Extraction of easily soluble fractions of Fe and other heavy metals from various substrates by electro-ultrafiltration (EUF) and their relation to the heavy-metal contents of plants

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Key words  Grapevine  Chlorosis  Calcareous soils  Electro-ultrafiltration (EUF)  Fe  Mn  Zn  Cu  Pb  Cd  Cr  Solubility  Iron sulphate  Garbage-sewage sludge compost  Peat

Summary  Easily soluble heavy-metal fractions from different soils, a garbage-sewage sludge compost and peat were extracted by EUF. Blanks were determined by extracting distilled water. As the rubber seal of the extraction chamber contained Zn, the obtained Zn values were not reliable. The relative standard deviations of extracted micronutrients were 29.1% for Fe and 20.5% for Mn, Fe, Mn, Zn, Cu, Pb, Cd and Cr were not only found in the filters but also in the extracts.

The extraction of CrIII and CrVI solutions showed that CrVI mainly migrated into the anode extract. CrIII was found mainly in the cathode filter and cathode extract, a smaller part however was obviously oxidized to CrVI and migrated into the anode extract. Consequently, CrIII and CrVI in soils could not be distinguished unequivocally by EUF.

The amounts of Zn, Cu, Pb and Cd extracted by EUF from various substrates were small compared with the quantities extracted by 2N HCl. The heavy metal contents of the leaves were mostly in the order of those of the EUF extract.

Several vineyard soils as well as peat were mixed with increasing quantities of ‘Griinsalz’ (green salt), a fertilizer consisting mainly of iron sulphate. High amounts of Griinsalz (100–200 g/200 g soil) were necessary to raise soluble Fe in calcareous soils. In peat, however, small Griinsalz additions (1 g/50 g peat) were sufficient. Soluble Mn and Cu increased too when Griinsalz was added to soil or peat. These results give valuable information on how grapevine chlorosis can be reduced by the use of Griinsalz or mixtures of peat and Griinsalz.

Introduction

The method of electro-ultrafiltration (EUF) has been used mainly for the determination of available fractions of N, P, K, Ca and Mg, whereas micronutrients have been studied so far to a lesser extent. Of the micronutrients, Fe is needed by plants in relatively large amounts. On calcareous soils, grapevines and other plants often show chlorosis as a consequence of induced Fe deficiency. Some investigations presented in this paper are part of a program dealing with prophylaxis and therapy of grapevine chlorosis by application of ‘Griinsalz’ as Fe fertilizer.

The solubility and availability of Fe and other micronutrients in the soil was studied by EUF extraction. Furthermore, a vineyard soil rich in Cu and a garbage-sewage sludge compost were extracted by EUF. In order to learn whether CrIII and CrVI can be distinguished
in soils by EUF, pure Cr salts were extracted. In combination with methodological investigations, these studies should give information on the question whether easily soluble heavy metal fractions can be characterized by EUF.

Materials and methods

Extraction by EUF

Heater, stirrer and thermostat of the extraction chamber were made of quartz in order to prevent heavy-metal contamination. The samples (3 replications; 5 g soil < 1 mm; 1 g peat < 1 mm; 1 g garbage-sewage sludge compost < 0.5 mm; all substrates air-dried) were extracted for 35 minutes (fractions I + II: 0–30 minutes; fraction III: 30–35 minutes, 80°C) as described by Németh. After removing the membrane filters, which were protected from soiling by coarse filter paper, each platinum electrode was sealed by a plexiglass plate which was pressed onto a rubber seal by strong rubber bands. Each electrode was filled with 10 ml N HCl solution (Merck Suprapur) and mechanically shaken for 20 minutes. The HCl extracts together with the filters were transferred into plastic tubes, heated overnight at 50°C and mechanically shaken for 1 hour. The contents of heavy metals, K, Mg and Ca in filters and extracts were determined by atomic absorption spectroscopy, P by photometry and SO₄ with an ion specific electrode.

Additional soil investigations

The pH was measured in N KCl with a glass electrode, the CaCO₃ content volumetrically with a Scheibler apparatus, P and K were extracted with Ca-lactate and Mg with a 0.025 N CaCl₂ solution after Schachtschabel.

Characterization of soils and 'Grünsalz'

Frei-Laubersheim: Vineyard soil, 0–20 cm depth; tertiary clay; composition see Table 1.
Nittel: Vineyard soil, 0–20 cm depth; weathered Muschelkalk (shelly limestone); composition see Table 1.
Alsheim: Vineyard soil, 0–20 cm depth; colluvial soil from loess; composition see Table 1.
Andel: Vineyard soil, 0–20 cm depth; lower terrace of the valley of the Moselle (diluvial loam); composition see Table 1.
Bernkastel: Vineyard soil, 0–10 cm depth; weathered argillaceous schist; composition see Table 1.

'Grünsalz' (Green salt): This by-product is obtained in large quantities from the extraction of titanium ores. The product used contained < 1% CaCO₃, 87–90% iron sulphate (ca 20% Fe); 6–7% magnesium sulphate (ca 0.7% Mg); 652 ppm Mn, 14 ppm Zn and 0.5 ppm Cu.

Investigation of plant material

Leaves and roots were decomposed under pressure with nitric acid in teflon tubes and analysed by atomic absorption spectroscopy.

Results and discussion

Methodological investigations

Blanks Two kinds of blanks were determined: a) Membrane filters were soaked in distilled water for 15 hours, transferred into plastic tubes filled with 10 ml N HCl, heated overnight at 50°C and shaken mechanically for 1 hour. The following heavy-metal contents were