Comparison of sampling soil solution techniques to assess metal fluxes to groundwater

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The elemental fluxes at the bottom of a soil profile is an important element in many soils studies. Unfortunately, the deep percolation through the bottom of the soil profile is difficult to evaluate, (*Kowalik 2006)*. Despite considerable research there is still no general consensus for the best methods for sampling the soil solution in either the field or the laboratory *(Reynolds et al., 2004; Weihermüller et al., 2007; Buckingham et al., 2008; Meissner et al., 2010)*. Each method has benefits and disadvantages with regard to chemical interactions between the type of sampler and the soil solution, and the range of tensions used to extract the water *(Bloem et al., 2009; Goss et al., 2010).* The soil structure may also have a significant influence on the exchange of water solutes between macro- and micropores and therefore on chemistry of draining waters *(Heinrichs et al., 1996)*. Thus, according to sampling method, there is a variation of soil solution concentrations. The aim of this study is to suggest ways of flux quantification which may be as close as possible to true chemistry and flux of solute in soil.

The study was undertaken on six PVC columns, containing pure Fontainebleau sand for three of them and 5% clay for three others. Minerals of As, Cr and Zn were added on each first 20 cm of the columns. '*Rhizon' soil moisture sampler* were installed to different depth from the surface. Three types of suction were applied on each replicate groups. The vacuums compared were :(i) the syringe probe ('S') ; (ii) vacuum sampler ('P'), is a sample tube under vacuum which allowed maintaining the soil moisture condition in the sampling profile similar to that in the natural soil profile and (iii) the deflected flow ('F') ; is a column divided into five pieces, water is transferred from one to the other pieces by Rhizon and Tygon tubing.

Major element sampled with syringes (figure I left) showed a distribution broadly similar to the theoretical distribution only in the presence of clay: constant concentration of major elements along the profile of the column. On the other hand metals added to the column showed a significant difference between the sand and clay columns. Inside the sand column, the peak concentration of metals dissolved from the source are lower than in clay. These concentrations are also lower than the one measured at the bottom of the sand columns.
Therefore the syringe probe appears to work well in clay but does not work in sand, it is thus necessary to test other sampling methods that can best represent the flux in all conditions.

Common to the three collector types the mean concentration of Mg (figure I, right), Ca, Na, Ni were broadly similar in contrary to mean concentrations of Cr, As and Zn $[Cr]_{'S'}>[Cr]_{'F'}>[Cr]_{'P'}$, $[As]_{'S'}>[As]_{'P'}>[As]_{'F'}$ and $[Zn]_{'S'}>[Zn]_{'P'}>[Zn]_{'F'}$. It is difficult to define a difference between protocols that may be valid for all metals. It seems that the syringe probe have a tendency to sample micropores preferentially, while the vacuum sampler ('P') and Deflected Flow ('F') collected more macropore water as argued by *(Reynolds et al., 2004)*.

The major point however, is that, in sand columns, none of the samplers were able to give correct estimates of the fluxes leaving the columns at one meter depth. In sand + clay columns this effect was not so pronounced and syringe samplers give approximate values of the fluxes. Therefore, is the soil is sandy, it is necessary to use unsaturated lysimeters (similar to the columns used in this study) to approach transient metal fluxes.

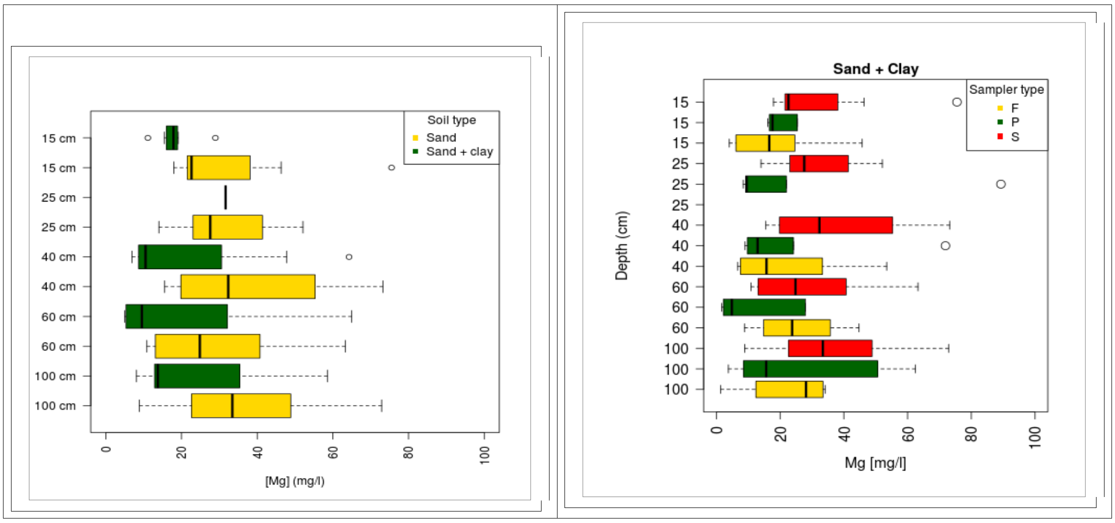

Figure I. Left : Box plot of concentrations distribution in sand columns (yellow) and sand and clay (green) taken by syringes. Right: Box plot of concentrations distribution in sand and clay columns for the three types of samplers: (i) syringe: 'S' (red), (ii) Vacuum sampler: 'P' (green) and (iii) deflected flow: 'F' (yellow).

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