Accumulation of copper and zinc in soil and plant within ten-year application of different pig manure rates

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ABSTRACT

Fertilization of crops with pig manure is a common practice throughout the world. Nevertheless, due to the relatively high copper (Cu) and zinc (Zn) contents in pig manure, continuous application of pig manure could have negative effects on soil and plant. The study aimed at the impacts of long-term applying different pig manure rates (equivalently 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008 and 0, 10, 25 and 50 t fresh weight/ha/year from 2009 to 2011, respectively) on Cu and Zn accumulation in soil and plant. During the 10 years of the experiment, a total of 2.04 to 10.20 kg/ha/year for Cu, 3.15 to 15.73 kg/ha/year for Zn were applied to the soil. Results from this study showed that long-term pig manure application resulted in serious accumulation of Cu and Zn in soil, total Cu and Zn concentrations increased by 204% and 107% at high application rates, respectively. Although topsoil Cu and Zn concentrations were below concentrations considered phytotoxic to crops, according to current Chinese legislation, it would take only less time than 16 and 27 years of high application rates to reach the allowable limits. Our result also suggested that Cu and Zn leaching occurred in the tested soil. The Cu and Zn concentrations in stalks and grains were not affected by the application of pig manure, and these values were lower than the threshold values for animal and human ingestion.

Keywords: long-term field experiments; maize; soybean; DTPA; leaching

With the rapid development of intensive pig farming in China in the last two decades, China has become the biggest pork-producing country in the world, producing 51.60 million t in 2012, which was twice more than those of European Union (22.60 million t) (Chinese Animal Husbandry Yearbook 2012). As a consequence, the quantity of pig manures has increased tremendously. Pig manure is traditionally applied to agricultural soils with double objective: as a fertilizer and to recycle waste material (Weber et al. 2007). However, animal feeds are frequently fortified with elements, such as copper (Cu) and zinc (Zn), to maintain various physiological processes and prevent animal health disorders. For all livestock, the majority of most heavy metals consumed in feed is excreted in the faeces or urine, and is present in manure that is subsequently applied to land (Nicholson et al. 2003). Many investigations showed that Cu and Zn concentrations in pig manure were significantly higher than other animal manures (Nicholson et al. 1999, Cang et al. 2004, Sager 2007), and consequently, pig manure could pose a higher risk of Cu and Zn pollution to farmland.

Even though Cu and Zn are essential nutrients for plant growth and development, these metals may become phytotoxic and cause metabolic disorders at high soil concentrations, and lead to a potential threat to human health through the food chain (Chang and Page 2000). In addition, the massive input of Cu and Zn following manure also promotes migration through leaching and runoff, negatively affecting water quality. Hence, it is important to evaluate the risk of crop and migration when pig manures containing heavy metals are applied to agricultural soil.

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Long-term field experiments provide direct observations of changes in heavy metal and are useful for predictions of future metal accumulation and soil-plant-environment interactions. According to recent studies, repeated application of poultry litter (Schomberg et al. 2008), pig slurry (Novak et al. 2004, Berenguer et al. 2008) or cattle manure (Lipoth and Schoenau 2007, Benke et al. 2008) can substantially increase the Cu and Zn contents in the upper soil layer. Moreover, several researchers have investigated the impact of liquid swine or solid cattle manures on the absorption of Cu and Zn by different plant species (Zhou et al. 2005, Hanč et al. 2008, Nikoli and Matsi 2011, Legros et al. 2013). For example, the result of Lipoth and Schoenau (2007) showed that Cu concentration in the straw of wheat (3.11 mg/kg) at the highest rate of swine effluent was significantly higher than the control (1.90 mg/kg). In another study, Cu and Zn concentrations in maize (*Zea mays* L.) were not influenced by the application of liquid swine manure (Berenguer et al. 2008). However, there is very limited information available about Cu and Zn accumulation and the potential risk of contamination at the field scale after long-term pig manure applications.

A 10-year field experiment with repeated application of different pig manure rates was conducted in the Northeast China, where there is a high density of animal farming and the intensive utilization of manure as fertilizers. The objectives of this research were to investigate the effect of long-term pig manure applications on the accumulation (total content) and bioavailability (diethylenetriamine-pentaacetic acid, DTPA extractable content) of Cu and Zn in soil; assess the potential risk of crop and leaching due to the use of pig manure; offer the optimal use rate of pig manure to agricultural soils in Northeast China.

MATERIAL AND METHODS

Study site and experimental design. A long-term field experiment was conducted since 2002 at the Shenyang Ecological Experimental Station of the Institute of Applied Ecology, Chinese Academy of Sciences (41°320'N, 123°230'E). The area is in the temperate sub-humid mainland climate, with a mean annual temperature of 7.5°C, and annual precipitation of 680 mm. The frost-free period is 147–164 days. The soil of the experimental field is a Luvisol (FAO 2006). The experiment included four treatments in this study: no fertilizer control (CK); low pig manure rate (M_L); middle pig manure rate (M_M) and high pig manure rate (M_H), which were equivalent to 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 0, 10, 25 and 50 t fresh weight/ha/year from 2009 to 2011, respectively. Table 1 presents the amount of dry matter applied each year. No other fertilizers were applied on these plots. Each fertilization treatment (main plot) is laid out in a randomized block design with three replicates. A three-course rotation was conducted (soybean, 2 × maize) in each main plot, and soybean, the 1st maize and the 2nd maize were planted in the three replicates, respectively.

Each year, pig manure was spread just before ploughing. The field was ploughed (15 cm depth) by horses in the spring, and the maize and soybean were sown on 1–5 May simultaneously, depending on the weather and soil conditions. Irrigation and herbicides were not applied and weeds were removed by hand-hoeing. Every year, harvesting took place in mid-October.

Sampling and analyses. Soil samples were taken from depths of 0–15 cm after crop harvest every year since 2002. Six soil cores were mixed to obtain a final soil sample. The soil samples were air-dried, followed by thorough grinding to pass through a 0.149-mm nylon sieve, and subsamples were then stored in plastic bottles for further chemical analysis. Maize grain yield and plant biomass were measured at physiological maturity by weighing all samples. At the same time, plant samples (stalks and grains) were collected and oven-dried at 70°C to determine moisture content. The plant samples were then ground by pulverizer to pass a 0.149-mm nylon sieve and stored in plastic bottles for heavy metal analysis. Manure samples were collected prior to application.

The soil samples were digested using HF-HNO_3-$HClO_4$; manure samples (0.1 g) were used for digestion by HNO_3-$HClO_4$; crop samples (2.0 g) were used for digestion by HNO_3-$HClO_4$ (Lu 2000), which were then measured by atomic absorption spectrophotometry (AAS) for content of Cu and Zn. Reagent blanks and standard reference samples were also analyzed to monitor analytical accuracy and precision. Three replicates of sample were analyzed.

Soil available Cu and Zn contents were obtained by extracting 3 g soil (2 mm) with 30 mL DTPA (diethylenetriamine-pentaacetic acid) solution. After 2 h of continuous shaking at 25°C, the soil suspension was centrifuged and filtered through a 0.45 mm membrane (Lindsay and Norvell 1978), which was then measured by AAS for content of Cu and Zn.

Calculations. To determine the potential risk to agricultural soils, some values were calculated from the raw data referring to Čásová et al. (2009).

The loading rate via pig manure application (kg/ha/year) was estimated by the ratio between the total amount of Cu or Zn applied during the experiment (kg/ha) and the number of years of the experiment (10 years).

Soil accumulation rate (mg/kg/year or mg/ha/year) was estimated by the ratio between the change of soil total metal concentration in plots (mg/kg or mg/ha) and the number of years of the experiment (10 years).

The output rate through plant removal (kg/ha/year) was estimated by the ratio between the total plant uptake amount of metal during the experiment (kg/ha) and the number of years of the experiment (3 years).

Statistical analysis. Data on Cu and Zn concentrations in crops and soil were analyzed using one-way ANOVA with SPSS Version 13.0 software (SPSS Inc., USA). The differences between treatments were compared using the least significant difference test (*LSD*) at the 0.05 level. In addition, simple correlations were performed between the total and DTPA metals concentrations in soil and the concentrations of metals in plant-tissue.

RESULTS AND DISCUSSION

Cu and Zn concentrations in pig manure and input of them. The range of Cu concentrations in pig manure was 118.67 to 673.58 mg/kg, with an average of 418.42 mg/kg, whereas Zn concentrations ranged from 183.42 to 1126.25 mg/kg, with a mean value of 625.30 mg/kg (Table 1), in line with concentrations reported in literature (Nicholson et al. 2003, Xiong et al. 2010). Almost all of the samples exceeded the limits for Cu (100 mg/kg) and Zn (400 mg/kg), respectively, in reference to the limits of manure compost in Germany (Verdonck and Szmidt 1997), since no available standards for trace elements in organic manures exist in China, suggesting that the land application of pig manure would have a high risk of Cu and Zn pollution. The Cu and Zn concentrations in animal manure were related to the amounts of Cu and Zn as additives being added to animal diets (Nicholson et al. 1999). Until now, China has had no standards for the reasonable use of Cu and Zn

Table 1. Concentrations and amounts of Cu and Zn applied to the soil derived from pig manure

	Treatment	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	Total
Amount applied (t/ha)												
	M_L	10.03	5.78	4.28	3.19	3.82	4.99	5.97	6.18	5.24	4.41	53.89
	M_M	25.03	14.38	10.68	7.97	9.52	12.48	14.92	15.46	13.11	11.00	134.55
	M_H	50.05	28.69	21.36	15.94	19.06	24.96	29.88	30.91	26.24	22.00	269.12
Amount applied (kg/ha)												
	M_L	1.19	0.94	1.70	2.15	1.37	3.16	1.54	3.49	2.41	2.46	20.40
Cu	M_M	2.97	2.34	4.24	5.37	3.41	7.90	3.85	8.73	6.03	6.14	50.99
	M_H	5.94	4.67	8.48	10.74	6.83	15.80	7.71	17.46	12.07	12.28	101.97
	M_L	1.84	1.18	1.80	3.25	1.16	3.10	3.22	6.75	5.91	3.27	31.47
Zn	M_M	4.59	2.93	4.50	8.12	2.91	7.76	8.03	16.88	14.77	8.16	78.66
	M_H	9.18	5.86	9.01	16.24	5.82	15.51	16.07	33.75	29.54	16.33	157.31
Concentrations (mg/kg)												mean
Cu		118.67	162.75	396.92	673.58	358.25	633.08	258.00	564.83	460.00	558.08	418.42
Zn		183.42	204.17	421.50	1018.83	305.33	621.50	537.83	1091.83	1126.25	742.33	625.30

M_L, M_M, and M_H refer to annual manure application rates being equivalent to 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011 additives in concentrated animal production. As a result of this, Cu and Zn additives are commonly oversupplied in animal feeding stuffs in China (Li et al. 2007, Xiong et al. 2010). Hence, it was important to establish the regulations of the use of additives permitted in pig feed for reducing the Zn and Cu contents in pig manure.

To determine the potential risk to agricultural soils, we further calculated the loading rates of Cu and Zn from pig manure. The result showed that the loading rates of Cu and Zn to soil ranged from 2.04 to 10.20 and 3.15 to 15.73 kg/ha/year, respectively (Table 2). Although these values did not exceed the EU standards (European Union 1986), which established the maximum limit of 12 kg/ha/year for Cu and 30 kg/ha/year for Zn, they were higher than those obtained in previous studies conducted in Denmark (0.58 kg/ha/year for Cu and 1.29 kg/ha/year for Zn) (Bach et al. 2002), the United Kingdom (1.60 kg/ha/year for Cu and 2.20 kg/ha/year for Zn) (Nicholson et al. 2003), and Spain (1.68 kg/ha/year for Cu and 2.32 kg/ha/year for Zn) (Berenguer et al. 2008), suggesting that the application of pig manure in China would result in a higher risk of soil pollution than in those European countries.

Change of total and DTPA Cu and Zn concentrations in soil and accumulation rate. The annual application of pig manure significantly increased soil total Cu and Zn concentrations (Figure 1, Table 2). Other studies also found an accumulation of these metals in soils when fertilizing with pig manure (Mantovi et al. 2003, Asada et al. 2010). By 2011, total Cu and Zn concentrations in M_H treatment increased by about 204% and 107%, respectively, but their levels (69.23 and 129.85 mg/kg) were still lower than the maximum allowable concentration (100 and 200 mg/kg) in Chinese agricultural soils (MEP 1995).

Soil accumulation rates for total Cu and Zn were markedly different between treatments, with higher rates as Cu and Zn load increased (Table 2). The accumulation rates were lower than the corresponding loading rates, meaning that the amounts of total Cu and Zn recovered in the surface soil layer (0–15 cm) were lower than the amounts applied with pig manure. Considering the accumulation rates and assuming a linear accumulation of Cu and Zn, the limit levels would be exceeded after only 16 and 27 years, respectively, of continuous application of pig manure at high rate, whereas it would take 112 and 160 years, respectively, to reach the ceiling in M_L plots. Based on the estimated time to reach the limit, low application rate of pig manure (10 t/ha/year) looked like to be a recommended agronomic rate in our region.

Compared with the control, there was also a significant enrichment of soil DTPA Cu and Zn in those plots receiving pig manure (Figure 2), as observed by some authors using other manures (Berenguer et al. 2008, Nikoli and Masti 2011). The increases can be attributed to two aspects. On the one hand, pig manure contained high amounts of organic Cu and Zn, which were easily decomposed into soluble Cu and Zn after the application of pig manure to soil (Ogiyama et al. 2005). On the other hand, the changes of soil properties caused by the application of pig manure affected metal availability, especially soil organic matter (SOC), which can supply organic chemicals to the soil

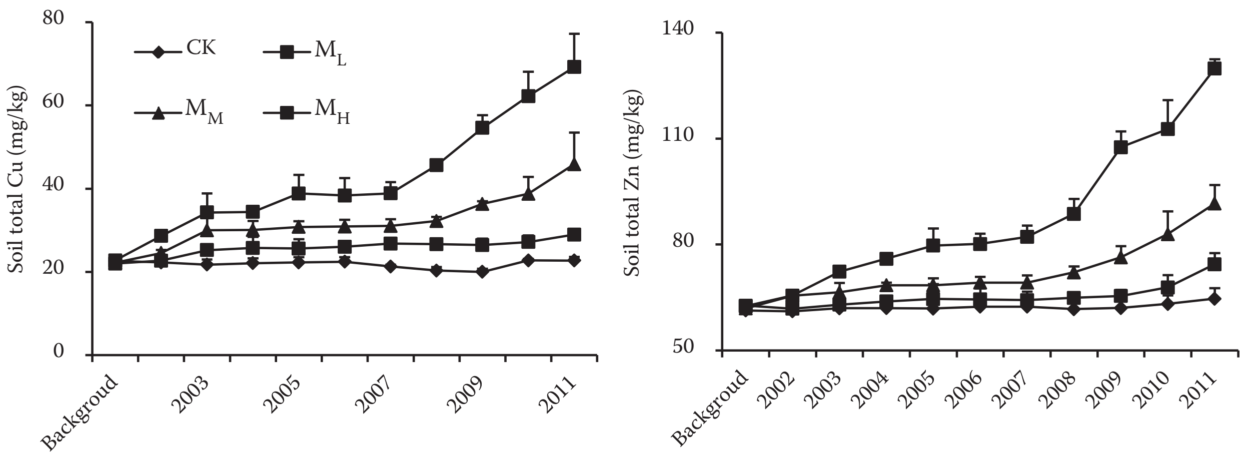

Figure 1. Trends in total Cu and Zn concentrations in topsoil (0–15 cm) during 10 years of pig manure application. CK, M_L, M_M, and M_H refer to annual manure application rates being equivalent to 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 0, 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011

Table 2. The application rate, soil accumulation rate and plant uptake rate of total Cu and Zn during 10 years of pig manure applications

Element	Treatment	Application rate (kg/ha/year)	Accumulation rate (mg/kg/year)	Accumulation rate[a] (kg/ha/year)	Plant uptake rate (kg/ha/year)
Cu	CK	0	0.01	0.02	0.05
	M_L	2.04	**0.70**[b]	**1.20**	0.07
	M_M	5.10	**2.36**	**4.08**	0.08
	M_H	10.20	**4.65**	**8.02**	0.09
Zn	CK	0	0.13	0.23	0.21
	M_L	3.15	**1.17**	**2.02**	0.29
	M_M	7.87	**2.97**	**5.13**	0.31
	M_H	15.73	**6.73**	**11.61**	0.32

CK, M_L, M_M, and M_H refer to annual manure application rates being equivalent to 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 0, 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011. [a]Calculations assume soil density of 1.15 g/cm^3 and soil depth of 0–15 cm. [b]Figures in bold indicate they differ significantly from 2002 (P < 0.05)

solution that can serve as chelates and increase metal availability (Asada et al. 2010).

Cu and Zn concentrations in crops and output of them. During recent 3 years grain yields and biomasses increased as the application rates of pig manure increased (Table 3). Thus, there was no evidence of yields diminishment due to Cu or Zn phytotoxicity. Another study also showed no

Table 3. Grain yield and biomass influenced by pig manure from 2009 to 2011

Year	Treatment	Maize (t/ha/year)		Soybean (t/ha/year)	
		stalks	grain	stalks	grain
2009	CK	5.09^{d}	5.28^{d}	2.83^{b}	1.51^{b}
	M_L	7.36^{c}	8.52^{c}	2.86^{b}	1.95^{b}
	M_M	8.31^{b}	10.74^{b}	2.94^{b}	2.33^{a}
	M_H	8.75^{a}	11.41^{a}	3.65^{a}	2.39^{a}
2010	CK	4.51^{d}	4.57^{d}	2.77^{c}	2.06^{c}
	M_L	5.79^{c}	5.64^{c}	3.83^{b}	2.62^{b}
	M_M	6.20^{b}	7.85^{b}	3.93^{b}	3.00^{a}
	M_H	6.67^{a}	8.67^{a}	4.44^{a}	2.99^{a}
2011	CK	5.38^{d}	6.01^{d}	1.12^{d}	1.58^{c}
	M_L	7.50^{c}	9.36^{c}	2.31^{c}	2.85^{b}
	M_M	8.34^{b}	10.60^{b}	3.06^{b}	3.26^{a}
	M_H	9.40^{a}	11.22^{a}	3.70^{a}	3.32^{a}

CK, M_L, M_M, and M_H refer to annual pig manure application rates being equivalent to 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 0, 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011. Values within a column followed by the same letters in the table indicate no significant difference at a 0.05 significance level, determined by LSD test (n = 3)

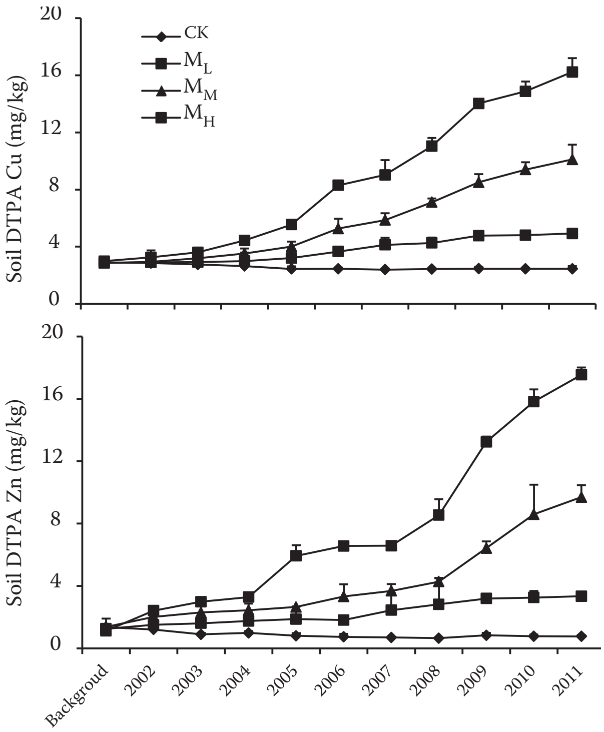

Figure 2. Trends in DTPA Cu and Zn concentrations in topsoil during 10 years of pig manure application. CK, M_L, M_M, and M_H refer to annual manure application rates being equivalent to 0, 100, 250 and 500 kg total N/ha/year from 2002 to 2008, and 0, 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011

Table 4. Cu and Zn concentrations in maize and soybean from 2009 to 2011

Year	Treatment	Cu (mg/kg)				Zn (mg/kg)			
		maize		soybean		maize		soybean	
		stalks	grain	stalks	grain	stalks	grain	stalks	grain
2009	CK	3.81^{b}	1.88^{a}	4.50^{a}	13.38^{a}	33.81^{a}	26.06^{a}	16.88^{a}	51.50^{a}
	M_L	4.13^{ab}	1.63^{b}	3.00^{a}	14.25^{a}	27.94^{b}	31.44^{a}	15.50^{b}	56.00^{a}
	M_M	4.13^{ab}	1.63^{b}	2.88^{ab}	12.25^{a}	25.94^{bc}	30.44^{a}	13.75^{c}	54.88^{a}
	M_H	5.44^{a}	1.50^{b}	2.38^{b}	14.13^{a}	21.81^{c}	29.06^{a}	12.13^{c}	53.00^{a}
2010	CK	9.88^{a}	1.75^{a}	7.00^{a}	11.75^{b}	37.13^{a}	22.00^{a}	17.75^{a}	48.50^{ab}
	M_L	9.88^{a}	1.63^{a}	8.00^{a}	12.13^{ab}	26.75^{b}	17.50^{b}	12.88^{b}	46.38^{b}
	M_M	8.56^{a}	1.38^{b}	7.00^{a}	12.63^{a}	24.81^{b}	19.19^{a}	12.50^{b}	46.63^{b}
	M_H	8.06^{a}	1.31^{b}	5.50^{b}	13.25^{a}	24.75^{b}	20.56^{a}	11.25^{b}	50.75^{a}
2011	CK	9.81^{b}	2.99^{a}	9.75^{a}	13.88^{a}	31.88^{a}	20.69^{b}	14.58^{a}	60.14^{a}
	M_L	11.88^{a}	2.44^{b}	8.13^{a}	11.38^{b}	29.58^{a}	23.82^{a}	11.81^{b}	57.64^{ab}
	M_M	9.75^{b}	2.31^{b}	7.25^{ab}	10.38^{bc}	23.68^{ab}	21.32^{ab}	10.00^{bc}	52.92^{b}
	M_H	8.94^{b}	1.50^{c}	6.38^{b}	9.00^{c}	19.72^{b}	23.13^{a}	9.17^{c}	53.47^{b}

CK, M_L, M_M, and M_H refer to annual pig manure application rates being equivalent to 0, 100, 250 and 500 kg totall N/ha/year from 2002 to 2008, and 0, 10, 25, and 50 t fresh weight/ha/year from 2009 to 2011. Values within a column followed by the same letters in the table indicate no significant difference at a 0.05 significance level, determined by the *LSD* test (n = 3)

sign of phytotoxicity in irrigated maize fertilized with liquid swine manure (Berenguer et al. 2008).

The measured concentrations of Cu and Zn exhibited by maize and soybean were within the normal range (Mantovi et al. 2003) and did not exceed the Chinese Food Hygiene Standards (NY861-2004) (Table 4). Unexpectedly, increasing rates of pig manure did not appear to increase the concentrations of Cu and Zn in plant-tissue among each year, so much so that the concentrations of Zn in stalks declined with increasing pig manure applied. Moreover, the lack of significant correlations between soil total or DTPA metals and plant-tissue metals also was found in this study (Table 5). These indicated that Cu and Zn concentrations in crops were not influenced by soil total or DTPA Cu and Zn. The same outcome was reported for Cu and Zn concentrations in maize following the addition of liquid swine manure (Berenguer et al. 2008) and liquid dairy cattle manure (Nikoli et al. 2011). Essentially, plant appeared to be capable of restricting heavy metal translocation from soil to roots and internal transport to avoid excessive heavy metal-induced damage (Ahumada et al. 2009). It was also suggested that increasing yields have resulted in decreased concentrations of trace elements in produce because of a 'dilution effect' caused by plant growth rates exceeding the ability of plants to acquire these elements (Jarrell and Beverly 1981).

Crop removal rates of Cu and Zn increased since biomasses of crop increased with the application of pig manure (Table 2), but these values were relatively small in comparison with the amounts applied through pig manure, and confirmed observations by Chang and Page (2000) and Berenguer et al. (2008). Plant uptake of Cu and Zn only represented < 3.4% and < 9.2 of the loading rates,

Table 5. Correlation coefficients for the relationships between soil total- and DTPA-metals and plant-metals

	Maize		Soybean	
	stalk	grain	stalk	grain
Total Cu	0.290^{ns}	–0.304^{ns}	–0.252^{ns}	–0.463^{ns}
DTPA-Cu	0.236^{ns}	–0.323^{ns}	–0.219^{ns}	–0.375^{ns}
Total Zn	–0.209^{ns}	–0.019^{ns}	–0.160^{ns}	0.102^{ns}
DTPA-Zn	–0.186^{ns}	0.032^{ns}	–0.100^{ns}	0.100^{ns}

^{ns}non significant at $P > 0.05$

respectively. This suggested that almost all the Cu and Zn applied through pig manure remained in the soil after harvest. Furthermore, the loading rates of Cu and Zn were higher than the sum of soil accumulation rates and removal rates, indicating that the leaching of Cu and Zn took place in those plots receiving pig manure.

In conclusion, excessive and continuous applications of pig manure may enhance serious contamination of Zn and Cu in arable soil within ten years. Nevertheless, long-term pig manure application did not significantly affect Cu and Zn concentrations in plant-tissue, and these values did not approach the threshold for Cu and Zn toxicity, even at high application rates. This study may assist in understanding the potential risk of Cu and Zn from pig manure land application, aiding in developing strategies to reduce the Cu and Zn input to pig manure and agricultural soils, and to promote policies to protect soil quality.

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