



## Phosphorus Speciation and Sorption Processes in Preferential flow paths and Soil Matrix in Forested Podzolic Till Soil

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The importance of preferential flow paths in nutrient leaching and subsurface transport has been identified in several studies mainly on agricultural soils. In forest soils research, decayed root channels, stone surfaces and other secondary soil structures have shown to affect unsaturated flow in glacial till soil. Until recently, the focus has been on nitrogen and carbon dynamics in the preferential flow paths. Preferential flow may also have a fundamental role in phosphorus (P) sorption processes and transport from forested till soils to surface waters. The main objectives of this study were to determine how preferential flow paths affect to P speciation, sorption and leaching in forested podzolic till soil.

Field experiments were conducted in mixed coniferous forest, with soil type of glacial sandy till classified as Haplic Podzol. The first experiment was conducted in Ranua, Northern Finland. The preferential flow paths were identified by introducing Acid Blue 9 dye tracer to a 1 m<sup>2</sup> study plot. The soil profile was vertically sliced and samples were collected from the stained preferential flow paths and unstained soil matrix. Ammonium-oxalate extracted trace elements and P, total and inorganic P, inorganic P fractions and organic P forms (31P-NMR spectroscopy) were analyzed from the samples. In the second experiment in Sotkamo, Eastern Finland, three 1 m<sup>2</sup> study plots were selected from a forested hillslope: top, middle and bottom slope. The detection of preferential flow paths and the sampling procedure was identical to the first plot experiment. Samples were analyzed for ammonium-oxalate extracted trace elements and P. Also, the effect of reaction time, P concentration and temperature on the sorption process in preferential flow paths and soil matrix was studied by kinetic batch-type sorption experiments.

Stone surfaces were the most dominant preferential flow paths and contained lower oxalate-extracted and total P concentrations than the soil matrix in all soil horizons. Other preferential flow paths, such as root channels and coarse-grained soil material, had higher oxalate-extracted and total P concentrations than the matrix in E-horizon, except for the B- and BC-horizon where the concentrations were equal on the average. Al-oxide-bound inorganic P was the most dominating inorganic P specie. Stone surfaces contained less Al-oxide bound inorganic P than the other preferential flow paths and the soil matrix. Fe-oxide bound inorganic P was only detected in the soil matrix for all horizons. Easily soluble P was only observed in the matrix of E-horizon. Ca-bound P was detected in the B- and BC-horizons with the lowest concentrations on the stone surfaces. In the E-horizon, the stone surfaces contained less organic P than the soil matrix. On the contrary, the other preferential flow paths contained more organic P than the matrix. In the B-horizon, stone surfaces had more organic P than the other preferential flow paths and the matrix. In the BC-horizon, organic P was detected only in other preferential flow paths than the stone surfaces. In the E-horizon matrix samples, most of the organic phosphorus was present as phytic acid. In preferential flow paths, other orthophosphate monoesters than phytic acid were more common. In the B- and BC-horizon, the stone surfaces contained higher amount of orthophosphate mono- and diesters and pyrophosphate than the other preferential flow paths and the soil matrix, but less orthophosphate.

In the forested hillslope study, preferential flow paths reached the depth of 0.5 m: the bedrock level of top and bottom slopes and the interface of B-and BC-horizon in the middle slope. In the upper study plot, the oxalate-extracted P, Fe and Al concentrations and the P sorption capacity were lower in the preferential flow paths than the soil matrix in all soil horizons. In the middle study plot, the P sorption capacity and the oxalate-extracted

P, Fe and Al concentrations were lower in the E-horizon preferential flow paths than the soil matrix and higher in the B-horizon preferential flow paths than the soil matrix. In the lower study plot, the preferential flow paths contained more oxalate-extracted Fe and Al than the matrix; however oxalate-extracted P concentration and P sorption capacity were lower than in the matrix. Temperature had an effect on the reaction kinetics of P sorption and the sorption capacity. The sorption reaction was significantly slower in the temperature of 3 °C than in 13 and 21 °C. In addition, the reaction was slower in the preferential flow paths than in the soil matrix for all soil horizons with low P concentration levels and short reaction times. The results implicate that during seasons with low soil temperatures and high soil humidity, the subsurface flow velocity can be higher than the time acquired for phosphorus sorption reaction to occur, which may cause phosphorus leaching and transport through preferential flow paths. Therefore it is important to consider the effect of preferential flow paths on phosphorus sorption processes while modelling phosphorus transport in forest soils.