Heavy metals in soils exist in various chemical forms, and the form strongly affects the plant availability and dynamics of the metals. Thus, clarifying the chemical forms of heavy metals in soils is important for evaluating agricultural productivity and soil contamination. Heavy metals occluded in manganese oxides are one of the primary chemical forms in soils, because manganese oxides have high adsorption activity for heavy metals. It has been reported that some soil sterilization methods decrease the amounts of manganese oxides and increase the amounts of water-soluble manganese in soils. These results imply that soil sterilization, which can cause dissolution of manganese oxides, might strongly affect the dynamics of heavy metals in soils. Close relation of cobalt to manganese in soils is well-known, and cadmium is important from the view point of heavy metal contamination. Therefore, the object of this study was to clarify the influence of sterilization on the chemical forms of manganese, cobalt, and cadmium in soils.

Soils were sampled from two paddy fields (Endoaquent). The soils were sampled at a depth of 5–15 cm. Fresh raw soil samples, which had been passed through 2-mm-mesh sieves and preincubated at room temperature for 7 days, were used as control samples. Parts of the preincubated soils were sterilized by chloroform fumigation method (24h at 25°C), which were used as fumigated soils. A sequential extraction method was used to determine the chemical forms of the heavy metals in the control soils and the fumigated soils. The fractions and chemicals for extraction were designated as follows: exchangeable (1 mol L⁻¹ ammonium nitrate adjusted pH to 7.0), dilute-acid-soluble (0.44 mol L⁻¹ acetic acid), manganese oxide-occluded (0.1 mol L⁻¹ hydroxyl ammonium chloride with 0.01 mol L⁻¹ nitric acid), organically bound (6 % H₂O₂ decomposition and 0.44 mol L⁻¹ acetic acid), iron oxide-occluded (0.2 mol L⁻¹ ammonium oxalate adjusted pH to 3.0 with 4g ascorbic acid), and residual (nitric acid and perchloric acid digestion). The concentrations of metals in the extracts were determined by ICP-OES or ICP-MS.

For all three metals, the decreases in the amounts of manganese oxide–occluded forms were equivalent to the sum of the increases in the amounts of exchangeable and dilute-acid-soluble forms. The amounts of the other three forms (organically bound, iron...
oxide-occluded, residual) did not change significantly upon fumigation. Some reports indicate organic matter derived from microbial cells can dissolve synthesis manganese oxide. The dissolution of the oxide which observed in this study might be caused by organic reducers come from dead microbial cells. Thus, the results of sequential extraction, probably be affected by organics, indicate that some of the cobalt and cadmium in manganese oxides was converted into exchangeable and dilute-acid-soluble forms, which suggests that soil sterilization may increase the plant availability of these heavy metals.