

## **Release of colloid-bound phosphorus in soils: comparing laboratory extraction experiment results with natural soil solution data**

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Colloids  $(1 \sim 1000 \text{ nm})$  are important carriers of phosphorus (P) in agricultural soil solutions and have been frequently studied by lab extraction experiments. However, little attention has been paid so far to evaluating how the proportion and composition of P-bearing colloids were affected by the water/soil ratio and the ionic strength of the extracting solutions used. Here, we conducted lab extraction of P-bearing colloids on surface soils from two transects (G and K) located in a small agricultural catchment from Western France, at different water/soil ratios (30:1, 20:1, 10:1 and 4:1) and different ionic strength (H<sub>2</sub>O, 0.001M NaCl and 0.01M NaCl), and compared the results with colloidal P quantification performed on natural soil solutions from the two same transects. Ultrafiltration combined with inductively coupled plasma mass spectrometry (UF-ICP-MS) and XANES spectroscopy were used to evaluate the proportion of colloidal P and the composition of the colloidal carriers. During laboratory extractions, we observed that total dissolved (<0.45  $\mu$ m) phosphorus (TP) and dissolved organic carbon (DOC) concentrations increased with decreasing water/soil ratio. Both TP and DOC concentrations decreased with the increasing ionic strength. According to these results, the water/soil ratio of the laboratory extraction experiments was optimized at 10:1 because DOC concentrations recovered at this ratio were similar to those in corresponding natural soil solutions. Meanwhile, the extracting solution was optimized at 0.001M NaCl which was close to the ionic strength of the natural soil solutions. Using these optimized conditions, we were able to extract approximately the same proportion of colloidal P in the laboratory extracts as found in the natural soil solutions, despite the persistence of slightly but significantly higher proportions in natural soil solution samples (50.4% as against 34.3% on average in laboratory extracts). The results also showed that the naturally observed and laboratory extracted colloids were of comparable composition, consisting both of a homogeneous mixture of Fe(Al)-oxyhydroxides and organic matter, which were comparable in composition to the P-rich soil aggregates. In laboratory extracts, the speciation of P was all homogenized, being dominated by colloidal P and truly-dissolved MRP in roughly the same proportion. In natural soil solutions, however, the TP released was dominated by truly-dissolved MRP (up to 70%) at one site of transect G; at the other site of transect G and both sites in transect K, the TP released was all richer in colloidal and truly-dissolved MUP. So far, the reason for this spatial variation in P speciation within and between transects in natural soil solution is still unknown and we have not been able to experimentally reproduce this difference with laboratory extractions. Thus, this study demonstrates that great care should be exercised when considering laboratory extraction results to assess the capacity of a soil to release P-rich colloids under natural field conditions. This study also suggests that laboratory extraction experiments should optimize their parameters according to the chemistry of the natural soil solutions, to better reflect the natural field condition.