next day, earthworms were cleaned in distilled water, dried with tissue paper, weighed and frozen at -80 °C.
- Prior to extraction with the QuEChERS method, the earthworms were lyophilized (in order to get the dry weight).



Results and discussion

- In all variants, the concentrations decreased over time following first-order decay kinetics and reaching a plateau after some time.
- Model lines comparing the BC treatments with each other and with soil-only results are shown in Fig. 1.
- The addition of BC to soils caused both an increase and decrease in the degradation rate ( $k_{deg}$ ) of conazole fungicides, illustrated in Fig. 2.
- For comparing the different factors (BC dose, BC type, soils and compounds), the non-degraded residues are presented as ratios of the plateau and initial concentration ( $C_{sp}/C_{si}$ ) in Fig. 3.
- Timepoint bioaccumulation factor (Mean BAFt ± SE) calculated for the timepoints after these stabilizations can be seen in Fig. 4.
- Toxicokinetics modelling was performed for dynamic bioaccumulation factor (BAFd) and modelled lines only are displayed in Fig. 5.
- The increase of BC concentration from 0.2 to 2 % on H-soil was the best example for an increase in the  $k_{deg}$  for EPC and TBC.
- High sorbing BC always decreased the  $k_{deg}$  for EPC in soil, while the TBC  $k_{deg}$  increased (except HH02 variant).
- Moderate BC may promote  $k_{deg}$  more than both low and high sorbing BCs in L-soil by non-selectively stimulating microbial activity by increasing TOC (%).
- Low sorbing BC may promote degradation more than moderate and high sorbing BCs in H-soil by selectively stimulating microbial activity.
- Comparing soils, it was observed that in spite of the addition of BC sorption, the strength was weaker in the L-soil compared with the H-soil.
- BAFt showed a bioaccumulation decrease with the BC % increase more in the L-soil variants than the H-soil variants.
- BAFd showed bioaccumulation variability more for EPC and less for TBC.
- Rising trend for BC sorption was low ≤ moderate < high sorbing BCs in combination with all soils.
- The soil effect suggested by BAFt showed that L-soil was more prone to have a higher EPC and TBC bioavailable environment for earthworms.
- TBC decreased bioavailability, suggesting faster uptake in L- compared with H-soil variants and also with the increase of BC % from 0.2 to 2.

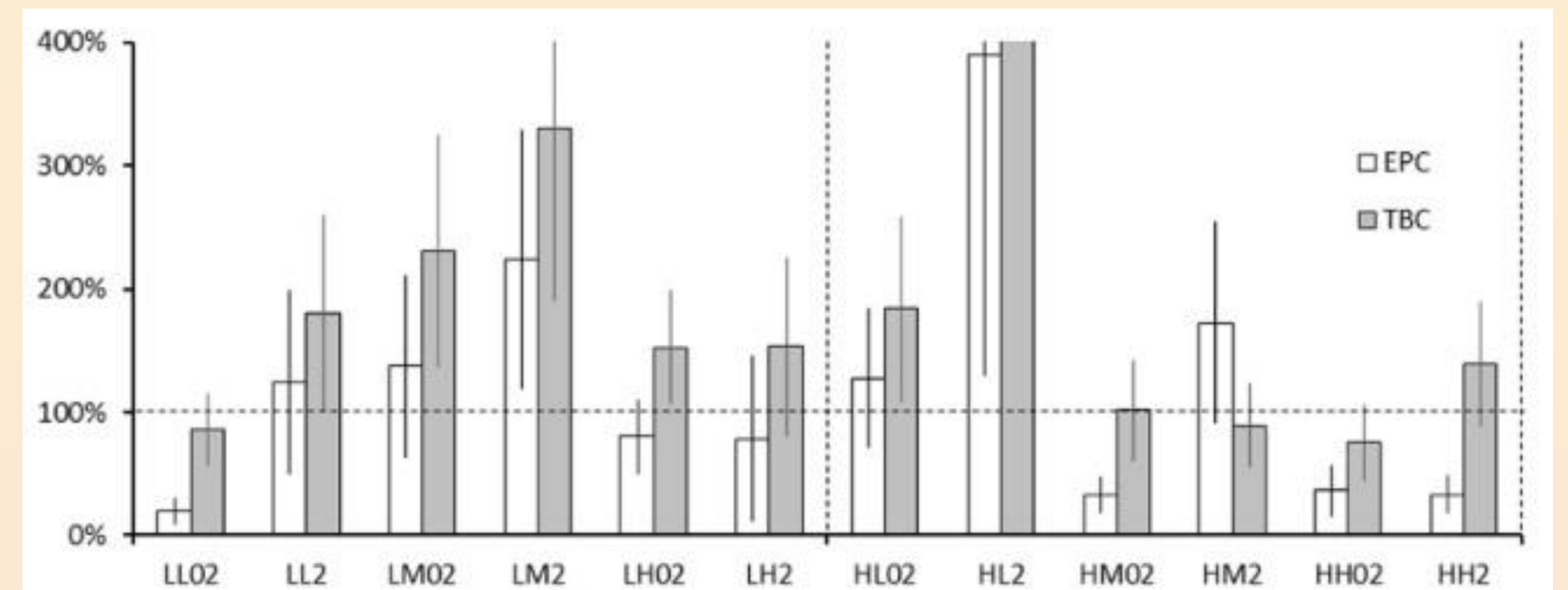
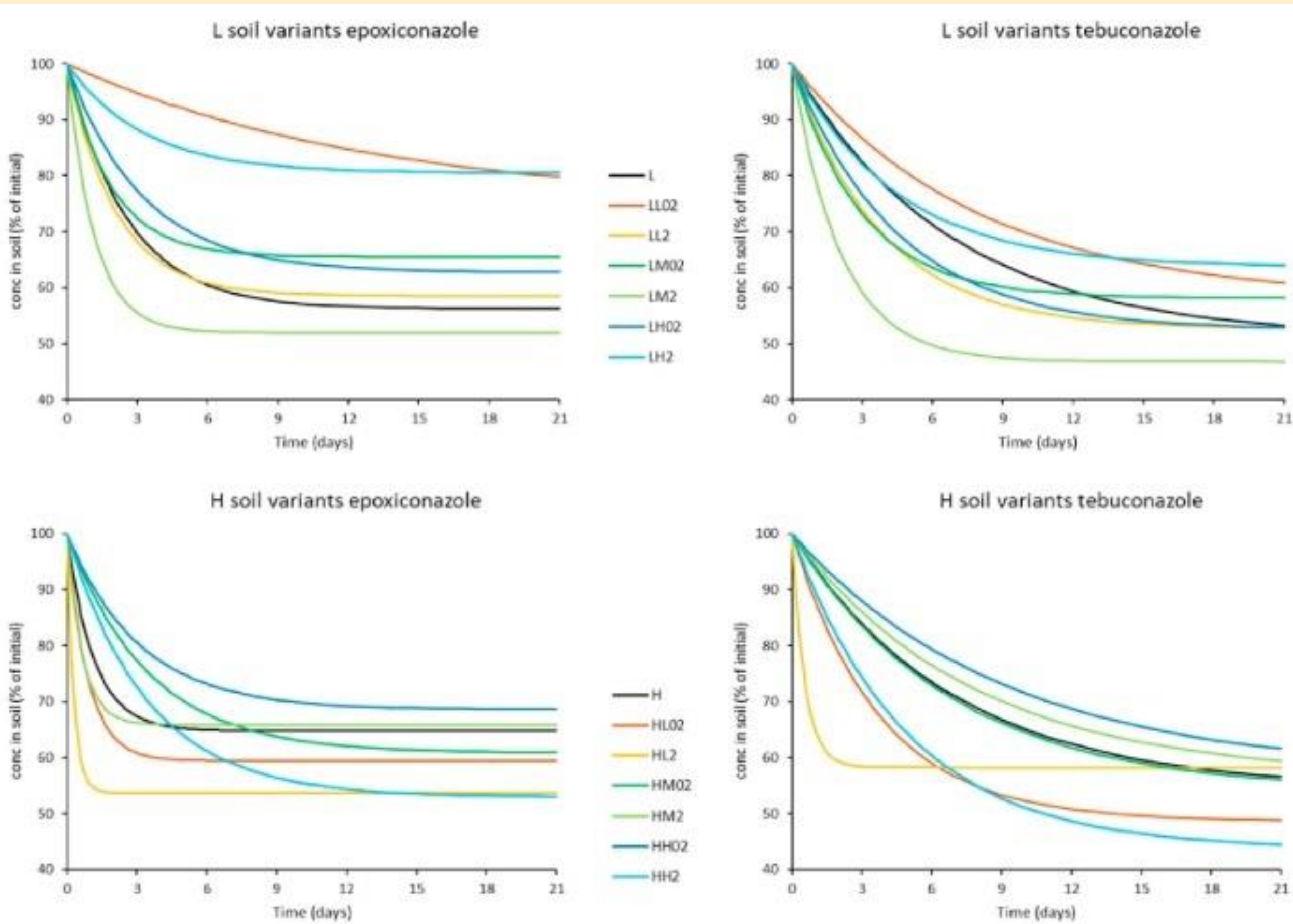


Figure 2. Biochar effect on the degradation rate ( $k_{deg}$ ) of EPC and TBC. The values show the % of the  $k_{deg}$  in biochar amended soil related to the  $k_{deg}$  in the soil without BC.

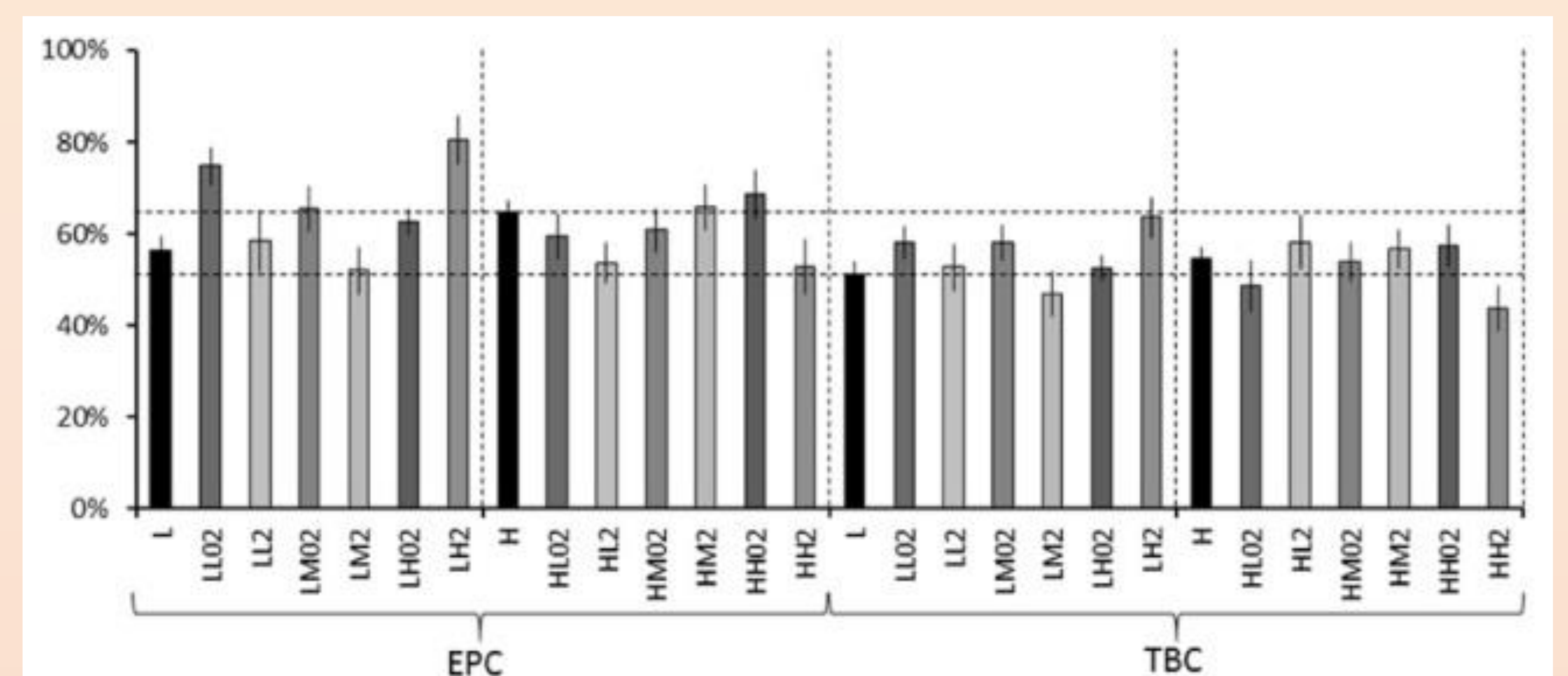


Figure 3. Non-degraded residues (plateau,  $C_{sp}/C_{si}$  in %) of EPC and TBC. Two horizontal dotted lines represent lowest L (TBC) and highest H (EPC) plateau without BC.

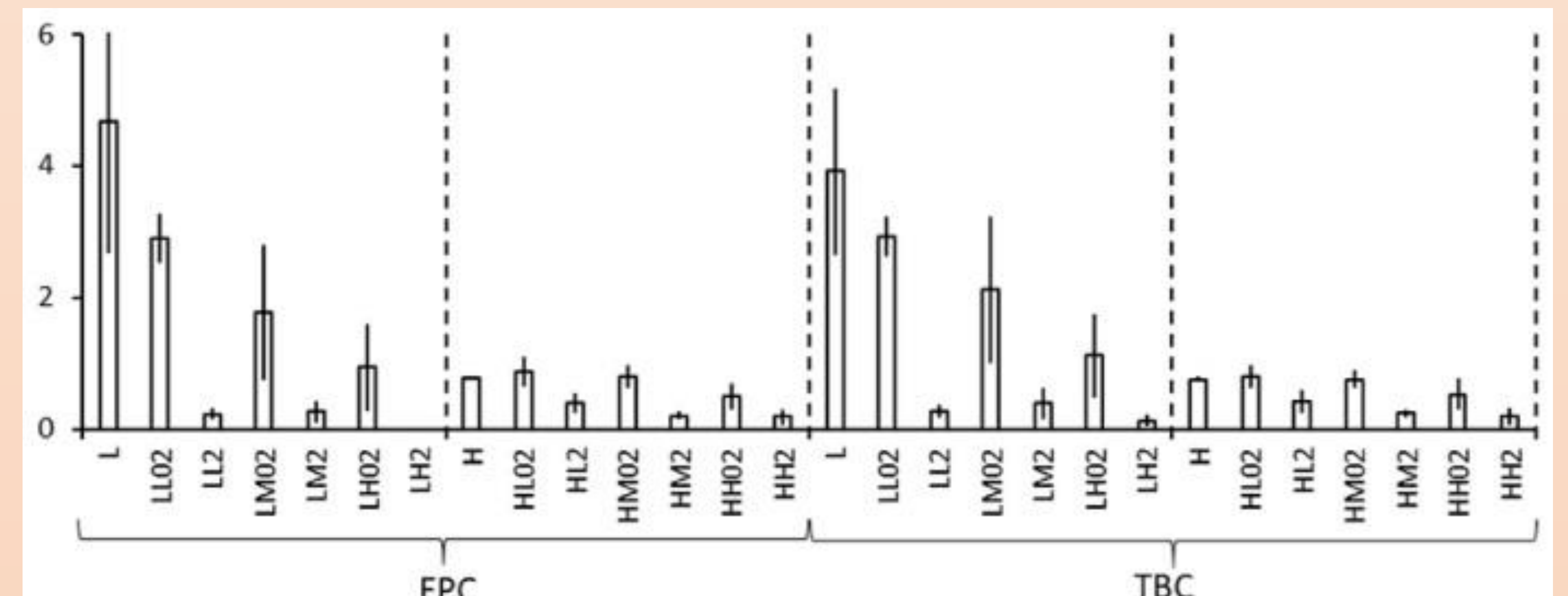
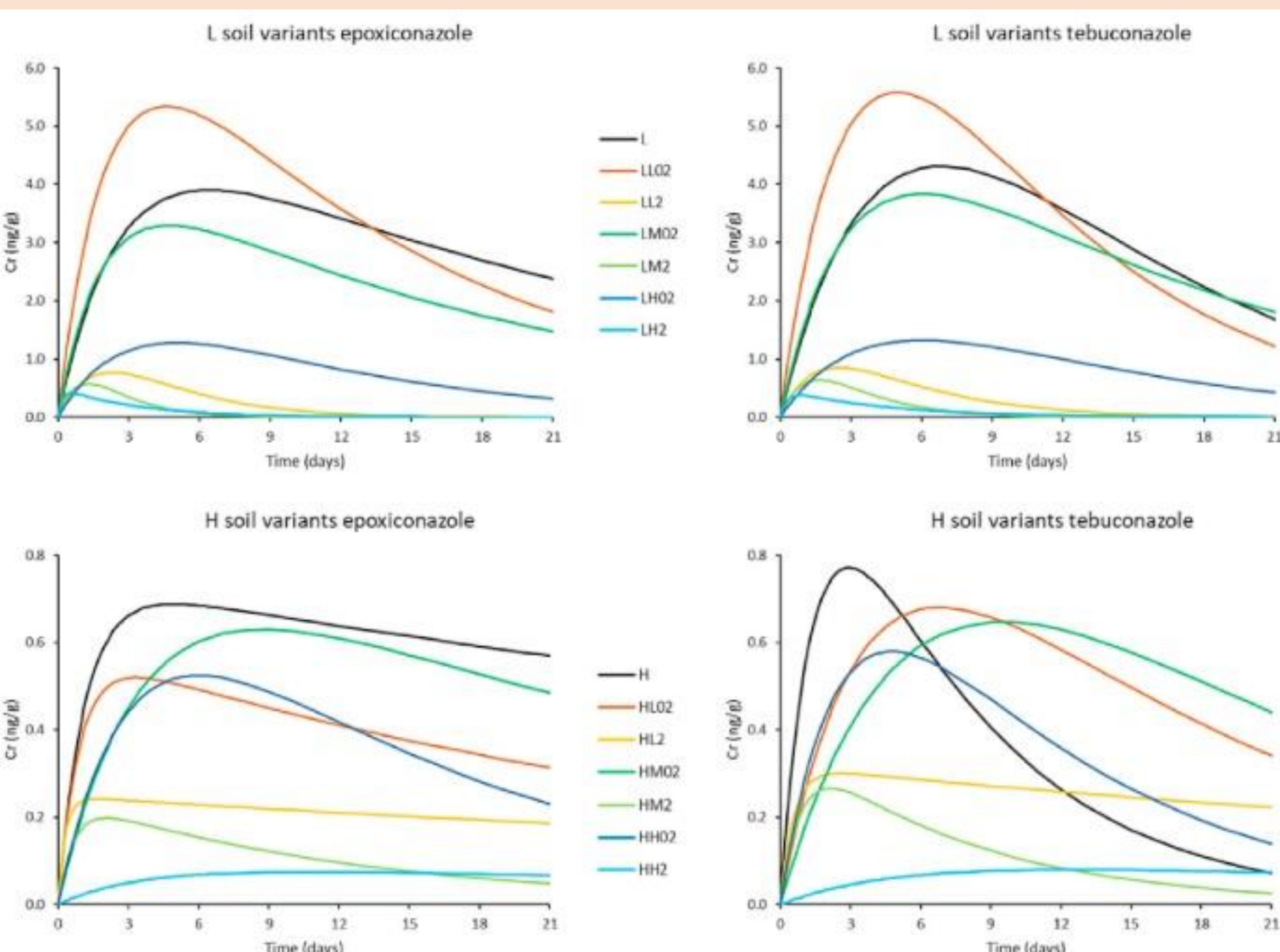


Figure 4. Timepoint bioaccumulation factor (BAFt) of EPC and TBC. BAFt were calculated for 7 days in H variants and after 21 days for L variants (except EPC LH2).

Conclusions

- The residual amounts of conazole fungicides were mostly decreasing with increased BC concentration in soil from 0.2 to 2%.
- Non-degraded residues ( $C_{sp}/C_{si}$ ) depended on the soil type, compound type, BC dose and type combined altogether.
- BC impacted fate and bioavailability of conazole fungicides in soil by changing (retarding and accelerating) degradation showing compound differences: EPC bioaccumulated more compared to TBC by BAFt, BAFd and soil differences.
- L-soil had higher bioaccessibility for EPC and TBC by BAFt compared to H-soil.
- BC differences were found to affect more L-soil by BAFt.
- A dose increase from 0.2 to 2 % of BC lowered the BAFt, more for L-soil variants compared to H-soil variants.

Acknowledgments

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