# The application of natural and $NH_4^+$-enriched chabazite zeolites as soil amendment: a bio-geochemical exploration

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**Abstract**

Little is known about natural and $NH_4^+$-enriched zeolite amendment effects on soil N pool dynamics, N gaseous emissions and soil microbial biomass.

In this thesis, the attention is focused on gaining new insights about these subjects by the mean of both long-term field investigations and short-term laboratory tests.

In first instance, N and C pools dynamics and $^{15}N$ distribution in an agricultural soil amended with both natural (5 and 15 kg $m^{-2}$) and $NH_4^+$-enriched (7 kg $m^{-2}$) zeolites have been investigated. Zeolite amendments increased soil cation exchange capacity in the bulk soil and affected soil microbial biomass. The $NH_4^+$ supplied with $NH_4^+$-enriched zeolites was probably immediately accessible to soil microbial biomass causing a higher N immobilization and a lower microbial C/N ratio. On the other hand, amendments with zeolites at natural state probably favoured the development of fungal biomass as testified by the higher microbial C/N ratio. $\delta^{15}N$ turnover in the soil-plant system indicated that a significant amount of N derived from $NH_4^+$-enriched zeolites remained in the soil until the growing season and that it was subsequently significantly up took by sorghum plants. On the other hand, in soils amended with zeolites at natural state, isotopic results showed that plants tissues were characterized by a $\delta^{15}N$ approaching that of chemical fertilizers, suggesting an enhanced N uptake from this specific source with respect to the unamended plot.

Similar evidences were recorded also during maize and wheat cultivation.

The effects of different chabazite zeolite amendments on soil gaseous emissions ($CO_2$, $N_2O$, $NO_x$ and $NH_3$) were evaluated in high resolution by the mean of a short-term incubation experiment. Different soil-zeolite mixtures were incubated for 24 h both immediately after the application of urea fertilizer and without a further N input. Immediate $CO_2$, $N_2O$, $NO_x$ and especially $NH_3$ emissions after fertilizer application were generally reduced in soils amended with zeolites at natural state, indicating a potential valuable material for reducing soil C-N gaseous losses. On the other hand, the application of $NH_4^+$-enriched zeolites supplied a fraction of N that was immediately subjected to gaseous losses.

Finally, the short-term effects of different chabazite zeolite amendments on soil microbial biomass (and activity) have been investigated. A silty-clay agricultural soil was amended in three different ways, including the addition of natural (5 and 15 wt%, respectively) and $NH_4^+$-enriched (10 wt%) chabazite zeolite rich tuffs. Dissolved organic carbon (C), total dissolved N, $NH_4^+$, $NO_3^-$, $NO_2^-$, microbial biomass C, N and $\delta^{15}N$ and ergosterol were periodically measured over a time course of 16 days in a laboratory incubation experiment. Soil amended with 5 wt% of zeolites at natural state showed increased ergosterol content as well as microbial C/N ratio, suggesting that fungal biomass was probably favored.

On the other hand, the $NH_4^+$-enriched zeolite showed strong interactions with soil microbial biomass N. Isotopic measurements supported microbial assimilation of the N introduced with this material since day 2 of incubation. The high dissolved organic C and microbial N suggested an increase of mineralization and immobilization processes. In addition, microbial N was related to $NO_3^-$ production over time and inversely related to $NH_4^+$, suggesting nitrification processes especially from day 7. Low microbial C/N ratio support bacterial prevalence in this substrate.

In conclusion, amendments with zeolites at natural and $NH_4^+$-enriched states differently affected soil N pool dynamics, gaseous emissions and microbial biomass. Natural zeolites have probably increased fertilization efficiency, reduced soil gaseous emissions and favored fungal biomass. On the other hand, notwithstanding the N inserted with $NH_4^+$-enriched zeolites has been proved to be exploited by plants, this material caused a priming effect on soil microbial biomass.