Preliminary Studies on Soil Accumulation, Potential Sources, and Soil Factors Affecting Cadmium Concentrations in Desert Durum Wheat

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Summary

The European Union (EU) has established maximum allowable cadmium (Cd) levels for wheat of 200 ug/kg. Desert Durum wheat sometimes exceeds this allowance. The objectives of these preliminary studies were to collect preliminary information on Cd accumulation in soils, use isotopic finger printing (with Pb) to infer potential sources of metals and as funds allowed evaluate soil properties affecting Cd accumulation in durum grain. The plow layer of soils used in our evaluation had bioavailable Cd of approximately 900 g/ha and bioavailable lead levels of approximately 9000 g/ha.. Phosphate fertilizers commonly used in the region contains approximately 150 mg/kg Cd and 3 mg/kg Pb. At typical fertilization amounts (600 kg/ha), there is a potential for annual additions of 90 g/ha and 2 g/ha of Cd and Pb, respectively. Results from the soil pedon samples show that there were no statistically significant increases in soil Cd or Pb after 35 years of P fertilization. Phosphorus fertilizer has a unique Pb isotopic ratio, distinguishing it from the soils and irrigation waters of the region. These data show very little Pb in wheat grain is derived from the fertilizer. By inference we assume that only a small percentage of the Cd in wheat grain is derived from the fertilizer as well. These preliminary findings suggest that P fertilizers are not a significant source of Cd and Pb to desert Durum wheat. Additional studies are needed to validate these findings and evaluate other biotic and abiotic factors affecting metal accumulation by wheat.

Introduction

Food is the major source of cadmium (Cd) exposure to humans (Gartrell et al., 1986; Gunderson, 1995; Pennington et al., 1986). The World Health Organization (WHO) has established a provisional daily intake of cadmium at 1 ug/kg body weight (Walker and Herman, 2000). The FAO and WHO established the Codex Committee for Food Additives and Contaminates (CCFAC) to address food safety issues and legislation. Based on consumption estimates and cumulative exposure projections, the CCFAC has recommended maximum levels (MLs) for various food commodities. The European Union (EU) has incorporated many of the criteria used by the CCFAC and have actually adapted many of the proposed MLs. For example, the ML for fruit, rooting vegetables, wheat, and leafy vegetables are 50, 100, 200, and 200 ug/kg, respectively (Berg and Licht, 2002).

These MLs are partially based on extrapolations from toxicological evidence from rice consuming populations affected with Cd induced renal proximal tubular dysfunction (Kobayashi 1978; Cai et al., 1995; Kobayashi et al., 2002). However, these estimates ignore differences in metal antagonist among various food sources and differences in the nutritional status of different populations (Chaney et al., 2004). For example, rice is low in zinc (Zn), iron (Fe), and calcium (Ca). High concentrations of one or more of these elements reduce the rate of Cd absorption in to the bodies of test animals and humans (Flannagan et al., 1978; Fox, 1988; Reeves and Chaney, 2002; Reeves and Chaney, 2004). Little consideration has been given to nutritional factors affecting the bioavailability of Cd. Nevertheless, buyers from the EU have scrutinized durum wheat produced in our desert region for Cd content and Arizona wheat shippers will have to modify culture and handling practices in attempts to comply with EU concerns.

Cadmium (Cd) is a natural contaminant in some soils and in most phosphate fertilizers. The amounts of Cd in phosphate rocks varies by source, ranging from 3 to 15 mg/kg in phosphate mined in Florida to as high as 150 mg/kg in phosphate rock mined in the western United States (Mortvedt et al., 1981). Most of the Cd in phosphate rock remains in the P fertilizers after processing. We have found monoammonium phosphate used in the desert has Cd at 150 mg/kg. Studies in Australia have shown high levels of cumulative P fertilization increased the Cd accumulation by crops (Williams and David, 1976). However, another study reported long-term P fertilization from experimental plots in the midwestern and southern United States did not increase Cd levels in plants (Mortvedt, 1987). We have no indication if P fertilization practices are a factor affecting Cd accumulation in the southwestern United States.

Crop species differ in their capacity to accumulate cadmium (Wagner 1993; Chaney et al., 1996). However even within crop species there can be considerable variation in Cd accumulation and redistribution. Greger and Lofstedt (2004) reported that most of the variation in Cd accumulation in the durum grain was due to variation in translocation from the root and shoot to the grain, rather than to variation in uptake by the roots. However, for durum wheat there was a good correlation between the Cd content of the flag leaf and the Cd content in the grain indicating the potential to use the flag leaf as a predictive tool.

Soil properties also play an important role in Cd accumulation by crops (MacLean, 1976; Eriksson, 1990). Soil pH is an important factor affecting Cd solubility and availability to plants (Gavi et al., 1997, Oliver et al., 1996). Generally, higher soil pH values favor soil sorption and decreases partitioning of Cd to the soil solution where it is available for plant uptake (Sauvé et al., 2000). Soils in the southwestern United States are generally buffered to a relatively narrow pH range above neutral, and it is unlikely that soil pH has a profound influence on the variability of Cd uptake in desert durum wheat. However, studies show that Cd uptake is enhanced by elevated levels of salinity, or specifically high soil chloride (Bingham et al., 1984; Li et al., 1994; Norvell et al., 2000; Khoshgoftarmanesh et al., 2006). It is possible that variation in the salinity of soils and irrigation waters used in wheat production affect Cd accumulation by grain in the desert.

A number of studies have shown Cd accumulation by crops is influenced by Zn availability (Haghiri, 1974; Abdel-Sabour et al., 1988; Chaney et al., 1994). In one particularly relevant study, the application of Zn rates up to 5 kg/ha were found to substantially decrease Cd concentrations in wheat produced on soils prone to Zn deficiency (Oliver et al., 1994). In another study, it was shown that the tendency for increased Cd uptake with increased salinity in wheat was reduced by Zn fertilization (Khoshogoftar et al., 2004). The potential for Zn fertilization to reduce Cd contents of wheat grain in the low desert southwestern United States has not been rigorously evaluated.

Studies have shown soil tests are potentially useful for predicting Cd accumulation by plants and grain (Oliver et al., 1994; Norvell et al., 2000). Both chelates and dilute salts based extractions have been utilized. In some instances more complex models including some measure of soil Cd as well as other soil properties such as pH (Adams et al., 2004) or soil chloride (Norvell et al., 2000) were required to predict Cd concentrations in grain.

The source of metals can also be inferred from measurement of metal isotopic ratio for materials from different sources. Lead is useful in this regard for the study of contaminates because multiple isotopes exist in nature. Lead is the natural by product of U and Th decay and has three radiogenic daughter isotopes: ^{208}Pb, ^{207}Pb, and ^{206}Pb. When ratioed to each other or to the one non-radiogenic isotope, ^{204}Pb, these isotopes provide a useful discriminator of contaminants. Unlike other stable isotopes (N, C, O, S), Pb isotopes do not fractionate through natural surficial processes, which makes them ideal for “fingerprinting” differing sources. Thus, from these data for Pb, we can infer sources of Cd as well. In these studies we will use this approach to distinguish fertilizer from other sources of metal contamination.

The objectives of these preliminary studies are to 1. collect preliminary information on Cd accumulation in soils, 2. use isotopic finger printing (with Pb) to infer potential sources of metals, especially Cd, in soils and durum wheat grain. These preliminary data are a prerequisite to developing longer termed strategies for eliminating Cd concerns in desert durum wheat.

Materials and Methods

Evaluation of accumulation in soils over three decades

Seven different soil pedons initially sampled in 1972 were again sampled incrementally to a depth of 1.5 m in 2007. Soils collected in 1972 and stored in glass jars, and those collected in 2007 were processed for digestion and extraction for metal content, and isotope ratio analysis. The acid digestion fraction would be an approximation of total metals while DPTA extraction would be an estimate of plant available metals. Data for soils collected at seven sites over 35 years were used to evaluate the effects of fertilization and other management practices on metal accumulation.

Evaluation of potential metal sources to wheat

The source of metals can also be inferred from measurement of metal isotopic ratio for materials from different sources. Lead is useful in this regard for the study of contaminates because multiple isotopes exist in nature. Lead is the natural by product of U and Th decay and has three radiogenic daughter isotopes: ^{206}Pb, ^{207}Pb, and ^{208}Pb. When ratioed to each other or to the one non-radiogenic isotope, ^{204}Pb, these isotopes provide a useful discriminator of contaminants. Unlike other stable isotopes (N, C, O, S), Pb isotopes do not fractionate through natural surficial processes, which makes them ideal for “fingerprinting” differing sources. Thus, from these data for Pb, we can infer sources of Cd as well. In these studies we will use this approach to distinguish fertilizer from other sources of metal contamination.

General Analytical Methodology

Soils, plant material, and fertilizers were digested using nitric acid and peroxide block digestion. Soils were also extracted for bioavailable metals (Cd and Pb) using DPTA or ammonium acetate. Water samples, soil, plant, and fertilizer digests, and soil extracts were analyzed for total element content by inductively couple plasma/ mass spectroscopy (ICP/MS). Pb isotopic ratios were separated using standard techniques and measured on a Multi Collector Inductively Coupled Mass Spectrometer (MC-ICPMS).

SUMMARY

Phosphate fertilizers commonly used in the region contains approximately 150 mg/kg Cd and 3 mg/kg Pb (Table 1). At typical fertilization amounts (600 kg/ha), there is a potential for annual additions of 90 g/ha and 2 g/ha of Cd and Pb, respectively.

A hectare of soil 30 cm deep would weigh approximately 4.5 million kg. Hence these soils would have bioavailable Cd and Pb levels of approximately 900 and 9000 g/ha, respectively.

Results from the soil pedon samples show that there were no statistically significant increases in soil Cd or Pb after 35 years of P fertilization.

Phosphorus fertilizer has a unique radiogenic Pb isotopic ratio, distinguishing it from the soils and irrigation waters of the region. These data show very little Pb in wheat grain is derived from the fertilizer. By inference we assume that only a small percentage of the Cd in wheat grain is derived from the fertilizer as well.

Conclusion

These preliminary findings indicate that P fertilizers are not a significant source of Cd and Pb to desert Durum wheat. Additional studies are underway to validate these findings and evaluate other biotic and abiotic factors affecting metal accumulation by wheat.

Table 1. Mean cadmium and lead contents of irrigation water and P fertilizer used for Durum wheat.

Source	Cd	Pb
Irrigation Water (ug/L)	0.06	0.13
P Fertilizer (mg/kg)	148	3.3

Table 2. Mean cadmium (Cd) contents in agricultural soils after 35 years of fertilization.

Metal	Year	0-30 cm average	0-150 cm average
		Acid Digest	
Cd (mg/kg)	1972	0.51	0.33
	2007	0.45	0.24
Stat.		NS	NS
		DPTA Extract	
Cd (mg/kg)	1972	0.21	0.13
	2007	0.14	0.05
Stat.		NS	0.001

Table 3. Mean lead (Pb) contents in agricultural soil pedons over 35 years of P fertilization.

Metal	Year	0-30 cm average	0-150 cm average
		Acid Digest	
Pb (mg/kg)	1972	17.6	12.6
	2007	18.1	10.5

Stat.		**NS**	**NS**
	DPTA-Extract		
Pb (mg/kg)	**1972**	**2.0**	**1.3**
	2007	**2.4**	**1.1**
Stat.		**NS**	**NS**

Table 4. Lead isotopic ratios of potential sources of metals and potential sink (wheat grain).

Source	206Pb/204Pb	207Pb/204Pb	208Pb/204Pb
Irrigation Water	19.044	15.698	38.816
Surface Soil (1972)[1]	18.864	15.635	38.602
Surface Soil (2007)[1]	18.923	15.644	38.622
P Fertilizer	72.658	18.469	38.828
Wheat Grain	19.488	15.730	38.881

[1]These data reflect ammonium acetate extractable Pb.

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