Impact of bacterial structural Fe(III) reduction on the CEC and exchangeable cations of a flooded rice cropped vertisol

F. Favre[1], J. Larvy Delarivière[2], V. Ernstsen[3], P. Boivin[1,2]

[1]IATE-P, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[2]Institut de Recherche pour le Développement (IRD), BP 1386 Dakar, Senegal
[3]Geological Survey of Denmark and Greenland (GEUS), Thoravej 8, 2400 Copenhagen NV, Denmark

Introduction

The cation exchange capacity (CEC) of soils is widely used to characterize soil sorption properties or to estimate water retention curves. CEC of clays due to ionic substitutions in the crystal units is usually considered to be constant, and only slightly variable with pH due ionization of hydrogen at crystal edges. However, Tessier et al. (1999) showed sharp CEC changes with soil-pH changes. Moreover, significant increase in CEC of iron-containing selected pure clays were found in laboratory reduction experiments. These CEC changes are due to reduction of structural iron (Fe_{Str}) or dissolution of positively charged oxide coatings as reviewed in Stucki, 1997. The same phenomenon was recently observed in the field by Favre *et al.* (in press) who found a twofold increase in CEC upon reduction in a flooded vertisol. Changes in cation fixation upon Fe_{Str} reduction and CEC increase was investigated on pure clay by Khaled and Stucki, 1991. They noted an increase in fixed cations such as K and Zn. Changes in cation selectivity for different $Fe_{Str}{}^{II}/Fe_{Str}{}^{III}$ ratio and CEC are likely to occur but has not been investigated up to now. This study is difficult to perform, because different methods are required for the exchangeable cation extraction (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+} and Fe^{2+}), each of them preserving oxidation state. This paper presents the observed changes in exchangeable cations during Fe_{Str} reduction on laboratory incubated samples from vertisols in Senegal.

Material and method

Two samples S1 and S2 coming from the Ap horizon of a rice cropped vertisol were air dried, crunched, sieved and mixed with demineralized water (ratio 1:1) in two incubators under nitrogen atmosphere. The soil characteristics are presented in Favre *et al.* (in press).
During incubation, EH was monitored using a platinum probe. Samples were collected from the reactors at different Eh values. S1 and S2 samples were analyzed for CEC and major exchangeable cations Ca, Mg, Na, K using the Cobaltihexamine (Cohex) method and in addition exchangeable iron and exchangeable ammonium were measured on S2 samples. $Fe_{Str}{}^{II}/Fe_{Str}{}^{III}$ ratio were measured using Mössbauer spectroscopy for S1 samples and chemical analysis for S2 samples.
Co was analyzed using AAS. Exchangeable Ca, Mg, Na and K were measured using capillary electrophoresis, and exchangeable Fe was measured using a spectrophotometer and NH_4^{+} with colorimetric method.

Results and discussion

CEC of the incubated samples increased markedly with decreasing redox potential (EH). This increase goes with an increase in $Fe_{Str}{}^{II}/Fe_{Str}{}^{III}$ ratio. Exchangeable cations Ca, Mg, Na and K remained constant upon reduction. S2 experiment showed that the increase in CEC was balanced by exchangeable Fe^{2+} and NH_4^+.

The increase in CEC due to increasing $Fe_{Str}{}^{II}/ Fe_{Str}{}^{III}$ ratio is in agreement with the results and interpretations of Favre *et al.* (in press) and previous studies (Stucki 1997). Both measurements on Mössbauer spectroscopy and chemical analyses methods confirmed these observations.

Constant values of exchangeable Ca, Mg, Na and K together with increasing concentration of ferrous iron in the soil solution is not very well documented in the literature. Other authors (e.g., Brinkman (1970) and Ponnamperuma (1972)) worked on soil solution only and they assumed that in temporarily waterlogged soils, the affinity of ferrous iron for clays is so high that the major exchangeable cations are expulsed in the soil solution. An increase in the concentration of major cations in soil solution of paddy soils incubated in the laboratory was interpreted in the same way by Narteh and Sahrawat (1999).

There are several ways to comment these contradictory observations. As far as we know, there is no other reported experiment where increase in CEC, $Fe_{Str}{}^{II}/ Fe_{Str}{}^{III}$ ratio and exchangeable cations were simultaneously monitored. The evolution in soil solution results from competition between Fe^{2+} and other cations for exchange sites. Fe^{2+} activity depends on dissolved oxides and other equilibria involving Fe^{2+}. The amount and state of reduction of Fe_{Str} determines soil CEC. The process depends on EH and pH and may have a different extent in soils depending of soil properties. Our experiments on a vertisol containing iron-bearing clays indicate high charges on the clay compared to the amount of ferrous iron in solution. Brinkman (1970) observed soils with kaolinite clays and very low CEC. When the EH drops in kaolinite-rich soils, the CEC remains nearly constant when the amount of dissolved iron gets height. The study of the iron-rich-clay vertisol also demonstrated that the amount of exchangeable major cations is very high compared to soil solution content. Consequently, a low and non significant change in exchangeable cation rates might result in significant changes in the concentrations of major cations in the soil solution.

In this experiment, the charges properties of the clays are sharply modified upon reduction and the consequences of the phenomenon can be measured in the bulk soil. The soil solution content results from an equilibrium highly dependent on iron reduction state. These results lead to new views and many questions about temporarily water logging soils. For example, sorption properties of cations and anions for various reduction states of clays should be determined. It seems necessary to investigate the impact of these phenomenon on the properties of temporarily waterlogged soils. In situ soil monitoring could allow to improve our knowledge of ferrolysis and other processes in water-saturated soils, particularly by comparing soils with iron-bearing clay types with various ratios of free and structural iron.