

## Mesocosms experiments with zeolite-amended marsh soils to reduce nitrogen leaching

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To prevent diffuse nitrogen (N) contamination from agricultural activities the Water Framework Directive institutes a series of good practices for a sustainable agriculture in vulnerable areas. Notwithstanding, N leaching is still a major issue at the European and global scale. To increase N retention capacity of lowland soils, natural zeolites were used in an experimental field near the town of Codigoro, in the eastern part of Ferrara province (Italy), pertaining to the Po delta reclaimed marsh soils, actually 3 m below sea level. To test their effectiveness a tridimensional model 100 x 50 cm in size (divided in two sections of 50 x 50 cm each) was built. Tank was completely filled with soil composed by 8±1% of sand, 49±2% of silt, 42±2.5% of clay and 8±1.5% of organic matter, with a bulk dry density of 1.15±0.05 g/cm<sup>3</sup>. In the uppermost 20 cm of one mesocosm, the equivalent of 7 Kg/ha of natural NH<sub>4</sub><sup>+</sup>-charged zeolite was mixed with the soil, whereas the second mesocosm was fertilized with the equivalent of 270 kg/ha of urea. The filling has been done manually, compacting successive layers of about 2 cm each. During this procedure, 5TE Decagon probes were inserted every 8 cm to monitor water content, temperature and bulk soil conductivity. Suction cups were also inserted at the same depths to monitor soil water composition. The two mesocosms were irrigated with a micronizer for 2 months at an average rate of 4 mm/d. The irrigation water was taken from the irrigation channel close to the experimental field. The regular irrigation created a percolation front slowly moving downward. At the end of the experiment, duplicate core samples were excavated and analyzed for mineral N (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) and for Cl<sup>-</sup> and Br<sup>-</sup> used as tracers. Soil water samples were also obtained by suction cups.

The mass balance of N within the two mesocosms highlighted that the natural zeolites acted as a strong buffer in N leaching, with most of the mineral N retained in the soil as adsorbed NH<sub>4</sub><sup>+</sup>. On the contrary, the mesocosm supplied with urea exhibited the greatest NO<sub>3</sub><sup>-</sup> concentrations in both soil solutions and cores.

## Aqueous carbonate speciation in equilibrium with Aragonite under subduction zones conditions

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In the course of subduction, carbonate minerals in the oceanic crust may survive dehydration and partial melting of the subducting slab [1-3] and transfer carbon from the surface into the deep mantle. However, the investigation of the solubility of carbonate minerals and aqueous speciation of carbon under the ranges of temperature and pressure relevant to subduction zones in the upper mantle remains largely unexplored experimentally and theoretically [4]. Here, we report a combined experimental and theoretical study of the equilibrium of CaCO<sub>3</sub> minerals with pure water and NaCl aqueous solutions in a larger *PT* range. The carbonate-bicarbonate speciation in the aqueous phase was first studied by *in-situ* Raman spectroscopy in a diamond anvil cell. Experimental solubilities of aragonite and relative amounts of the dissolved C-species were obtained and used to constrain a theoretical thermodynamic model of the fluid speciation and solubility in equilibrium with aragonite. In pure water at 300–400°C, the experimental and theoretical results indicate that CO<sub>2</sub> is a minor species in fluids in equilibrium with aragonite at *P* > 10 kbar. Instead, the CaHCO<sub>3</sub><sup>+</sup> species becomes important until *P* > 50 kbar, where carbonate ion and CaCO<sub>3</sub><sup>0</sup> become the dominant C-species. At higher temperatures, the theoretical model indicates that CO<sub>2</sub> again becomes a major species in fluids in equilibrium with aragonite depending on the pressure. The presence of sodium chloride in the fluid expands the pressure domain where the speciation of carbonate is highly variable.

[1] Yaxley & Green, (1994) *EPSL*. **128**, 313-325. [2] Molina & Poli, (2000) *EPSL*. **176**, 295-310. [3] Kerrick & Connolly, (2001) *EPSL*. **189**, 19-29. [4] Martinez *et al*, (1994) *Chem.Geol.* **207**, 47-58.