



Comparison of Different Methods for Extracting Soil Selenium

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Soils of Finland are natively low in selenium (Se), which has led to inadequate Se intake of the population and livestock. Annual Se fertilization, applied since 1984 as sodium selenate, has proved to be a feasible way to correct this nutritional problem. However, the fate of added Se in soils is not yet clear, even though only about 10% of the selenate applied annually to the soil is taken up by the crop. The main part of fertilizer Se is supposed to remain in the soil, being reduced and immobilized in insoluble form. Fertilizer Se is thus gradually accumulating in soils. Theoretically, fertilization has increased the Se content of the plough layer of Finnish agricultural soils by about 20%. However, this accumulation has not been verified in soil testing. In the Se monitoring programme, the most easily soluble fraction extracted by hot water has not shown any increase. Semi-total analysis by aqua regia extraction has also been used but substantial deviation in the inherent Se concentrations in the soil parent material overruled the effects of fertilization. Methods targeted to extract residual fertilizer Se are needed to monitor the changes in soil Se status and to assess the possible environmental risks of repeated Se fertilization.

In this study, several methods were compared in their efficiency to extract Se from a cultivated sand and clay soil. Se was extracted with hot water, and soluble and ligand exchangeable Se fractions were extracted with four different phosphate solutions (0.1 M and 1 M K_2HPO_4 - KH_2PO_4 -buffer both at pH 4 and 7). Total Se adsorbed on Al and Fe oxides was extracted with oxalate solution (0.18 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ + 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, pH 3.3). In addition, a sequential extraction procedure was adopted to fractionate Se into four chemical pools: salt soluble Se (1 M NH_4Cl), Se associated with Al oxides

(0.5 M NH_4F) and Fe oxides (0.1 M NaOH) by ligand exchange mechanism and that bound in acid soluble form (0.25 M H_2SO_4). Total Se concentration in each extract was analysed by an electrothermal atomic absorption method.

The sum of Se extracted in the sequential extraction procedure was 0.15 and 0.05 mg Se kg^{-1} of clay and sand soil, respectively. Very little Se was detected in the salt or acid soluble fractions. In the clay soil, 60% and 35% of the extracted Se was associated with Fe and Al oxides, respectively. In sand soil the Se concentrations were equal in both oxide-associated fractions. The difference in the proportions of Se associated with Fe and Al oxides between the two soils agreed with their oxide concentrations. As for single extractants, increase of phosphate concentration from 0.1 M to 1 M triplicated, and increase of pH of the buffer from 4 to 7 doubled the amount of Se extracted. The most efficient phosphate-buffer solution (1 M, pH 7) dissolved 70% and 50% of the amount of Se obtained as the sum of sequential extraction procedure from clay and sand soil, respectively. Hot water dissolved Se more than did NH_4Cl but only 10% of the amount obtained with sequential fractionation analysis. As for oxalate method, a high amount of iron co-dissolved interfered with the analysis, rendering the results of the method unreliable.

Even though labour-intensive, the sequential extraction procedure seems to be promising for studying the soil Se status. Its sensitivity to reflect fertilization-induced changes has to be further tested by analysing time series of soil samples with different amounts of accumulated Se. Among the single extractions, phosphate-buffer solutions proved to be more efficient than hot water in extracting soil Se. Further studies are needed to unravel if Se replaceable by phosphate can be used as an index of bioavailable pool in soil.