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Pore Mn^{2+} dynamics of the rhizosphere of flooded and non-flooded rice during a long wet and drying phase in two rice growing soils

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HIGHLIGHTS

- Soil pore Mn^{2+} concentrations were higher in flooded soil than in saturated soil.
- After rice harvest, Mn^{2+} concentrations remained high for at least one week.
- Concentrations of Mn^{2+} were generally higher in red sodosol than in grey vertosol.
- Two peaks of Mn^{2+} were recorded: at 4 weeks after flooding and during rice flowering.
- In the post-flooded, drying stage, the oxidation of Mn^{2+} was slower at greater depths.

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ABSTRACT

Flooded rice soils produce elevated concentrations of soluble manganous manganese (Mn^{2+}) that could be potentially toxic to subsequent crops. To provide insight into how soil pore Mn^{2+} changes its concentration in a rice and post rice drying soil, we used an artificial microcosm system to follow Mn^{2+} concentrations in two different soil types (red sodosol and grey vertosol) and under two irrigation regimes (flooded and saturated). Soil pore water was collected from four different depths of soil (2.5 cm, 7.5 cm, 15 cm and 25 cm) and Mn^{2+} concentrations were analysed during and after the rice phase over a one year cycle. Mn^{2+} increased with the advancement of anaerobic conditions at all soil depths, but the concentration was higher in flooded soil compared to saturated soil. Initially, the highest concentration of Mn^{2+} was found at a depth of 7.5 cm, while at the later stage of rice growth, more Mn^{2+} was found in the deepest sampling depth (25 cm). Plants grown in saturated soils showed a delay in flowering of approximately 3 weeks compared to flooded cultures. Moreover, plants grown in flooded soil produced more tillers and leaf area than those grown in saturated soil. Peak concentrations of soil Mn^{2+} were associated with the reproductive stage of rice growth. Mn^{2+} concentrations decreased after drainage of water. In post rice soils, Mn^{2+} remained elevated for some time (lag phase), and then rapidly declined. Regression analysis revealed that the process of oxidation of Mn^{2+} to Mn^{4+} following water drainage decreased with soil depth.

1. Introduction

The predisposition for manganese to be reduced in flooded soil has been appreciated for many years (Ponnamperuma, 1972; Fageria et al., 2011; Shaheen et al., 2014), and is particularly evident under flood irrigated rice (Doran et al., 2006). Rice soils generally start to become anoxic within a week after flooding, and the nature of some soil nutrients change as the soil transitions from aerobic to anaerobic conditions (Patrick, 1981). When a post rice crop is sown following the drainage of water from the rice bay, the anaerobic state of the soil also progressively changes and becomes more aerobic, with a consequent change in the concentration of manganous manganese (Mn^{2+}) (Patrick and Jugsujinda, 1992).

Manganese is an essential plant micronutrient that is toxic at higher concentrations (Rezai and Farboodnia, 2008). Its solubility

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is dependent on the oxidation state of the soil, with the more oxidized forms (Mn^{3+} and Mn^{4+}) being insoluble and unavailable to plants, while the reduced form (Mn^{2+}) is highly soluble and readily plant available. Measurement of total manganese in soil is not very informative as it does not reflect the ratio of Mn^{4+} to Mn^{2+} and hence relative availability to plants (Leeper, 1970). Soil type may also influence the availability of Mn^{2+}. For example, clay soils accumulate Mn^{2+} in the anaerobic interior of aggregates, and crops in acid soils are more vulnerable to Mn toxicity (McVittie et al., 2012) as Mn solubility increases with declining soil pH.

In aerobic soils, manganese is found mostly as insoluble Mn^{4+} or Mn^{3+} oxides and oxyhydroxides (Post, 1999), while in anaerobic environments the most common form of Mn is the more soluble Mn^{2+} (Ponnamperuma, 1972). In flooded conditions, the major indicative redox couples (according to reduction states) include: O_2/H_2O, NO_3^-/N_2, $Mn(^{4+/3+})/Mn^{2+}$, Fe^{3+}/Fe^{2+}, SO_4^{2-}/H_2S, and CO_2/CH_4 (Gao et al., 2002). As a consequence, some nutrients change their form and their concentrations do not remain constant after flooding. For example, nitrogen may be readily lost from flooded soils through denitrification, and sulfur may be lost to the atmosphere under prolonged periods of waterlogging through its reduction to H_2S (Tiedje et al., 1984).

An increase in soluble manganese has been observed in soils experiencing extended periods of water saturation (Han and Banin, 1996). Typically, the predominant form of Mn in aerobic soil is the easily reducible oxide (Mn^{4+}) and the least dominant species is exchangeable Mn^{2+}. While saturated, the Mn oxides (Mn^{4+}) are reduced into their exchangeable and carbonated forms (Han and Banin, 1996). These changes in redox conditions occur as anaerobic microorganisms use oxidized forms of manganese oxide as an alternative electron acceptor in the absence of oxygen, and its reduction drives the oxidation of organic compounds under anaerobic conditions (Lovley, 1991). The oxygen consumption rate in flooded soils varies according to temperature and level of microbial activity, but is poorly correlated with soil redox condition (Gao et al., 2002). In general, after flooding, oxygen is rapidly consumed followed a period where the residual oxygen declines more slowly. Once oxygen is able to diffuse back into the soil, Mn^{2+} is oxidised to insoluble Mn^{4+}.

The reduction of Mn^{4+} to Mn^{2+} is governed by various biogeochemical and physical processes (Soto-Neira et al., 2011). This reaction is affected by the redox potential (E_H) and pH (Bailey and Beauchamp, 1971; Sparrow and Uren, 2014). For example, in a flooded soil, Mn^{2+} first appears at an E_H of 200 mV while the critical value for the oxidized-to-reduced transition is 150 mV (Patrick and Jugsujinda, 1992). The E_H in rice soil can be shifted by the water conservation techniques used (Tian et al., 2013). Drainage of water from the flooded rice soil allows for the entry of atmospheric oxygen into soil, and its entry can allow for the transformation of the soil from the anaerobic form into a partial aerobic state. Where drainage is impeded, this transformation can be delayed (Manchanda et al., 2003), but the dynamics of redox changes can be difficult to follow, as measurements of E_H are prone to errors and are difficult to interpret when examining complex flooded soils (Gao et al., 2002). In this context, the measurement of soil Mn^{2+} could provide an additional indicator of redox state (Doran et al., 2006), and allow a clearer picture of soil chemistry to emerge.

Changes in Mn^{2+} in rice field soils after flooding have been reported previously (Doran et al., 2006), in a study evaluating the influence of rice plant roots on the redox behaviour of soil. This included assessment of oxygen diffusion from the top of the soil and the impact of roots on the formation of reducing conditions. Mn transformations in the field, however, are difficult to study as Mn leaching may occur following heavy rainfall or irrigation (Han and Banin, 1996), and clay soil shrinkage occurs upon drying. For these reasons, Yuan and Ponnamperuma (1966) suggested using soil microcosms to observe metal transformation (Doran et al., 2006; Shaheen et al., 2014). While the increase in soil Mn^{2+} with flooding is comparatively well known, there is little published information on the dynamics of soil Mn^{2+} in the rhizosphere over the transition from flooded rice to an aerobic drying phase and the effect of carryover Mn^{2+} beyond flooding on subsequent aerobic crops. The aim of this study was to examine changes in the concentration and distribution of Mn^{2+} in the soil profile over the course of a rice crop and in the subsequent drying phase. Microcosms were utilised for this study because they can emulate the complexity of field conditions but allow a greater degree of control for sensitive assessment of micronutrient fluctuations and are not subject to extreme climatic variations.

2. Materials and methods

2.1. Soil collection and analysis

Soils were collected from Yanco Agricultural Research Station and Leeton Research Station, in the rice-growing region of southern Australia. At Yanco (34°36′37″S, 146°24′39″E), the soil was classified as a red sodosol while at Leeton (34°35′52″S, 146°21′49″E), the soil was classified as a grey vertosol (Isbell, 1996). These soils were selected as they typify soils of the Riverina region of southern NSW in which rice is typically grown, and vary both in total amount of Mn and in the predominant clay species. At both sites, soils were excavated in 10 cm layers to a depth of 30 cm using an excavator, with each layer separately stockpiled. Soil samples from each layer were collected and composite samples were analysed by Environmental Analysis Laboratory, Lismore NSW (Table 1). Easily reducible manganese was analysed at the Soil Science Laboratory, NSW Department of Primary Industries (NSW DPI) in Wagga Wagga, Australia using the ammonium acetate and hydroquinone method as described by Sparks et al. (1996). Preliminary soil screening for total manganese was undertaken by nitric acid digestion and analysis by inductively coupled plasma atomic emission spectroscopy (Eaton and Franson, 2005).

2.2. Construction of microcosms

Microcosms were constructed from polyvinyl chloride (PVC) cylinders (internal diameter, 0.15 m; length 0.40 m). Four holes were drilled (i.d. of 0.02 m) vertically on the wall of the pipe at a distance of 0.125 m, 0.15 m, 0.25 m and 0.35 m from the top of the pipe (Fig. 1). A nut (length 0.022 m and head i.d. 0.0094 m) was screwed to the edge of each hole of the pot by keeping the head end inside the pot. A 0.015 m hole was drilled on the opposite side of the lowermost hole and a small airlock was attached and sealed with a stopper. The base of each pipe was closed with a plastic cap sealed using a commercial silicone sealant.

Sampling frits were constructed using porous aquarium air stones (length 0.03 m: inside capacity 1 mL) for soil water extraction with minimal sediment as described by Doran et al. (2006). One third of the surface area was protected from blocking by soil particles by wrapping with Valspar scrim tape (0.025 m) and the remainder was sealed with silicon sealant. Teflon tubing was selected as it maintains its shape when buried in the soil, can withstand high pressures and enables water from the frit to be collected outside of the vessel without disturbing the soil. A Teflon tube (l = 0.10 m, o.d. 0.0016 m, i.d. 0.0006 m) was inserted through the opening of the air stone. The base of the Teflon tube connected to the air stone was reinforced with a covering of nylon tube and