



Changes in exchangeable cations and micronutrients in soils and grains of long-term, low input cropping systems of subtropical Australia



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ABSTRACT

Demand for agricultural products is increasing, but there remains considerable uncertainty regarding many of the impacts of long-term cropping systems on soil properties. Using six soils from low input cropping systems of subtropical Australia, the effects of long-term cultivation (≤ 70 y) on three macronutrient cations (Ca, Mg, and K) and three micronutrient cations (Cu, Zn, and Mn) was examined. For Ca, Mg, and K, exchangeable concentrations generally remained constant and were not influenced by the period of cultivation. As a result, concentrations of these nutrients in grain tissues of wheat (*Triticum aestivum*) also remained constant over time. However, concentrations of DTPA-extractable Cu, Zn, and Mn often (but not always) decreased significantly over time, with Cu decreasing 21%, Zn by 34%, and Mn by 46% (when averaged across soils where significant differences were found). In some soils, these decreases in DTPA-extractable micronutrients also resulted in concomitant decreases in grain tissue concentrations. These decreases in DTPA-extractable Cu, Zn, and Mn concentrations do not result only from the export of nutrients in grain tissues, but also, from an increase in soil pH caused by a cultivation-induced mixing of alkaline subsoil into the surface soil. The data presented here demonstrate the potential impact of long-term cropping on nutrient availability, and in particular, the need to consider changes in nutrient availability and its potential impact on plant and human nutrition.

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1. Introduction

The growing global demand for agricultural products and biofuels is being driven by an increasing human population as well as increasing consumption per capita. However, arable land is being lost at a rate of ca. 12 million ha per year due to soil degradation (Pimentel and Pimentel, 2003). Thus, this increased agricultural production must occur from a shrinking soil-resource. Despite the potential impact of agricultural production on soil properties, there remains much unknown about the nature of these effects. Changes in soil C, N, and P have been the most intensively studied in long-term cropping systems, with cultivation and product removal often causing substantial reductions in their concentrations (Beck and Sanchez, 1994; Dalal and Mayer, 1986b; David et al., 2009; Hedley et al., 1982; Motavalli and Miles, 2002; Tiessen et al., 1982; Wang et al., 2011). Of particular interest in the present study is the potential impacts of long-term, low input cropping on concentrations of Ca, Mg, and K (macronutrients) and Cu, Zn, and Mn (micronutrients).

For Ca, Mg, and K, the exchangeable concentrations (i.e. those held electrostatically by the negatively charged soil colloids on the cation exchange capacity [CEC]) represent the major plant-available reservoir,

with exchangeable cations buffering uptake from the soil solution. In addition, in some soils, release of “fixed” K from interlayer sites can also potentially be of importance over longer periods of time (Sparks and Huang, 1985). Similarly, for the micronutrients, Cu, Zn, and Mn, uptake from the soil solution is buffered by the non-specifically adsorbed cations on the CEC, but specific adsorption is also of importance, as is chelation by organic matter (Reed and Martens, 1996). To assess the plant-availability of these micronutrients, chelating agents (such as DTPA, diethylenetriaminepentaacetic acid) are commonly used to decrease the free-ion concentration, thereby allowing their replenishment (and measurement) from the various labile pools.

Whilst limited studies have investigated changes in these macronutrients (Berthrong et al., 2009; Loke et al., 2014; Morari et al., 2008; Williams and Lipssett, 1961), we are aware of only one study that has examined changes in these micronutrients in long-term production systems (Sanchez et al., 1983). Yet changes in the availability of micronutrients within the soil is of importance not only for plant nutrition (and hence yield), but also for human nutrition. For example, Zn deficiency is the most widespread micronutrient deficiency limiting crop production in the world (Alloway, 2008; Alloway, 2009). Furthermore, an estimated two billion people worldwide are thought to have inadequate intakes of Zn (Hotz and Brown, 2004). Indeed, worldwide micronutrient malnutrition affects more than half of the world's population (FAO, 1997).

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The aim of the present study was to examine the effects of long-term cultivation and product removal on Ca, Mg, and K (as macronutrients) and Cu, Zn, and Mn (as micronutrients). Soils were collected from six locations in subtropical Queensland, Australia. At each location, samples were collected from an undisturbed site as well as from adjacent sites that differed in the length of time that they had been cultivated. Changes in Ca, Mg, and K were assessed using their exchangeable concentrations, whilst Cu, Zn, and Mn were assessed from their DTPA-extractable concentrations. Changes in these soil concentrations were also related to the removal of these nutrients within the grain of wheat (*Triticum aestivum*). The data presented here provides important information on the potential impacts of long-term cropping systems on soils and their agricultural products.

2. Materials and methods

2.1. Soil and plant sampling

To investigate the effects of long-term agricultural cultivation on the concentrations of base cations (Ca, Mg, and K) and on micronutrient cations (Cu, Zn, and Mn), soils were collected from six locations in subtropical Queensland (Australia) (Supplementary Fig. S1). As described previously (Kopittke et al., 2016), the six soil types were referred to as Billa Billa, Cecilvale, Langlands-Logie, Riverview, Thallon, and Waco (Table 1). Other than varying rates of N and P (Table 1), the soils of these low-input systems had not been fertilized, with the number of cultivation operations varying depending upon soil type (Table 1). Where stubble was not retained, it was burnt (Table 1).

At each location, soils were collected from multiple adjacent sites (paddocks) that had been cultivated for different periods of time, ranging from 0.5 to 70 y. At these sites, soils were generally cultivated to a depth of 20–30 cm. Furthermore, samples were collected from an immediately adjacent undisturbed area that still contained the native vegetation and had not been disturbed since cultivation commenced (see Dalal and Mayer (1986a) for more information). Across all six locations, there were a total of 83 individual sites, with each site representing a different soil with a different period of cultivation. Specifically, samples were collected from 12 to 16 sites across the six locations, representing cultivation for ≤ 25 y at Billa Billa, ≤ 35 y for Cecilvale, ≤ 45 y for Langlands-Logie, ≤ 20 y for Riverview, ≤ 23 y for Thallon, and ≤ 70 y for Waco.

At each individual site, 25 samples were collected across an area of 0.1 ha on a 5 × 8 m sampling grid at a depth of 0–0.1 m. From these 25 samples, five were then mixed to form a single composite sample (thus, each site consisted of five composite samples). Whenever

grown, samples of wheat grain were also collected, oven-dried at 65 °C for 48 h, weighed, and ground to pass a 1 mm sieve.

2.2. Analyses

Exchangeable cation composition was determined using alcoholic 1 M NH₄Cl at pH 8.5 (Rayment and Lyons, 2011), with concentrations of Ca, Mg, and K measured using atomic absorption spectroscopy (AAS). The effective cation exchange capacity (ECEC) was calculated as the sum of the exchangeable cation concentrations (Ca, Mg, K, and Na). For micronutrients, concentrations of DTPA-extractable Cu, Zn, and Mn were extracted as described by Lindsay and Norvell (1978) and measured using AAS. Plant tissues were digested in concentrated HNO₃ before analysis using inductively coupled plasma atomic emission spectroscopy (ICP-OES).

2.3. Statistical analyses

All statistical analyses were undertaken using Systat 13.1 (Cranes Software, India). Changes in elemental concentrations were examined using a linear regression:

$$C_t = C_0 - at \quad (1)$$

where C_t is the concentration of the cation after t years, C_0 is the concentration of the cation prior to disturbance, and a is the average annual decrease in the concentration of the cation.

3. Results

3.1. Concentrations of cations in soil

Overall, concentrations of exchangeable cations (Ca, Mg, and K) were generally not influenced by the period of cultivation, with changes in each exchangeable cation concentration typically related to the duration of cultivation in only one or two of the six soils (Fig. 1). Indeed, for exchangeable Ca, concentrations decreased significantly with increasing cultivation for Thallon (predicted concentrations decreasing from 26 to 22 cmol_c kg⁻¹) but no significant relationship was found for the five other soils (Fig. 1A, B). Similarly, for exchangeable Mg, a significant relationship was found for Waco (increasing from 6.7 to 10 cmol_c kg⁻¹) but not for the other soils (Fig. 1C, D). Finally, for K, exchangeable concentrations were observed to decrease in two soils, with a predicted decrease of 0.57 cmol_c kg⁻¹ (30%) for Thallon and 0.60 cmol_c kg⁻¹ (53%) for Langlands-Logie (Fig. 1E, F). Changes in ECEC were generally not significant, with the ECEC remaining relatively constant over time except in Thallon (Supplementary Fig. S2).

Table 1
Selected physicochemical properties of the six soils collected from undisturbed sites (with native vegetation) at a depth of 0–10 cm. Where stubble was not retained, it was burnt. The stubble retention is given as the proportion of the total number of crops where stubble was retained. The P was added as single superphosphate.

Soil series	Classification ^a	Period of cultivation (years)	pH (1:5 water)	EC (dS m ⁻¹ 1:5 water)	Sand (%)	Silt (%)	Clay (%)	Organic C (%)	Bulk density (g cm ⁻³)	Clay minerals ^b	Stubble retained ^c (% crops y ⁻¹)	N fertilizer (kg ha ⁻¹ y ⁻¹)		P fertilizer (kg ha ⁻¹ y ⁻¹)	
												Range	Mean	Range	Mean
Billa Billa	Vertisol	0.5–25	7.4	0.20	48	18	34	1.5	0.95	Q, RI, K, I	73	0	0	0–20	2.0
Cecilvale	Vertisol	3–35	7.4	0.11	44	15	41	1.7	1.0	RI, Q, K, I	67	0–61	18.3	0–33	7.7
Langlands-Logie	Vertisol	0.5–45	7.4	0.25	34	16	50	2.2	0.99	Q, RI, K	77	0–30	7.5	0	0
Riverview	Ultisol	0.5–20	6.4	0.035	73	9.3	18	1.2	1.3	K, Q, I, H	14	0	0	0	0
Thallon	Vertisol	2–23	7.2	0.083	18	23	60	0.78	0.95	K, I, S, Q	64	0	0	0	0
Waco	Vertisol	1–70	8.1	0.13	13	14	72	1.7	0.85	S, K, Q, I	49	0–45	32.6	0–8	1.0

^a Soil Survey Staff (2003). In the Australian Soil Classification (Isbell, 2002), these soils are a Kandosol (Riverview) and Vertosols (all other soils).

^b Listed in order of decreasing abundance: S, smectite; K, kaolinite; I, illite; Q, quartz; RI, randomly interstratified; H, Hematite.

^c Average value across the entire period of cultivation.

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