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Variations in the cation exchange capacity of a ferralsol supplied with vinasse, under changing aeration conditions

Comparison between CEC measuring methods

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A B S T R A C T

The spreading of vinasse may favour soil anoxia and affect cation exchange capacity (CEC). Our aims were to assess the reliability of CEC measurements in reducing conditions, quantify CEC variations in a ferralsol under changing aeration conditions, and understand the mechanisms involved. In a first experiment, soil slurry was incubated for a succession of 7 oxic, 28 anoxic and 28 oxic days, vinasse being supplied when anoxia began. CEC was measured at intervals by exchanging Mg^{2+}, Cu-trien or $Co(NH_3)_6^{3+}$, the solutions being characterized before and after exchange. In a second experiment, soil CEC was measured after the elution of NH_4^+ solutions of pH 5 to 7. In a third experiment, we assessed the reduction of $Co(NH_3)_6^{3+}$ by Fe^{2+} and checked for induced changes by geochemical simulations. During the first oxic period, CEC varied according to method, in the order: Cu-trien < Mg2+ < $Co(NH_3)_6^{3+}$ < NH_4^+. It increased by 2 $cmol_c\ kg^{-1}$ when pH increased from 5 to 7. After 28 days of anoxia, CEC estimates were 2.75, 1.43 and 5.1 times their initial values for the 0.05 M Mg^{2+}, Cu-trien and $Co(NH_3)_6^{3+}$ methods respectively; pH after exchange was about the same as initial slurry pH (6.9), except after $Co(NH_3)_6^{3+}$ exchange when it was 9.4. This complex was partly reduced by Fe^{2+} leading to NH_3 release, pH increase, $Fe(OH)_3$ and $Co(OH)_2$ precipitations, Co(II) adsorption and overestimation of CEC. After the return to oxic conditions, the CEC did not return to its initial value. At all dates, CEC measured by 0.05 M Mg^{2+} method agreed with the exchangeable cation measurements.

1. Introduction

Spreading liquid food industry by-products enriches the soil with nutrients and organic matter, but also enhances the risk of anoxia (Gemtos et al., 1999), since it increases soil moisture, stimulates O_2 consumption by supplying organic C (Lahlah et al., 2009) and decreases soil structural stability (Tejada and González, 2005, 2006). It thus increases the risk of anaerobic microbial activity (Stemmler et al., 2004) and can induce reduction of Fe in oxyhydroxide form or contained in the clay crystal structure (FeStr) (Lovley, 1991; Ona-Nguema et al., 2002; Stucki, 1997; Kostka et al., 2002; Berthelin et al., 2006). The reduction of the latter form results in an increase in the cation exchange capacity (CEC) of the clays (Stucki et al., 1984b; Favre et al., 2002, 2006) due to an increase in layer charge and a simultaneous loss of hydroxyls released in solution. In some conditions, the weathering of clays occurs during reduction (Stucki et al., 1984b). After anoxic periods, which favour adsorption of reduced Fe and Mn and the release of other cations, the oxidation of Fe can contribute to soil acidification and clay ferrolysis (Brinkman, 1970; Amatekpor, 1989), although this depends on the leaching of the cations desorbed during the anoxic period. To describe the fate of trace metals, soil acidification and mineral weathering, it is therefore important to describe the CEC variations occurring in intermittently reduced soils.

All the methods for measuring soil CEC and exchangeable cations involve replacing exchangeable cations with another cation. They differ from each other in (i) the cation exchanged (K^+, Ca^{2+}, Zn^{2+}, and Cu^{2+} (Khaled and Stucki, 1991), Ba^{2+} (Ciesielski and Sterckeman, 1997a,b), NH_4^+ (Metson, 1956; AFNOR, 1999), Cobalt–hexamine (Ciesielski and Sterckeman, 1997a), Cu-trien (Meier and Kahr, 1999), among others), (ii) the pH of the exchange solution, either buffered (pH = 7 (Metson,

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1956) or pH = 8.2 (Brady and Weil, 2002)) or *a priori* the same as the soil pH (Ciesielski and Sterckeman, 1997b; Meier and Kahr, 1999), (iii) whether the exchange solution is percolated through soil aggregates (Metson, 1956; AFNOR, 1999; Ciesielski and Sterckeman, 1997b) or mixed with the soil with single or successive exchanges (Ciesielski and Sterckeman, 1997a,b; Meier and Kahr, 1999), and (iv) whether the measurements are of the amount of exchanged cation that either disappeared (Ciesielski and Sterckeman, 1997a,b; Meier and Kahr, 1999) or of the amount recovered after a second exchange with either Na^+ (Metson, 1956; AFNOR, 1999) or Mg^{2+} (Khaled and Stucki, 1991). The difference between desorbed cations after this second exchange and the amount of retained cations after the first exchange led Khaled and Stucki (1991) to distinguish between exchangeable and fixed cations, although the proportion of fixed to exchangeable cations depends on the cation concerned. Indeed, some cations are retained more specifically on some sites (Khaled and Stucki, 1991; Ciesielski and Sterckeman, 1997b). For example, K^+ may be trapped in the clay interfoliar space and reduce its thickness (Khaled and Stucki, 1991), and then exchanges more easily with NH_4^+ than with other cations (Ciesielski and Sterckeman, 1997b). Trapping of NH_4^+ (Osborne, 1976; Evangelou and Lumbanraja, 2002) and Cs radionuclides (Hird et al., 1996) have also been observed. It has been shown that CEC varies with the amount and nature of the soil clay, soil organic matter content and solution pH, although the proportion of pH dependent charges varies with the solids (Brady and Weil, 2002). The main exchangeable cations include Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+ and Na^+ (Ma and Eggleton, 1999), but Al^{3+} is recovered in acidic conditions (Brady and Weil, 2002).

Some studies have shown that CEC increases in reducing conditions. Khaled and Stucki (1991), working on isolated clays and inducing chemical reduction of clay Fe (Stucki et al., 1984a), noticed that Fe reduction increased the total negative charge of ferruginous smectite and montmorillonite by about one third, but noted that this increase did not always lead to an increase in CEC since K^+ or Ca^{2+} could then be trapped in the clay inter-layers, whereas retained Zn^{2+} and Cu^{2+} could be almost totally desorbed after initial adsorption. By contrast, Favre et al. (2002), using $Co(NH_3)_6^{3+}$ exchange on a vertisol with smectite and kaolinite in a rice paddy field, noted that CEC more than doubled in reducing conditions and that CEC changes were still reversible after 22 rice crops. They explained CEC variations in terms of reduction of smectite Fe and reductive dissolution of Fe oxyhydroxides partly covering the clay particles. They ignored kaolinite CEC increase since the soil pH did not greatly increase during anoxic periods and the Fe content of the kaolinite could be ignored, although Fe_2O_3 in similar clays such as halloysite can reach 12.8% w/w (Joussein et al., 2005). The mechanism of FeStr reduction has been intensively studied and documented by Stucki et al. (1996), who calculated the relationship between the Fe(II)Str content of clay, CEC and released hydroxyls (Lear and Stucki, 1985). Recently, using $Co(NH_3)_6^{3+}$ exchange on a ferralsol from Reunion Island supplied in rum vinasse, we measured CEC increase of more than fourfold during an anoxic period, while the disappearance of $Co(NH_3)_6^{3+}$ was not balanced by the desorption of Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+} and Mn^{2+} (unpublished results). Thermodynamic data suggest that $Co(NH_3)_6^{3+}$ complex could be partly unstable in reducing conditions (Charlot, 1983), as has been shown for other Co(III) complexes (Santhakumar et al., 2006).

Therefore, the objectives of this study were to (i) assess actual variations in the CEC of a ferralsol under changing aeration conditions using different methods, (ii) analyse the results with regard to variations in soil pH as well as Fe and Mn reductions and mobilisations, and (iii) identify the mechanism that caused overestimation of $Co(NH_3)_6^{3+}$ adsorption in reducing conditions. Trace metals were abundant in the sampled ferralsol (Doelsch et al., 2006b) and rum vinasse from the same island was supplied at the beginning of the anoxic period. CEC was measured with $Co(NH_3)_6^{3+}$, Cu-trien, Mg^{2+} or NH_4^+ exchange, using (after adaptation) the methods of AFNOR (1999), Meier and Kahr (1999), Khaled and Stucki (1991) and AFNOR (2002) respectively.

2. Materials and methods

2.1. Soil and rum vinasse

A Ferralsol was sampled at La Mare experimental station on Reunion Island (20°40′ S and 55°32′ E). The experimental field has been used for sugarcane growing for 20 years, the last harvest was in late July 2005. Average annual precipitation is about 1500 mm, with a potential evapotranspiration of 2300 mm. Sampling was performed on the 0–20 cm soil layer, on 10th January 2006. The soil was air-dried (15.6% w/w residual moisture), stored in hermetic bags at about 20 °C and flown to Montpellier. It was then mechanically crushed, sieved at 2 mm and stored again under the same conditions until the beginning of the experiments. Its properties were as follows: 668 $g\,kg^{-1}$ clay; 251 $g\,kg^{-1}$ silt; 81 $g\,kg^{-1}$ sand; 22.9 $g\,kg^{-1}$ organic C; 2.07 $g\,kg^{-1}$ organic N; 2.52 $mg\,kg^{-1}$ $N–NH_4^+$; 37.3 $mg\,kg^{-1}$ $N–NO_3^-$; 163.2 $g\,kg^{-1}$ total Fe, 4.15 $g\,kg^{-1}$ total Mn, 0.126 $g\,kg^{-1}$ total Cr, 0.076 $g\,kg^{-1}$ total Ni. Metals released by DTPA extraction were: 46.7 $mg\,kg^{-1}$ Fe and 174.4 $mg\,kg^{-1}$ Mn. The soil pH (water) was 5.48 and the pH (KCl 1 M) was 4.60. The main clay mineral was halloysite, but clays also contained amorphous phases (unknown proportions). Iron was present in all granulometric fractions, as hematite. The ≤2 µm fraction probably also contained maghemite. The 2–50 and the 50–200 µm fractions contained the same minerals and other minor compounds (probably ilmenite and ferrosilite). The 200–2000 µm fraction also contained magnetite and ferrosilite.

Rum vinasse from sugarcane molasses was collected at the bottom exit of a distillation column in the Savannah distillery, on 24 February 2006. It was frozen at −20 °C, flown to Montpellier in plastic boxes and stored again at −20 °C until experiments began. The vinasse contained 76.8 $g\,l^{-1}$ of dry matter, including 703.65 $g\,kg^{-1}$ of organic matter with a mean C/N ratio of about 17.65. The corresponding 24.1 g organic C l^{-1} vinasse included about 6.6 g C l^{-1} as carbohydrates, 3.5 g C l^{-1} in identified organic acids (in decreasing order of C concentrations: trans-aconitate, lactate, malate, acetate, cis-aconitate, citrate, pyruvate, tartrate, formate, iso-citrate, butyrate, propionate), 2.2 g C l^{-1} in identified polyols (in decreasing order of C concentrations: glycerol, mannitol, inositol, arabitol, sorbitol), 10.7 g C l^{-1} as isopropanol, 1.39 g l^{-1} as phenols, and 0.7 g C l^{-1} as proteins. Lipids were not found. The vinasse also contained mineral compounds, including K (7.1 g l^{-1}), NO_3^- (1.35 mg N l^{-1}), NH_4^+ (11.7 mg N kg^{-1}), Fe (53.3 mg l^{-1}), Mn (10.9 mg l^{-1}), Cr (1.5 mg l^{-1}), Ni (0.5 mg l^{-1}), Pb (0.2 mg l^{-1}), as well as Na, Ca, Al, Mg, Cu, and Zn. Its pH was 5.93.

2.2. Experiment 1: CEC variations with changes in aeration

2.2.1. Incubation and treatment (Fig. 1)

Soil slurry was incubated successively for 7 days in oxic conditions, 28 in anoxic conditions and 28 in oxic conditions, the vinasse being supplied when anoxia began. Batch incubations were performed in sealed 324 ml flasks continuously shaken at 25 °C in darkness. The flasks were initially filled with 90 g of fresh soil and 108 ml of de-ionised water. Aeration was maintained during the first 7 days by shaking the flasks in flat position and ventilating them after 3 or 4 days by opening the flasks three times (for 30 s each time, stirring the air above the flasks) and shaking manually between openings. After the first 7 days, the flasks were supplied with 13.5 ml de-ionised water and 13.5 ml vinasse. For 28 days, they were then kept in anoxic conditions, created by alternating 3 successive cycles of 3 min vacuum and 3 min N_2 replacement. Anoxia was considered to start with the first vacuum phase. Flask air pressure was then equilibrated with ambient laboratory air. The flasks were then shaken to equilibrate the slurry with the headspace atmosphere and incubated in upright position. Finally the flasks were incubated in well aerated conditions for 28 days. The aeration during this period began with 1 min of powerful air bubbling and slurry mixing, followed by continuous gentle bubbling of air