Speciation of Heavy Metals in New York City Soils

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Abstract:
Selective and sequential leaching methods were used to study the speciation of Cr, Mn, Ni, Cu, As, Cd and Pb in soil samples collected from New York City residential and community gardens. Eight air dried samples, four of which were different size fractions of a same soil sample, were used in this study.

A three-step sequential extraction procedure was followed. The exchangeable and carbonate fraction was obtained by equilibrating 40-mL 0.11-M acetic acid with 5-g of soil for 16 hours. This was followed by washing of the residue, and extraction of the reducible fraction with 40-mL 0.1-M hydroxyammonium chloride (pH adjusted to 2.0 with HNO_3). The residue was digested with H_2O_2 and then the oxidizable and organic fraction was extracted with ammonium acetate (pH adjusted to 2). The residue was then digested with H_2O_2/HNO_3 and extracted with 1.0-M HNO_3 for total metal concentrations. The results show that there are almost no heavy metals in the exchangeable or carbonate fraction, with the exception of Cd (2-20%) and Zn (9-32%). The reducible fraction also only contains a small percentage (generally <10%) except for Cd (19-46%) and Mn (45-59%). Appreciable amounts of Cu (39-70%), Pb (25-63%) and Cr (50-70%) exist in the oxidizable or organic fraction, while most As, Ni and Fe were not organically bound or oxidizable. No systematic difference is observed among the different size fractions, except that the percentage of organic-bound Pb was lower for fine fractions (25-30%) than for coarser fractions (44-46%).

Selective extracts were obtained by shaking 2.0 g of sample with 10 mL of the following reagents: (1) 1.0-M KNO_3; (2) 1.0-M ammonium-acetate; (3) 0.04-M NH_2OH-HCl solution; (4) 1.0-M NH2OH-HCl solution; (5) 0.1-M Na_2-EDTA solution; (6) 1.0-M acetic acid; (7) 0.2-M sodium pyrophosphate; and (8) Ammonium acetate with pH adjusted to 4.8. The results reinforce the findings from the sequential study but reveal further details. In general, heavy metals do not exist in an exchangeable form, nor do they associate with carbonate or oxides. There is ~20% of soil Pb in the easily soluble organic and exchangeable fraction, part of which can be exchanged with 1-M ammonium acetate. By comparison, the majority of Cu in organic phase (28-53%) is not exchangeable. Mn-oxide binds small amounts of Cd (10-22%) and Zn (7-22%). Little Cr was observed in the organic fraction, suggesting that 50-70% of Cr is in the oxidizable form.

The metal speciation data has profound implications on several aspects. For example, Pb and Cr is largely not bound to carbonates or oxides, and only a fraction of the organic-bound Pb is exchangeable. This on one hand implies that most Pb and Cr are not easily absorbed by plants, but also suggests that remediation measures such as raising pH wouldn't be very effective. Large amounts of Pb are likely already in a stable form (e.g., Pb-phosphate compounds) that is not bioavailable to plants or human. By comparison, Cd occurs in almost all phases, suggesting easier uptake by plants and its availability is more affected by pH changes.

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