Contents lists available at ScienceDirect

Applied Clay Science

Research paper

Carbohydrate concentrations and enzyme activities as influenced by exchangeable cations, mineralogy and clay content

Fatemeh Rakhsh*, Ahmad Golchin

Soil Science Department, Faculty of Agriculture, University of Zanjan, Zanjan, Iran.

ABSTRACT

Enzymes can exist in bound or free form within the soil, but the impact of interactions between extracellular enzymes with the amount and type of clay minerals and exchangeable cations on the activities of enzymes and decomposition or retention of carbohydrates in soil is still poorly understood. Appropriate amounts of homoionic Na-, Ca- and Al-clay minerals from Georgia kaolinite, Illinois illite and Wyoming montmorillonite were mixed with pure sand to prepare artificial soils with different clay contents, exchange cations and clay types to examine the effects of exchangeable cations, mineralogy and clay content on the concentrations of hot water and dilute acid extractable carbohydrates and activities of acid and alkaline phosphatases and CM-cellulase. There was a significant effect of clay content on the concentrations of carbohydrates and activities of enzymes. The concentrations of carbohydrates increased when the clay contents of soils increased from 0 to 5 and 10%, respectively, showing that the clay contents influence the capacity of soils for stabilization of carbohydrates. But opposite trends were found in enzyme activities. The enzyme activities decreased significantly as the clay contents of the artificial soils increased. The concentrations of carbohydrates and activities of enzymes were significantly affected by exchangeable cations. In soils with 5 and 10% clay, the concentrations of carbohydrates were maximum in Al-soils and minimum in Ca-soils, in contrast, the activities of enzymes were maximum in Ca-soils and minimum in Al-soils. There was a significant effect of clay mineralogy on the concentrations of carbohydrates and activities of enzymes. The concentrations of carbohydrates were highest in soils with Wyoming montmorillonite clay mineral and lowest in soils with Georgia kaolinite clay mineral. But the activities of enzymes were lower in soils with Wyoming montmorillonite clay mineral than soils with Georgia kaolinite and Illinois illite clay minerals, indicating the influence of specific surface area (SSA) and cation exchange capacity (CEC) of clay minerals on carbohydrate retention and enzyme activities. The results of this study indicate that carbohydrates are stabilized in soils through the interaction with clay minerals and a small amount of clay (5%) significantly increases carbohydrate retention and reduces enzyme activities in soils. Exchangeable cations exert their influence on enzyme activities and hence carbohydrate dynamics by controlling the activities of enzymes through modifying the physicochemical characteristics of soils.

1. Introduction

Better understanding of carbon cycling is necessary to decrease the emission of greenhouse gases and global climate changes resulted from it. Soil organic carbon (SOC) is a significant pool that plays important role in global carbon cycling (Scharlemann et al., 2014; Wang and Hsieh, 2002). The SOC consists of two main fractions; the labile and the non-labile organic fractions. Carbohydrate constitutes an important component of the labile fraction that represents about 5–25% of soil organic matter (SOM) (Uzoho and Igbojionu, 2014). Its fate in soils varies depending on the SOM dynamics and transformation processes, especially decomposition, mineralization and immobilization (Paul

et al., 2002). Carbohydrate plays fundamental roles in the soil which include; conservation of soil physical properties (Martins et al., 2012), stabilization of soil aggregates (Yousefi et al., 2008) and sustenance of soil microbial activities through the provision of readily available energy (Ros et al., 2003).

Besides being a source of energy for microorganisms, the soil carbohydrates play a significant role in the formation of stable aggregates and metal ion complexes (Six et al., 2004). Soil carbohydrates consist of plant- and microbial-derived polysaccharides that are an immediate by-product of microbial utilization of organic carbon (OC). Microbial extracellular polysaccharides are regarded important in ecophysiological processes from the viewpoints of resistance to desiccation and survival

---

* Corresponding author.
  E-mail address: rakhsh.fatemeh@znu.ac.ir (F. Rakhsh).

in extreme environments (Helliwell et al., 2014). Adsorption of monosaccharides and polysaccharides on clay minerals has been demonstrated (von Lützow et al., 2006) to be markedly influenced by the type of clay, pH and exchangeable cations (Theng, 2012). Adsorption of polysaccharides in acid clays may involve complex formation through exchangeable aluminum. Multiple bonding of a polysaccharide molecule to more than one mineral particle would influence aggregation and hence a range of physical properties of soil. Polysaccharide molecules are generally strongly hydrophilic and contribute to water retention in soils.

Carbohydrate distribution in soils varies with the particle size fractions. Whereas high concentrations have been reported in the sand fractions of soils (Allard, 2006; Spaccini et al., 2001), reports of a chromic Luvisol in semiarid northern Tanzania indicated large concentrations in the clay fraction (Solomon et al., 2000). Also, large depletion of neutral sugars and uronic acid carbohydrate components in the silt fraction has been reported for Alfisols in Australia (Oades et al., 1987), Inceptisols in Canada (Angers and Mehuys, 1990) and Inceptisols of southern Germany (Guggenberger et al., 1994). The discrepancy in carbohydrate distribution of soil particle size fractions has been attributed to differences in the mineralization pattern of sugars derived from plants and carbohydrate inputs of microbial origin (Uzoho and Igbojionu, 2014; von Lützow et al., 2006). Presence of carbohydrates in precise soil particle fractions indicates their potential accessibility for microbial degradation (Spaccini et al., 2001).

Procedures for the estimation of soil carbohydrate concentration differ. Typical methods include hydrolysis procedures using cold water, hot water, dilute and concentrated acids (Gieseking, 2012). According to Gregorich et al. (1994), as the concentration of acid and temperature of hydrolysis increased the amounts of carbohydrates extracted increased. Cheshire (1979) noted that the non-specific extraction procedures using concentrated acids or bases could not identify the differences between the pools of total carbohydrate and the more specific ones. While a strong correlation has been obtained between the specific fractions and the hot water extractable carbohydrate (Debosz et al., 2002). Cold water extractable carbohydrate could be associated with the most labile and microbial accessible fraction that includes the non-structural plant carbohydrates and the extracellular microbial carbohydrate, usually extracted with hot water (Haynes and Francis, 1993; Redmile-Gordon et al., 2014). The magnitude of extractable carbohydrates decreased in the order total > dilute acid soluble > hot water soluble > cold water soluble in response to the chemistry of the extractants (Herbert et al., 1995). (Cheshire, 1979).

The extracellular enzymes decompose the polymers exist within the plant and microbial cell walls and depolymerize macromolecules to soluble substrates for microbial utilization and thereby mediated the decomposition of SOM (Burns and Dick, 2002). The activity of extracellular enzymes, independent of their producers and ecosystem processes, is affected by several factors among the most important ones are the physicochemical parameters of soil and vegetation and management practice (Saviozzi et al., 2001; Sinsabaugh et al., 2008; Trasar-Cepeda et al., 2008). The interaction of enzymes with soil components and the mobility or enzymes in the soil environment have been the subjects of many researchers and attracted some attention (Masciandaro et al., 2008; Vepsäläinen, 2001). Depolymerization of various macromolecules which is necessary for decomposition of organic matter (OM) and thus mineralization of plant nutrients are controlled by soil total enzymatic activity which is derived from active microbial population and the enzyme pool immobilized in organo-mineral complexes (Burns et al., 2013; Schimel and Bennett, 2004; Tabatabai, 1994).

Enzymes were associated with soil particles of various sizes and types were different (Ceccanti et al., 2008; Marx et al., 2005). Components of the soil matrix (e.g., different minerals or OM) stabilize enzymes differently (Burns et al., 2013; Servagent-Noinville et al., 2000). Enzymes may be broken down by proteolytic enzymes, by

abiotic processes (including thermal denaturation and reacting with minerals), or by being taken up intact by microbes and metabolized intracellularly (Shukla and Varma, 2010). They may be stabilized by interactions with minerals and OM (Burns et al., 2013). Upon release of enzymes from soil microbes, these enzymes become covalently bound to SOM or physically adsorbed onto soil colloids. The covalently bound enzymes persist in soil and perform their functions whereas the physically adsorbed enzymes are readily inactivated due to the adverse conditions of the soil. Thus soil is a natural system where enzymes become immobilized by interaction with clay and humus (Naidja et al., 2000). Enzymes adsorbed to clay minerals either within the lattices of 2:1 layer silicates or on the external surfaces may or may not retain their catalytic capacity (Boyd and Mortland, 1990; Tietjen and Wetzel, 2003).

Acid and alkaline soil phosphatases which are extra- and intracellular enzymes play a major role in the hydrolysis of organic phosphorus compounds in soils. These enzymes are important for various functions in soils. They are involved in nutrient cycling, reflect microbial activity and act as indicators of soil changes (Alkorta et al., 2003; Burns et al., 2013). The sensitivity of acid and alkaline phosphatases to pH, make it possible to evaluate the effects of soil pH on the presence or relative activity of these enzymes (Dick et al., 2000; Turner, 2010). These enzymes may be existed in the free state or be intimately sorbed to soil organic and inorganic fractions (Nowak et al., 2002; Rejsek et al., 2012; Shindo et al., 2002). Cellulose comprises almost 50% of plant biomass formed by photosynthetic fixation of CO_2 and is regarded as the most abundant organic compound in the biosphere (Eriksson et al., 1990). The production of cellulose by plants is about 180 billion tons per year globally, making carbohydrate the largest organic carbon reservoir on the earth (Festucci-Buselli et al., 2007). Although a limited amount of soil cellulose comes from fungi and bacteria, it is mainly derived from the plant residues incorporated into the soil (Richmond, 1991). The most important enzymes involved in the decomposition of cellulose in the plant residues, cellulase, cleave the β −1, 4 bond in the cellulose chain and convert it to simple sugars. Cellulase can be synthesized through microorganisms during their growth on cellulosic substances. Abiotic factors such as soil pH, temperature, the contents oxygen and water, the chemistry of OM and its accessibility to soil organisms or its location within the soil matrix, mineral nutrients and trace metals released from fungicides or herbicides all influence on cellulase activity (Alef and Nannipieri, 1995; Arinze and Yubedee, 2000; Deng and Tabatabai, 1994).

Although the effects of soil texture on carbohydrate concentrations and enzyme activities of soils have been investigated in many studies, but research showing the direct effects of clay type is rare (Bergaya et al., 2006; Chenu and Stotzky, 2002; Spaccini et al., 2001) and the simple effects of exchangeable cations and their interactive effects with clay types in these regards are unknown (Bolt et al., 2013a; Theng, 2012). Therefore, this study aimed to: (i) investigate the effects of clay types (Georgia kaolinite, Illinois illite and Wyoming montmorillonite) on the carbohydrate concentrations and enzyme activities of soils, (ii) determine how enzyme activities are affected by mono-, di- and trivalent exchangeable cations (Na^+, Ca^{+2}, Al^{+3}) present on the exchange complexes of clay minerals, and (iii) examine the influences of clay contents on enzyme activities and carbohydrate concentrations of soils.

2. Material and method

Since natural soils are complex and formed from various parent materials and under different environmental conditions, it is difficult to analyze factors controlling soil organic matter decomposition and retention in these soils (Babin et al., 2013; Ding et al., 2013). The physical, chemical and biological complexity of natural soils restrict manipulation of soil characteristics independently (Guenet et al., 2011).

To study the interactions between soil minerals, organic matter and microbes, thus simplified systems or artificial soils of known chemical