Impact of long-term application of phosphate fertilizer on cadmium accumulation in crops

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Abstract
Field studies were conducted since 2002 at five locations across the Canadian prairies to study the long-term effects of P fertilizer application rate and Cd content on seed Cd concentration of durum wheat (\textit{Triticum turgidum} L.) and flax (\textit{Linum usitatissimum} L.). Cadmium concentration was higher in durum wheat than flax and varied with location. Cadmium concentration in the seed of both crops increased with application of P fertilizer even when the fertilizer contained only trace concentrations of Cd, indicating that P fertilization directly influenced Cd concentration of crops apart from the effect of Cd addition. Seed Cd concentration was higher when the fertilizer contained greater Cd concentrations, particularly when rate of fertilizer application was also high. Cadmium concentration in crops was directly proportional to the total amount of Cd applied over time, but the effect of fertilizer application varied with soil characteristics. Highest availability of Cd added in P fertilizer was on light-textured or acidic soil, while availability of applied Cd was lower on heavier-textured or higher pH soils. Therefore, soil characteristics that affect phytoavailability must be taken into account when assessing the risk of transfer of Cd into the food chain from P fertilization.

Key Words
Cadmium, heavy metal, linseed.

Introduction
Cadmium (Cd) is a trace element that can accumulate to high levels in specific crops. Cadmium has been linked to negative health effects, so it is desirable to reduce the Cd concentrations of crops entering the human diet. Cadmium concentration in crops is influenced by a wide range of factors, including crop genetics, soil characteristics such as texture, pH and salinity, weather, crop sequence, crop management practices and soil Cd concentration (Grant \textit{et al.} 1999). Cadmium is present at varying concentrations as a contaminant in phosphate (P) fertilizers (Grant \textit{et al.} 2002; Grant and Sheppard 2008; Taylor 1997) and repeated applications of Cd in P fertilizers may increase Cd content of soils, potentially increasing Cd content of crops. However, the long-term availability of the Cd applied in phosphate fertilizer will vary with soil characteristics. This study was conducted to determine the long-term influence of Cd applied in monoammonium phosphate (MAP) fertilizer on Cd concentration of durum wheat and flax, across a range of soils and environments.

Methods
Field studies were conducted at five sites across the Canadian prairies from 2002 to 2009, to determine the influence of repeated applications of monoammonium phosphate fertilizer on accumulation of Cd in crops. At each location, three rates of P fertilizers (0, 20, 40 and 80 kg P ha\textsuperscript{-1}) from three different sources varying in Cd concentration (0.38 mg Cd/kg, 71 mg Cd/kg, and 211 mg Cd/kg) were applied annually and sites were seeded following a durum wheat-flax-durum wheat–flax crop sequence. Treatments were applied to the same plots each year so that the cumulative effects of P applications could be assessed over time. Treatments were arranged at each location in a randomized complete block design with four replications. Crops were harvested at maturity using a small plot combine and seed yield and concentrations of Cd and nutrient elements were determined for flax in 2007 and durum wheat in 2008. Seed samples were ground in a coffee grinder and digested with a mixture of HNO\textsubscript{3}-HClO\textsubscript{4} (9:1). Digests were analysed for Zn on an ARL (Sunland, CA, USA) ICP unit and for Cd on a Varian (Palo Alto, CA, USA) 300/400 atomic absorption spectrophotometer at a wavelength of 228.8 nm using a graphite furnace with deuterium correction (detection limit 0.01 ng Cd /mL). Reliability of the analysis was assessed by including standard reference materials from NIST (i.e., durum wheat flour #8436, peach leaves #1547, tomato leaves #1573 and wheat
flour #1567a), and internal standards (with concentration values confirmed from ‘round-robin’ analyses with 7-10 co-operating laboratories) in each of the plant digests. Statistical analysis was conducted using Proc Mixed of SAS (Littell et al. 1996), with differences among treatments being considered significant at the \( p < 0.05 \) level.

**Results and discussion**

Seed Cd concentration was measured in flax grown in 2007 (data not presented) and durum wheat grown in 2008 (Figure 1). At a given site, flax seed was higher in Cd concentration than was durum wheat grain. Grain Cd in the unfertilized crop varied as much as three-fold from location to location, indicating that soil and environmental characteristics have a dominating effect on Cd concentration of crops (Figure 1). Highest Cd concentrations in the unfertilized control in both the flax and the durum wheat occurred on the Carman site, a light-textured, acidic soil. Previous studies had shown that this soil had a high solution Cd concentration, indicating high Cd phytoavailability (Lambert et al. 2007).

![Figure 1. Effect of 8 years of application of varying rates of MAP fertilizer with low, medium and high Cd concentration on concentration of Cd in durum wheat grain at five sites in Western Canada (2008).](image_url)
Phosphorus application increased grain Cd content at all sites in both flax and durum wheat, even when Cd concentrations in the P fertilizer were low, indicating an effect of fertilization on Cd availability for crop uptake apart from the direct addition of Cd. However, grain Cd increased to a greater extent with MAP application on most of the sites when the fertilizer contained a higher concentration of Cd. When the data were averaged over sites, Cd concentration in durum grain showed a quadratic relation to the total amount of Cd added over the seven years of the study with an $R^2$ of 0.89.

While the pattern of crop response to fertilizer application was similar from location to location, the magnitude of response differed substantially. The largest effect of fertilizer application on flax was at the Ellerslie site where seed Cd increased from 103 µg Cd/kg in the control to 441 µg Cd/kg in the high Cd high P treatment. Similarly at the Sylvania site seed Cd increased from 127 µg Cd/kg in the control to 365 µg Cd/kg with the high rate of high-Cd MAP. Durum wheat grain Cd at the Sylvania site increased by more than four-fold from 55µg Cd/kg in the control to 223 µg Cd/kg with the high rate of high-Cd MAP. Cadmium concentration in durum wheat at the Ellerslie site also increased substantially from 35µg Cd/kg in the control to 113 µg Cd/kg with the high rate of high-Cd MAP. The Sylvania site was a sandy loam soil, which may have led to the high availability of added Cd on this site. The Ellerslie site was a silt clay loam with pH near 6.2 and the Carman site was a loam with a pH near 5.2. Cadmium concentration in flax and durum wheat at the Carmen site, a coarse-textured soil with low pH, also increased substantially with application of high Cd MAP. Grain Cd response to fertilizer application was much smaller at the Phillips and Spruce sites, which were clay to clay-loam sites with pH of 7.0 or higher.

Conclusions
Cadmium concentration in durum wheat increased with application of MAP fertilizer, even when the fertilizer did not contain significant amounts of Cd. Therefore MAP fertilizer can increase Cd concentration of crops through mechanisms other than the direct addition of Cd. However, the impact of MAP fertilizer on Cd concentration of crops increased with Cd concentration in the fertilizer, particularly at high fertilizer rates and with repeated application. Soil characteristics such as texture or pH appear to be important in influencing the long-term phytoavailability of the added Cd. Therefore, soil characteristics that affect phytoavailability must be taken into account when assessing the risk of transfer of Cd into the food chain from P fertilization.

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References