

Distribution of heavy metals in superficial soils in the Upper Manzanares River Watershed, Sucre state, Venezuela

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In this study, cadmium, copper, lead, manganese, mercury and zinc concentrations were determined in samples of surface soils (0–5 cm), sieved at $\leq 63 \mu\text{m}$, collected from 10 different locations in the upper Manzanares River watershed. Chemical sequential extraction based on Campanella et al. (1995) scheme was used and metal ions were partitioned among the different geochemical fractions in soil (carbonates oxyhydroxides of iron, aluminum and manganese, humic substances, organic matter, and sulfides). Soil aliquots were digested with concentrated nitric acid for total extraction of cadmium, copper, lead, and zinc. Total mercury was extracted with a mixture of nitric, hydrochloric and sulfuric acids. The solutions were analyzed by flame (Cu, Mn and Zn), graphite furnace (Pb and Cd) and cold vapor (Hg) atomic absorption spectroscopy. Methods were validated with Standard Reference Materials, namely SRM Montana Soil 2711(NIST), together blanks, blank spikes and matrix spikes, subsequently analyzed with each batch of samples, to monitor and control the quality of the analyses. The pH range was from 5.87 to 8.35, and good correlations ($p < 0.01$) were found between pH with Zn, Cu and Pb. The range of concentrations were 0.2–1.6 $\mu\text{g.g}^{-1}$ to Cd; 45–100 $\mu\text{g.g}^{-1}$ to Cu; 1.0–3.0 $\mu\text{g.g}^{-1}$ to Hg; 55–167 $\mu\text{g.g}^{-1}$ to Mn; 21–70 $\mu\text{g.g}^{-1}$ to Pb and 24–80 $\mu\text{g.g}^{-1}$ to Zn. The mean values of Hg, Pb, Cu and Cd were higher than world average for

farm soils. Mercury and copper were mostly associated to humic substances and sulfur, cadmium to carbonates and lead to oxihydroxide of iron, aluminum and manganese followed by carbonates. The analysis confirmed that the highest content of mercury, lead, copper and cadmium were found in the farming area. Additionally, sequential extractions show that the mobility factors are high to Cd and Pb. It is probable that fertilizers have contributed to the high level of these metals there. The residents of these sites probably do not have any information about the contents of heavy metals permissible in fertilizers and pesticides, as this is not always shown on the labels; in case of fertilizer, only the beneficial nutrients, such as zinc, potassium and phosphate are shown. Also, the fertilizers are sold directly to the public, and consumers are not warned about the presence and high quantities of toxic metals. Therefore, it is of high priority to monitor toxic heavy metals in these areas, because the main threat of these heavy metals deposited in soil around the upper Manzanares River watershed is due to agriculture, involving both crops and livestock, and soil run-off become a source of metal contamination to river water and tributaries, which are widely used for household and irrigation of crops produced around middle and lower Manzanares River watersheds.

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