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Manganese oral and respiratory bio-accessibilities in wastes and soils and the influence of their geochemical characteristics.

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In the 1950's, one of the largest Mn deposits in the world was discovered in Mexico. The Mn-$PM_{2.5}$-inhalation can produce neurological damage. Some studies have reported signs of Mn-toxicity in children of the Mexican manganese region, but no information on its bio-accessibility in the dust is available. Therefore, this research seeks to measure Mn-available for absorption in the gut/lungs and its relationship with geochemical characteristics, according to its oral and respiratory bio-accessibilities, in minerals-subproducts-waste of the mining-metallurgical-complex, sources of $PM_{2.5}$-particles.

We carried out representative sampling. The samples were classified based on their general characteristics and dominant manganese species, determined by different techniques (XRF, XRD, SEM-EDS-DLS, ICP-OES). Four groups were established: $MnCO_3$-samples, a mixture of oxides-samples (MxOy), MnO_2-samples, and polluted-soils (weak signal of $MnCO_3$ and oxyhydroxides).

The pH in all samples varied from 6.9-8.2, the E.C. from 0.12 to 2.87mS/cm) and solubilities in water (pH=4.5, pH=5.5) from 0.00006 to 1.42%. The respiratory-bio-accessibility measured with the Gamble solution (G.S.) was negligible (<0.005%), and the fraction $PM_{2.5}$ was high in all samples (53-84.5%.). Mn total concentrations varied in the soils from 0.14 to 6.78%, and in the remaining samples from 16.12 to 35.70%.

The $MnCO_3$-samples showed higher oral bio-accessibility (60.4-95.9%) than the MnxOy-samples (44.63-68.06%) and soils (23.49-53.60%), and much higher than MnO_2-samples (3.57-11.38%). The high values of Mn carbonates are due to their favorable decomposition under gastric-conditions (pH=1.5). In contrast, the $MnCO_3$-samples and soils had significantly lower ALF respiratory bio-accessibilities (35.01-74.54) than the MnO_2 and MnxOy-samples (97.79-99.98%). The critical factor favoring the Mn dissolution on ALF seems to be its coordination with organic ligands in a slightly acidic media. On the other hand, the lower values of carbonate samples and soils seem to be related to their high content of clays and the competitive Mn^{2+}adsorption.

Conclusions. Water-insoluble $PM_{2.5}$ particles exhibit high Mn bio-accessibility in lung macrophage lysosome's simulated acidic intracellular environment. The bio-accessibility depends on Mn compounds. The oxides present the highest values. Consequently, control measures have been taken in the mining-metallurgical complex to reduce the human risk associated with atmospheric pollution. Afforestation of mining-deposits and waste recycling projects are underway.