New application of density fractionation: assessing trace element/soil matrix associations within organic waste-amended agricultural soils

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Zinc (Zn) is a trace element (TE) that occurs naturally in soils, however spreading Zn-rich organic waste (OW) on farmlands may lead to hazardous Zn levels. Common problems are related to phytotoxicity, introduction into the food chain and groundwater contamination. Assessing the associations between OW-borne Zn and the soil matrix is paramount to predict its short- and long-term behavior in the environment. This is usually pursued by using either single/sequential extractions (SSE) or spectroscopic methods such as XAS. Nevertheless, SSE reflects element extractability rather than the nature of its interactions with bearing phases, while XAS requires synchrotron radiation sources that are not available in certain regions of the world. We applied a third approach in this study – namely soil density fractionation – to isolate and characterize the constituents of the soil matrix (i.e. potential Zn bearing phases) and thereafter identify their associations with natural and OW-borne Zn. The target density fractions were the following: <1.9 g cm^{-3}, 1.9–2.25 g cm^{-3}, 2.25–2.5 g cm^{-3}, 2.5–2.7 g cm^{-3}, >2.7 g cm^{-3}, plus an extractable fraction. The soil analyzed was a clayey Hapludox soil that received controlled pig slurry applications over 11 years, causing a 2-fold increase in Zn concentration within the surface layer: from 105.8 mg kg^{-1} of Zn (control soil) to 206.6 mg kg^{-1} of Zn (amended soil). Among the six selected density fractions, two of them were the most contrasting and representative. (I) The light fraction (<1.9 g cm^{-3}) contained high OM concentration but accounted for only ~5% of the bulk soil mass. (II) The mineral-rich fraction (2.5–2.7 g cm^{-3}) contained mainly quartz, kaolinite, vermiculite, a small amount of hematite and accounted for ~80% of the soil mass. In the control soil (no pig slurry application), 79.7% of the Zn was found in the mineral-rich 2.5–2.7 g cm^{-3} fraction. In the soil amended with pig slurry, the proportion of Zn found in the 2.5–2.7 g cm^{-3} fraction decreased to 57.3%, as Zn was also found in the OMrich <1.9 g cm^{-3} fraction (13.2%) and in the extractable fraction (16.6%). Other fractions were less representative in both soils (control and amended). The extractable, <1.9 g cm^{-3} and 2.5– 2.7 g cm^{-3} fractions accounted for roughly $^{1}/_{3}$ each of the OW-borne Zn fate in the amended soil. Finally, these results were compared with data we previously reported for the same field experiment using well-stablished SSE and XAS techniques. Density fractionation not only agreed but also complemented the understanding of previous observations. This work demonstrates that density fractionation may be used as either main or complementary approach for assessing the biogeochemistry of TE such as Zn in the context of OW recycling in agricultural soils.