

What happens with the nitrogen in sewage sludge once this material is pyrolyzed?

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The transformation of sewage sludge (SS) into char by pyrolysis achieves sludge hygienization, a necessary step prior to a possible application on agricultural soils. Former studies indicated that during this process part of the organic nitrogen (No) of this material is incorporated into the aromatic network of the charred product and forms the so called black N (BN). De la Rosa and Knicker (2011) showed further that at least some of the BN is bioavailable. However, neither the pathways of BN formation nor its chemical structure is well understood.

Therefore, we studied the production of inorganic N (Ni) and the forms of No after subjecting two types of SS to hydrothermal carbonization (HTC) and dry pyrolysis (Dry-Py). The samples were collected at two different stages of the wastewater treatment (hereafter A_SS and T_SS) at the Experimental Wastewater Treatment plant CENTA, located in Carrion de los Céspedes (Southern Spain). Four chars were produced by HTC at 200°C and 260°C, and with residence times of 30 min and 3 hours. Dry pyrolysis char was obtained after heating at 600°C for 1 hour. The organic N forms were revealed by solid-state ¹⁵N nuclear magnetic resonance (NMR) spectroscopy.

All pyrolysis conditions resulted in a decrease of the amount of total N (Nt). Whereas HTC preserved between 83-59% of original N, only 2% were recovered in the char after Dry-Py. With respect to Ni, the amounts of ammonium and nitrite increased between 2 and 4 times compared to the non-treated SS after HTC. After Dry-Py no Ni was detected in the solid residue. The solid-state ¹⁵N NMR spectra of the non-treated SS are dominated by the signals assignable to amide-N. With increasing temperature and residence time applied during HTC, a shift of the signal intensity toward the region of pyrrole-N was evidenced. The largest contribution of pyrrole-N was identified in the sample obtained after heating at 260°C for 3h although the ¹⁵N-intensity in the chemical shift region of amide/carbazole N dominated the spectrum. In contrast, Dry-Py resulted in a dominance of pyrrole-N. In conclusion, our study demonstrated the impact of the pyrolysis conditions on the quantity and quality of N-forms in chars of SS. Considering the N fertilization potential, HTC chars may be more suitable than chars produced by Dry-Py if fast fertilization is needed due to the presence of Ni. On the other hand, the binding of N in heterocyclic structures retards its bioavailability. Thus Dry-Py chars will be a better choice, if slow N-release is wanted. However, deeper and specific researchers are necessary to confirm this hypothesis.

De la Rosa JM, Knicker H (2011) Bioavailability of N released from N-rich pyrogenic organic matter: An incubation study. *Soil Biology and Biogeochemistry* 43: 2368-2373