



## **Sorption of nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in soils amended with natural zeolites and biochar**

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Innovative agricultural practices increasingly include the application of natural zeolite-rich rocks (NZ, zeolites) or biochar (BC) to soils to improve their characteristics, crop yield and mitigate the effect of climate change.

Amendment practices with pre-NH<sub>4</sub><sup>+</sup> enriched zeolites (CZ) and BC have recently shown to accelerate nitrification, and thereby N losses via NO<sub>3</sub> leaching and emission of N<sub>2</sub>O, a potent greenhouse gas (GHG). The simultaneous use of nitrification inhibitors (NI) could be a useful mitigation strategy by maintaining the soil physico-chemical improvements by zeolites and BC. The efficacy of NIs relies on their availability to soil microbial biomass to inhibit/reduce ammonia oxidation.

The main objective was to study sorption of inhibitor molecules on soils amended with NZ/CZ and BCs. Sorption of NIs is likely affected by the soil amendments since they are characterized by a variety of physico-chemical properties. For example, zeolites show high cation exchange capacity (CEC), molecular sieving and reversible dehydration, while biochar also shows high CEC, high organic carbon content (OC) compared to zeolites, and hydrophobicity varying with feedstock and pyrolysis temperature.

The sorption behavior of NI was tested in soil added with 10% w/w of NZ and CZ and in pure NZ and CZ. BC obtained from different feedstocks and pyrolysis temperatures were added at 3 % w/w and at 1 % w/w for comparing the effects of application rate.

The NI 3,4-dimethylpyrazole phosphate (DMPP) was chosen as model NI because of several favorable characteristics, such as the very low application rates (< 1 % of the N added) and absence of toxicity for soil fauna and crops. Sorption was studied using 6 different concentrations of DMPP (1, 10, 50, 100, 200, 500 mg L<sup>-1</sup>) in phosphate buffer (pH 7) and containing 3 mM NaN<sub>3</sub>. Concentrations were measured by HPLC analysis, and isotherms fitted using Langmuir equation.

Both amendments significantly increased soil CEC but contrasting effects were observed concerning DMPP sorption: pure CZ and NZ showed a very low sorption of DMPP, thus zeolites decrease its sorption in the soil while BC generally increased DMPP sorption. The fact that DMPP is neutral in the studied pH range suggest that no CEC processes occurred between the employed amendments and DMPP but that probably the sorption process was driven by OC, which is known to be one of the primary carriers for DMPP sorption in soils. In this light, one of the main differences between zeolites and BC consist indeed in their OC content, which is very low in NZ/CZ and high in BC.

The low OC in zeolite amendments is suggested to cause the low sorption of DMPP while higher DMPP sorption in soils amended with BC, can be due to the additional OC, however the differences in sorption with pyrolysis temperature are very likely related to hydrophobic interactions.

Our results suggest higher availability of DMPP in zeolite amended soils than in BC amended soils, due to higher sorption in the latter.