Molecular characterisation of fertilizing materials of residual origin for a better understanding of interactions with pollutants

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The increasing demands on food and drinking water due to the rising world population induces increasing production of organic waste such as manure and sewage sludge. The main sustainable valorization pathway for these biodegradable waste is land farming despite it potentially contain metal traces elements and organic micro contaminants. The consequence can be a pollution of soils, aquatic resources, crops and finally human food chain. Depending on the characteristics of these organic fertilising material of residual origin as well as the treatment it was submitted to, pollutants can be more or less degraded or bio-available. Indeed, processes such as composting can participate to degrade organic pollutants or modify heavy metals bio availability.

In this context a better knowledge of the characteristics of organic fertilising material of residual origin is essential to envisage the interactions between organic fertilizing materials of residual origin and pollutants which are eventually present. The impact of several pre-treatments processes such as drying, hygienisation, stabilisation or composting was studied. For this purpose, horse and cattle manure, recirculated, limed, dried, digested or composted sludges were characterized at the molecular level using elemental analysis and double-shot thermochemolysis. In parallel the same samples were analysed for chemical functions and biochemical content according to the methods described in Lachassagne et al (2015), and for their fertilizing properties. Moreover these properties were put in regards to their ability to desorb copper during landspreading.

Composted, and reed bed sludge presented high material (organic and mineral material) content and high protonic exchange capacity in particulate phase of sludge. In limed, filter pressed, digested thickened sludge a large protein, polysaccharide and “humic like” substances content was measured in the soluble phase while the distribution of the corresponding fluorescence intensity in the floc (observation of confocal laser scanning microscopy) was low. Large DOC content observed in soluble phase of limed sludge, centri-dried and anaerobic granular sludge corresponded to high protein contents under the 3D-fluorescence observation. High content of carboxyl and phosphoric functional groups was measured in particulate phase of composted and dewatering sludge while they were present in high percentages in soluble phase of limed, digested, thickened sludge.

The low C to N ratios (table 1) demonstrated stable organic matter. This ratio is higher for composted sludge than for digested or dried sludge. In parallel the H to C atomic ratio is lower for composted and digested sludge which is characteristic of humified materials.

The characterization of sludge by thermochemolysis at 350°C (first shot) showed the presence of fatty acids, hydroxyacids, diacids and steroids. Iso and anteiso C_{15} and C_{17} compounds of bacterial origin, demonstrated thanks to the branched to linear ratio a higher bacterial contribution for the digested sludge is observed whereas the composted sludge are more stable. This is confirmed by the hydroxyacids / fatty acid ratio (H/A) or diacids/monoacids (D/A). The second shot at 600ºC produced cellulose, lignin and proteins moieties and a series akenes/alkanes. The toluene/styrene ratio higher than 1 outlined the natural origin of organic compounds.

Table 1. Elemental analysis of different sludges

	circulated	dried	Composted	digested
C (weight %)	34.97 ±0.10	31.86 ±0.08	25.86 ±0.46	29.24±0.06
H (weight %)	5.50 ±0.27	4.86 ±0.02	3.35 ±0.02	4.72±0.23
N (weight %)	6.09 ±0.03	5.67 ±0.12	3.43 ±0.22	5.84±0.02
C/N weight	5.74	5.62	7.54	5.01
H/C atomic	1.89	1.83	1.55	1.94

Double-shot thermochemolysis is a technique particularly well adapted to the molecular characterization of organic waste from different origin. The pyrolysis results showed differences at the molecular level which can influence the interactions with pollutants and soil organic matter. Low copper desorption efficiency (<5%) were measured in the samples. Copper was more mobile in limed and filter-pressed sludge compared to other CAS (conventional activated sludge) due to the reduction of copper distribution in exchangeable or reducible fraction.

Lachassagne, D., Soubrand, M., Casellas, M., Gonzalez-Ospina, A., Dagot, C. Impact of sludge stabilization processes and sludge origin (urban or hospital) on the mobility of pharmaceutical compounds following sludge landspreading in laboratory soil-column experiments. 2015. Environmental Science and Pollution Research 22(21), pp. 17135-17150

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