

## Short communication

# Continuous biosolids application affects grain elemental concentrations in a dryland-wheat agroecosystem

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## ABSTRACT

Continuous land application of biosolids in a beneficial-use program changes trace-element availability to plants over time. Consequently, what regression model, if any, could best predict wheat (*Triticum aestivum* L.) grain concentrations in a biosolids-amended dryland agroecosystem? We calculated paraboloid, linear, quadratic, and exponential-rise-to-a maximum equations for grain Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn concentration versus number of biosolids applications and/or soil  $\text{NH}_4\text{HCO}_3$ -dithylenetriaminepentaacetic acid (AB-DTPA) extract concentrations for two sites that had each received six applications of Littleton/Englewood, CO, USA Wastewater Treatment Facility biosolids. The paraboloid-regression models were superior (higher  $R^2$  values, lower S.E. of the estimate) to other models. Soils classified the same as the Weld soil (used in this study) at the family level (fine, smectitic, mesic Aridic Argiustolls) encompass 25 soil series in 10 US states with an aerial extent of  $2.3 \times 10^6$  ha. The paraboloid-regression model approach probably would be applicable to these similarly classified soils.

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## 1. Introduction

The beneficial use of biosolids (sewage sludge) to recycle organic matter and plant nutrients is supported and regulated by USEPA (40 CFR Part 503 regulations; USEPA, 1993). Continuous applications based on the agronomic N rate for wheat are common in dryland agroecosystems (Barbarick and Ippolito, 2007). Since trace-element availability varies with time after biosolids application (Barbarick and Ippolito, 2008), this practice raises the question: What regression model, if any, would best predict the relationship between soil  $\text{NH}_4\text{HCO}_3$ -dithylenetriaminepentaacetic acid-extractable (AB-DTPA) levels and grain concentrations?

Lavado et al. (2005) found that soils amended with non-digested biosolids growing corn (*Zea mays* L.) produced significantly larger ethylenediaminetetraacetic acid (EDTA) soil extractable Cu and Zn and total soil Cr, Cu, Ni, and Zn than in digested biosolids. In another biosolids study on Mollisols in Argentina, Lavado et al. (2007) reported that neither EDTA soil extraction nor total soil digests provided any significant relationships between soil content and plant concentrations of potentially toxic elements in wheat and corn.

Norvell et al. (2000) found that the predictability (based on  $R^2$  values) of durum-wheat-grain Cd with soil-extractable DTPA Cd was improved from 0.45 to 0.66 by adding the water-extractable soil  $\text{Cl}^-$  concentration to the regression model. This resulted in a three-dimensional-regression equation that prompted the authors to conclude that elevated soil  $\text{Cl}^-$  levels were the major cause of increased grain Cd. They would not have reached this conclusion if they had not completed a three-dimensional-regression with water-extractable  $\text{Cl}^-$  as a variable.

Barbarick and Ippolito (2008) showed that planar-regression models (another three-dimensional model) that predicted AB-DTPA Zn, P, Cu, and Fe based on elemental additions and number of biosolids applications were superior (i.e., higher  $R^2$  values and lower S.E. of the estimate) to linear, quadratic, or exponential-rise-to-a-maximum models using only elemental additions as the dependent variable. They used the planar-regression models to predict how extractability changed by varying the number of biosolids applications.

Our hypothesis is that paraboloid-regression models using AB-DTPA concentrations plus the number of applications as independent variables will allow better predictability of wheat-grain concentrations of Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn (i.e., higher  $R^2$  values and lower standard errors) than linear, quadratic, or exponential-rise-to-a-maximum regression models on two sites amended with Littleton/Englewood Wastewater Treatment Plant (L/E) biosolids.

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## 2. Materials and methods

Our biosolids study was initiated in the summer of 1993 near Bennett, CO, USA (latitude 39.9563, longitude 104.462). Mean annual precipitation for this area is about 350 mm, mean maximum and minimum temperatures are 19 °C and 2 °C, respectively, and the annual growing season is about 150 d (NRCS, 1974). We used two sets of plots on the same farm (designated A for those established in 1993; B for those established in 1994) since the crop rotation was hard red winter-wheat summer fallow.

The soils at both sites were classified as Weld loam (fine, smectitic, mesic Aridic Argiustoll; NRCS, 2008a). The Weld soil series occupies  $3.2 \times 10^5$  ha in eastern CO (NRCS, 2008b). Initial soil characteristics (before treatment) were organic matter content ~1% to a depth of 150 cm; surface (0–20 cm) soil pH of 6.9, and subsoil pH ranged from 7.2 to 8.3 from 20 to 150 cm in depth for the two sites. The electrical conductivity of saturated-soil extracts were  $<1$  dS  $m^{-1}$  to the 150 cm depth at both sites.

The L/E biosolids were anaerobically digested and delivered by L/E after approximately 60 d of sand-bed drying. Biosolids samples were collected prior to application and kept refrigerated at approximately 3 °C until analyses were completed. Table 1 shows elemental content for the biosolids applied to both plots. We applied biosolids at rates of 0, 2.24, 4.48, 6.72, 8.96, and 11.2 dry Mg biosolids  $ha^{-1}$  to 1.8 by 17.1 m plots in 1993, 1995, 1997, 1999, 2001, and 2003 at site A and in 1994, 1996, 1998, 2000, 2002, and 2004 at site B. Barbarick and Ippolito (2007 and 2008) provide further study-site details. The 4.48 Mg biosolids  $ha^{-1}$  rate is the recommended agronomic rate for dryland winter wheat, typically supplying ~35 kg N  $ha^{-1}$  (Barbarick and Ippolito, 2007). The study was arranged in a randomized complete block design with four replications of each treatment at each site. In late July or early August (about 50 d before planting), the dried biosolids were weighed (solids content of 530–930 g  $kg^{-1}$ ), evenly spread over the plots utilizing a front-end loader, hand raked to improve the uniformity of distribution, and immediately rototilled to a depth of 10–15 cm.

Each July from 1994 through 2005, we completed yield determinations by harvesting a 1.8- by 15.2-m area. The 2000–2001 crop was lost due to hail damage. Grain elemental concentrations of Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn in concentrated  $HNO_3$  digests (Huang and Schulte, 1985) were determined using an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES; Soltanpour et al., 1996).

Immediately following each wheat harvest, composite soil samples were collected (two to three cores per plot) from the 0–

20 cm (tillage layer) depth near the center of each plot to avoid biosolids redistribution problems that can occur following tillage operations over many cropping years (Ippolito et al., 2007; Yingming and Corey, 1993). The soil samples were immediately air-dried and crushed to pass a 2-mm sieve. We determined concentrations of soil Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn in AB-DTPA (Barbarick and Workman, 1987) extracts using ICP-AES.

We statistically analyzed the grain concentration data for each site using a split-plot analysis (Steel and Torrie, 1980) where biosolids rates were main plots and biosolids application frequency were the subplots. We separated site A and B since plant growth and sampling took place during different growing seasons. We used a probability level ( $P$ ) of 0.10 to determine if grain concentrations varied with year. We then developed regression models using the AB-DTPA soil concentrations and/or application frequency in calculating regression equations to predict grain concentrations.

Our regression models were:

$$\begin{aligned} \text{paraboloid : grain concentration} &= a + b \\ &(\text{number of applications}) + c(\text{number of applications})^2 \\ &+ d(\text{AB-DTPA concentration}) + e(\text{AB-DTPA concentration})^2 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{linear : grain concentration} \\ &= a + b(\text{AB-DTPA concentration}) \end{aligned} \quad (2)$$

$$\begin{aligned} \text{quadratic : grain concentration} &= a + b(\text{AB-DTPA concentration}) \\ &+ c(\text{AB-DTPA concentration})^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{exponential rise to a maximum : grain concentration} \\ &= a + b(1 - e^{-(\text{AB-DTPA concentration})}) \end{aligned} \quad (4)$$

where: AB-DTPA = AB-DTPA extractable element concentration in  $mg\ kg^{-1}$ ;  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  = empirical constants.

We used a  $P$  of 0.10 to determine significance. Model equations,  $R^2$  values, and standard errors were determined using SigmaPlot<sup>®</sup> (2006) version 10.

## 3. Results and discussion

Grain Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn concentrations were significantly different over years at both sites (data not provided).

**Table 1**

The average Ba, Cd, Cu, Mn, Mo, Ni, P, and Zn content of the Littleton/Englewood, Colorado biosolids applied to dryland winter wheat at two sites near Bennett, CO, USA from 1993 to 2005.

	Ba (mg $kg^{-1}$ )	Cd (mg $kg^{-1}$ )	Cu (mg $kg^{-1}$ )	Mn (mg $kg^{-1}$ )	Mo (mg $kg^{-1}$ )	Ni (mg $kg^{-1}$ )	P (g $kg^{-1}$ )	Zn (mg $kg^{-1}$ )
Site A								
1993	ND <sup>a</sup>	6.0	558	ND	26	85	27.1	942
1995	423	4.0	458	250	13	42	17.4	816
1997	ND	2.9	459	ND	8	35	35.9	422
1999	ND	5.6	256	ND	8	15	10.2	198
2001	ND	0.6	398	ND	13	8	19.9	428
2003	ND	1.7	594	ND	15	11	24.2	418
Site B								
1994	421	6.7	493	246	22	65	16.6	816
1996	144	6.1	657	290	24	52	23.0	652
1998	ND	3.4	236	ND	6	15	11.8	301
2000	ND	2.4	352	ND	6	1	36.0	370
2002	ND	0.9	326	ND	16	8	19.3	351
2004	498	2.5	652	256	18	14	29.8	767

<sup>a</sup> ND: not determined.

**Table 2**  
Regression model  $R^2$  values and standard errors for wheat-grain concentrations versus AB-DTPA-extractable soil concentrations of Zn, P, Cu, Ni, Ba, and Mn after six applications of Littleton/Englewood biosolids at two sites near Bennett, CO, USA.

Element	Regression model <sup>a</sup>	Site A		Site B	
		$R^2$	S.E. <sup>b</sup>	$R^2$	S.E.
Ba	Paraboloid	0.619	1.5	0.318	2.4
	Linear	0.551	1.5	NS	NS
	Quadratic	0.565	1.5	NS	NS
	Exp. rise	Model did not fit		NS	NS
Cd	Paraboloid	0.828	0.05	0.812	0.06
	Linear	0.406	0.09	NS	NS
	Quadratic	0.486	0.08	0.339	0.11
	Exp. rise	0.486	0.08	Model did not fit	
Cu	Paraboloid	0.780	0.8	0.588	4.4
	Linear	0.222	1.3	NS	NS
	Quadratic	0.570	1.0	NS	NS
	Exp. rise	0.502	1.1	NS	NS
Mn	Planar	0.833	1.9	0.630	3.2
	Linear	0.399	3.4	NS	NS
	Quadratic	0.400	3.4	NS	NS
	Exp. rise	Model did not fit		NS	NS
Mo	Paraboloid	0.832	0.07	0.667	0.15
	Linear	0.552	0.10	NS	NS
	Quadratic	0.553	0.10	NS	NS
	Exp. rise	Model did not fit		Model did not fit	
Ni	Paraboloid	0.680	0.5	0.332	1.4
	Linear	NS	NS	0.204	1.5
	Quadratic	NS	NS	0.307	1.4
	Exp. rise	NS	NS	0.253	1.5
P	Paraboloid	0.778	287	0.869	424
	Linear	0.349	470	0.741	564
	Quadratic	0.553	395	0.798	507
	Exp. rise	0.548	397	0.788	519
Zn	Paraboloid	0.775	2.6	NS	NS
	Linear	0.319	4.3	NS	NS
	Quadratic	0.405	4.0	NS	NS
	Exp. Rise	0.415	4.0	NS	NS

<sup>a</sup> Probability levels for all regression analyses were <0.05 except for those models labeled as NS for “non significant”.

<sup>b</sup> S.E.: standard error of the estimate.

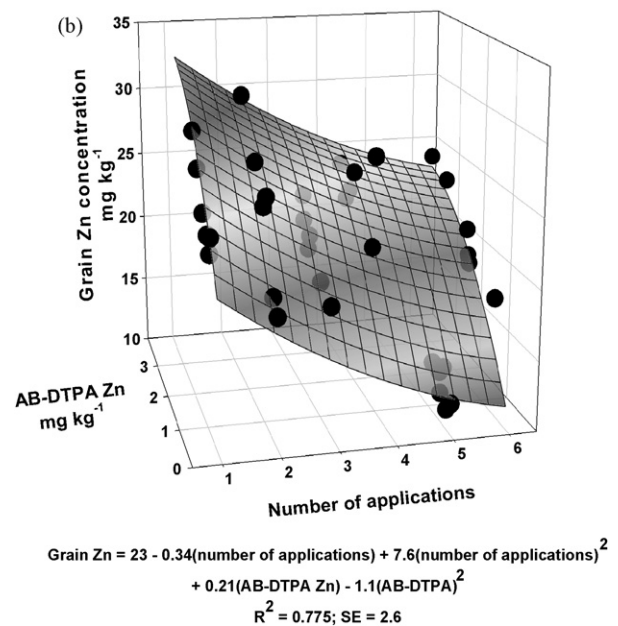
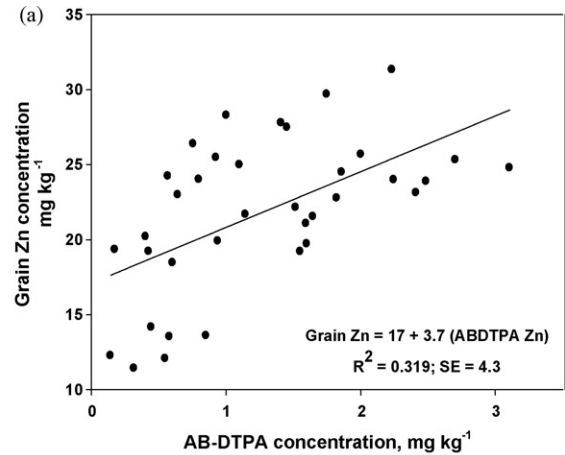
We expected these results since dryland wheat production is primarily controlled by moisture availability. The mid to late 1990’s were periods of excessive moisture; during the 2000’s the sites have experienced drought (Barbarick and Ippolito, 2007).

The paraboloid-regression model (Eq. (1)) provided higher  $R^2$  values and lower S.E. of the estimate for every element tested at both sites (Table 2). We therefore accepted our hypotheses that the paraboloid-regression model is superior to the other models

**Table 3**  
Parameters for paraboloid-regression models for prediction of wheat-grain elemental concentration (in  $\text{mg kg}^{-1}$ ) by the following equation: grain concentration =  $a + b(\text{number of applications}) + c(\text{number of applications})^2 + d(\text{AB-DTPA}) + e(\text{AB-DTPA})^2$ .

Element	Site A								Site B							
	a	b	c	d	e	$R^2$	S.E. <sup>a</sup>	a	b	c	d	e	$R^2$	S.E.		
Ba	6.9	-0.74	1.5	0.045	0.98	0.619	1.5	8.1	1.7	-0.46	-0.34	0.46	0.318	2.4		
Cd	-0.54	0.34	1.8	-0.046	-1.4	0.828	0.05	0.49	-0.21	0.64	0.021	-1.8	0.812	0.06		
Cu	1.9	-0.041	1.8	-0.066	-0.17	0.780	0.8	32	18	-24	-2.2	2.5	0.588	4.4		
Mn	29	5.7	0.68	-0.95	-0.012	0.833	1.9	20	10	2.5	-1.3	-0.17	0.630	3.2		
Mo	0.69	-0.028	-2.4	-0.0066	8.8	0.832	0.07	0.16	0.35	4.1	-0.061	-26	0.667	0.15		
Ni	4.2	-1.5	3.6	0.13	-2.4	0.680	0.5	-15	0.021	27	0.017	-10	0.332	1.4		
P	2900	-840	330	120	-13	0.778	290	3100	-570	220	110	-3.2	0.869	420		
Zn	23	-3.4	7.6	0.21	-1.1	0.775	2.6	-	-	-	-	-	NS	NS		

<sup>a</sup> S.E.: standard error of the estimate.



**Fig. 1.** Linear regression (a) and paraboloid regression (b) models for wheat-grain Zn at site A versus soil AB-DTPA Zn concentrations in a dryland agroecosystem that received six applications of Littleton/Englewood, CO, USA biosolids.

tested. The paraboloid-model parameters for each element are presented in Table 3. For comparison and as an example for one element at site A, a linear plot of grain Zn versus AB-DTPA Zn (Fig. 1a) and a three-dimensional graph of grain Zn versus number of applications and soil AB-DTPA Zn levels (Fig. 1b) are provided.

The paraboloid model is akin to a three-dimensional quadratic equation; and, this model probably better accounts for grain concentration changes under different climatic (moisture availability) regimes over the years.

As Barbarick and Ippolito (2008) demonstrated, the “aging” of applied biosolids-borne trace elements to various mineral phases reduces their availability over time so that the better mechanistic model to predict trace-element grain concentrations would be one that accounts for when and how many times biosolids are applied. As Norvell et al. (2000) showed for durum-wheat-grain Cd, the introduction of a second factor (water-extractable  $\text{Cl}^-$ ) with the soil DTPA Cd level provided not only a better statistical model but also a superior mechanistic model.

As indicated earlier, the NRCS (2008b) estimates that the Weld soil encompasses  $3.2 \times 10^5$  ha in eastern CO. Soils classified at the same family classification as the Weld soil (fine, smectitic, mesic, Aridic Argiustolls) make up  $2.3 \times 10^6$  ha in 25 soil series in the US states of Arizona, Colorado, Kansas, Montana, Nebraska, New Mexico, Nevada, South Dakota, Utah, and Wyoming (NRCS, 2008b). Since the paraboloid-regression models rely on the soil AB-DTPA concentrations in the top 20 cm of Weld soil, which would comprise a portion of the mollic epipedon, we can reasonably expect the 25 soil series classified as fine, smectitic, mesic, Aridic Argiustolls would provide similar statistical-modeling responses to continuous biosolids application. This approach provides biosolids managers with another predictive tool regarding the fate of biosolids-borne elements.

#### 4. Conclusions

Paraboloid-regression models for predicting wheat-grain elemental concentrations in a dryland agroecosystem receiving continuous biosolids applications were superior to more commonly used linear, quadratic, and exponential-rise-to-a-maximum equations. The addition of number of biosolids applications along with soil AB-DTPA concentrations as independent variables to predict grain concentrations are mechanistically accurate since the availability of biosolids-borne elements tend to decrease with time after soil application.

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