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Fluorine in soils under pasture following long-term application of phosphate fertiliser in New Zealand

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ABSTRACT

An understanding of the rate at which fluorine (F) accumulates in soil from phosphorus fertiliser and how much is lost via leaching are important because of the challenge elevated F may pose to soil, plant and animal health. This study measured F accumulation in a soil under pasture (Inceptisol) that received single superphosphate (SSP) fertiliser over 63 years in a long-term fertiliser trial. It also assessed the downward movement of F in soil and effect of irrigation in a long-term irrigation trial. Results showed total F concentrations in topsoil (0–7.5 cm) that received 188 kg SSP ha^{-1} and 376 kg SSP ha^{-1} fertiliser increased from 251 mg kg^{-1} to 349 and 430 mg kg^{-1}, respectively. The rates of F accumulation were estimated at 1.1 and 2.1 kg ha^{-1} yr^{-1} respectively, low compared to previous studies. The F concentration in the 376 kg SSP ha^{-1} treatment decreased with depth, but was significantly higher than the control treatment to 50 cm, suggesting movement of F down the soil. Fluorine concentrations also decreased with depth to 50 cm in soils that received either no irrigation or up to 770 mm yr^{-1} from irrigation. However there was no significant difference in the amount of F with depth between irrigation treatments. We postulate that F was moving predominately in drainage water in the period immediately after P fertiliser application in mid-winter and wasn't enhanced by irrigation. This study should be repeated for other soil types to help our understanding of the potential for ongoing F accumulation in soil and implications this may have on future land use.

1. Introduction

Fluorine (F) is a naturally occurring trace element that is an incidental impurity (1–3%) in phosphorus (P) fertilisers that have been derived from fluorapatite (Loganathan et al., 2003; McLaughlin et al., 1996). There is interest in many parts of the world regarding the accumulation of F in agricultural soils from the application of P fertilisers (Kim et al., 2016; Stacey et al., 2010; McGrath and Tunney, 2010) because of the potential adverse effects that F at elevated concentrations may pose to soil, plant and animal health. For instance, at elevated concentrations in soil, F can adversely affect a wide range of plant functions including germination, photosynthesis, respiration, enzyme activity and biomass yield (Panda, 2015; Mishra et al., 2014; Singh et al., 2013; Jha et al., 2009; Stevens et al., 1997). For example, Arnesen (1997) investigated the effect of increasing F concentrations on clover and ryegrass growth in a sand and a sandy loam soil. At 400 mg kg^{-1} there were visible signs of toxicity in both plants and soils, with negligible growth of clover in the sand. At 800 mg kg^{-1}, there was only plant growth in the sandy loam soil, but it was reported growth was very stunted. Studies have also reported a reduction in soil microbiological processes such as dehydrogenase and phosphatase activity and nitrification in soils with increased soil F concentrations (Ropelewska et al., 2016; Rathore and Agrawal, 1989). For example, Tscherko and Kandeler (1997) found that the soil microbial biomass (SMB) and dehydrogenase activity decreased when soil F concentrations exceeded 100 mg kg^{-1}. In comparison, Poulsen (2011) reported phosphatase activity decreased significantly in soil, but at a soil F concentration of 1000 mg kg^{-1}. The development of chronic fluorosis in grazing ruminants such as cattle and sheep through the inadvertent ingestion of F-enriched soil could potentially impair animal performance (McLaughlin et al., 2001).

To effectively manage the potential impact of increased F in agricultural soils, it is essential there is good information available on the rate at which F accumulates and what factors affect accumulation. While there are some estimates of F accumulation rates in soils from P fertiliser application in New Zealand (Kim et al., 2016; Loganathan et al., 2006; Loganathan et al., 2001) and elsewhere (McLaughlin et al., 2001; McGrath and Tunney, 2010), there is very little data available for irrigated soils under pasture. Further, little research has investigated the movement of F down the soil profile via leaching in agricultural soils, which could affect soil accumulation rates. It has generally been considered that the mobility of F from P fertilisers in most soils is low (Loganathan et al., 2007; Murray, 1983), with accumulation limited to the top few centimetres of soils as a result of sorption to oxides and

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hydroxides of iron (Fe) and aluminium (Al) and layer silicate clay minerals (Harrington et al., 2003; McLaughlin et al., 1996; Murray, 1983; Omueti and Jones, 1977). However, Robinson and Edgington (1946) investigating the effect of single superphosphate (SSP) application on soil F concentrations soils with low F sorption capacity, reported that at a depth of c. 35 cm total F concentrations were elevated by 31% and 39% in a sandy loam and gravelly sandy loam respectively, compared to soils that received no F. Specht and MacIntire (1961) found in a leaching trial with a sandy acid soil, with low amounts of clay and Al oxides, only 55% of the F added from fertiliser was recovered in the soil. These studies suggest that F may be relatively mobile in coarse textured soils.

Over the last two decades, there has been large-scale expansion and intensification of pastoral agriculture in New Zealand, particularly on stony soils that are extensively irrigated and receive P fertiliser (Carrick et al., 2013). It is currently not clear how readily F can accumulate in these types of irrigated soils. This information is important to our understanding of future land use activities of these soils, and whether F is likely to accumulate to concentrations which may adversely affect soil, plant and animal health. The aims of this study were therefore undertaken to investigate two factors affecting F accumulation in soils i) F accumulation rates in a irrigated pasture soil that has received regular addition of SSP (*viz* F) over a period of 63 years and ii) assess the effect of SSP application and irrigation on the vertical movement of F from topsoil to the subsoil.

2. Materials and methods

Soil samples were obtained from two long-term field trials at the Winchmore Irrigation Research Station, New Zealand (43.8° S, 171.8° E). The soil at Winchmore is a shallow free-draining Lismore stony silt loam (Udic Ustochrept in USDA Soil Taxonomy), formed from moderately weathered greywacke loess over gravels. Details of the site history, together with soil preparation and establishment are provided in other publications (Kelliher et al., 2012).

2.1. Fertiliser trial

Twelve plots comprising four replicates of three fertiliser treatments arranged in a randomised block design were selected for this study. Fertiliser has been applied (top dressed) annually as SSP (9% total P) in late winter to each plot since 1952. The treatments included a control (Nil P), 188 kg SSP ha^{-1} yr^{-1} (188PA) and 376 kg SSP ha^{-1} yr^{-1} (376PA). This is equivalent to 0, 17 and 34 kg P ha^{-1} yr^{-1}. Lime was applied in 1947 (5 t ha^{-1}) and again in 1972 (4.4 t ha^{-1}) to all treatments. The trial received rainfall (740 mm) plus an average of 4.3 irrigation events (100 mm per event) per annum (total c. 1150 mm yr^{-1}). Each plot of each treatment was grazed rotationally by separate flocks of sheep to avoid nutrient transfer between treatments, with the stocking rates designed and adjusted to optimise pasture utilisation. No stock grazing occurred in winter.

2.2. Irrigation trial

Eight plots comprising four replicates of two irrigation treatments arranged in a randomised block design were selected. The two treatments were a dryland treatment that only received rainfall and a treatment that received irrigation when the topsoil (0–100 mm) moisture reached 20% (50% available soil moisture (asm) with 0% asm being wilting point). On average, this resulted in 7.7 irrigations per year, 100 mm of water at each event. Both irrigation treatments received 250 kg ha^{-1} of SSP applied in late winter to each plot annually from 1949 until 2003. This is equivalent to 22 kg P ha^{-1} yr^{-1}. Lime was applied to the trial in 1948 (5 t ha^{-1}) and 1965 (1.9 t ha^{-1}) to all treatments. Each treatment was rotationally grazed by a separate flock of sheep as for the fertiliser trial.

2.3. Soil samples

2.3.1. Temporal samples

Soil samples (0–7.5 cm depth) were retrieved from the soil archive for each treatment from the fertiliser trial i.e. Nil, 188PA and 376PA sampled in the spring each year from the years 1952, 1958, 1962, 1967, 1973, 1979, 1986, 1990, 1996, 2003, 2011 and 2015. Archived soils were air dried, sieved (<2 mm) and stored in plastic containers at ambient temperature and humidity.

2.3.2. Depth samples

Vertical soil sampling was carried out in 2009, from each replicate of the Nil and 376PA treatments from the fertiliser trial and also from the dryland and 20% moisture treatments from the irrigation trial. Conventional soil sampling with a corer was not practicable because of the high stone content with soil depth. Instead bulk soil samples were taken as previously outlined (Condron et al., 2014). Briefly, pits for each treatment were excavated with a mechanical backhoe, and soil and stones were collected from six depths (0–7.5, 7.5–15, 15–25, 25–50, 50–75 and 75–100 cm) using a 40 × 40 × 25 cm^3 steel frame. Each sample was weighed and separated into soil and stones (the roots having been removed) using sieves and weighed again. From each sample, approximately 3 kg of fresh soil subsample was set aside for analysis. From each subsample, a portion was weighed, dried at 105 °C for 24 h and weighed again. By applying the subsample's water content to the sample's fresh soil and stone weights and accounting for the sample's volume, the sample's stone content and bulk density were determined.

2.4. Analysis

Soil was air-dried and sieved (<2 mm) prior to analysis. Soil pH was measured in a deionised water suspension with a soil:solution ratio 1:2.5 (Blakemore et al., 1987). Total carbon (C) was measured by a combustion method (Kelliher et al., 2012). Amorphous iron (Fe) and aluminium (Al) oxides were determined by oxalate-extraction (McKeague and Day, 1966). Determination of total F in soil samples was by the alkaline fusion/ion-selective electrode method of McQuaker and Gurney (1977). In this method, 0.5 g of oven-dried (105 °C) and sieved (<180 μm) soil sample is fused with 17 M sodium hydroxide in a nickel crucible at 600 °C at 45 min in a muffle furnace, and the resulting fusion mass is dissolved in hot deionised water. The solution is adjusted to pH 8–9 (to precipitate iron and aluminium), filtered, and buffered (TISAB) to constant ionic strength. Fluoride was determined in the aqueous extracts using an ion-selective electrode (Frankenberger et al., 1996). Quality control measures for F analysis included use of blanks, analysis of duplicate samples and a reference quality control sample (CRM BCR-461; 568 ± 60 mg F kg^{-1}). Concentrations of F in procedural blanks were less than the detection limit of 20 mg L^{-1}. Results of duplicate analysis of samples were within 10% of each other. The recovery of F from reference material were within the limits of the certified value.

Statistical analyses were performed by GENSTAT for Windows v17. Data were not transformed before being subjected to Analysis of Variance (ANOVA) to test for the effects of treatment and depth. Effects were considered significant if they differed at the probability level of 5% based on Fisher's unprotected least significant difference (LSD) test.

3. Results and discussion

3.1. Temporal trends

Total soil F concentrations in the Nil treatment from the long-term SSP trial decreased slightly ($P < 0.011$) from 250 mg kg^{-1} in 1952 to 233 mg kg^{-1} in 2015 (Fig. 1). The decrease is possibly a function of F that was present in the SSP applied during the trial establishment in 1947 being lost from the topsoil, either by leaching and/or in animal