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Article

Copper Residue in Animal Manures and the Potential Pollution Risk in Northeast China

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Abstract: A total of 224 animal manures and feeds, randomly sampled from different sizes of intensive farms in three northeastern provinces, were analyzed to determine Cu concentration. At the same time, the load of animal manure Cu on farmlands and loss to rivers in sewage irrigation areas of Liaoning Province was estimated. The results showed that the mean Cu concentrations in pig, cattle, and chicken feeds were 179.8, 16.6 and 20.8 mg kg^{-1}, respectively. Cu concentrations in manures ranged from 1.5 to 1521.2 mg kg^{-1}. The mean value of 642.1 mg kg^{-1} in pig manure was higher than the mean values of 65.6 mg kg^{-1} and 31.1 mg kg^{-1} in chicken and cattle manures, respectively. The load of animal manure Cu on farmland in the study area ranged from 12.3-35.4 kg km^{-2} annually. In particular, the Xiaolinghe area received a higher level than the other areas. The possible amount of manure Cu entering river water as a result of soil erosion was lower than 0.76 kg km^{-2}. The highest loss rates were found in the south of Anshan and the west of Jinzhou. It is suggested that animal manures contain a high level of Cu. Long-term agricultural application of animal manure may increase the potential risk of Cu pollution in soil and surface water.

Key words: animal manure; Cu; sewage irrigation area; agricultural application

1 Introduction

China's economic boom in recent decades has stimulated human demand for animal products and has consequently led to a vast expansion of animal production. Heavy metals such as Cu and Zn are widely used in animal diets, not only as essential micronutrients but also for their stimulating effect on animal growth (Nicholson *et al.* 1999). However, owing to abuse of mineral additives in animal production, high residues of Cu, As, and Zn in animal manures have been reported in China (Cang *et al.* 2004; Li *et al.* 2007). Samples of pig manure collected in Jilin Province, China exhibited a mean value of 765.1 mg kg^{-1} Cu and a wide range of 97.9–1704.7 mg kg^{-1} (Yao *et al.* 2006). Recently, we also found that the Cu concentration in a pig manure sample reached as high as 2016.7 mg kg^{-1} in Beijing (Xiong *et al.* 2010).

The soil is a long-term sink for heavy metals (Nicholson *et al.* 2003). There is concern about excess inputs of heavy metals such as Cu to agricultural soils of China (Luo *et al.* 2009). Manure production in China is approximately 32×10^8 t annually (Wang *et al.* 2006). According to Luo *et al.* (2009), the contribution of animal manure to the total of Cu in soils is approximately 68.5%. Xiong *et al.* (2010) reported that pig and chicken manures might be the primary contributors of Cu to farmlands of Fuxin and Beijing. Therefore, it is important to understand the role of Cu in animal manures and its potential risk for farmlands.

Accumulation of heavy metals could not only affect soil fertility and product quality (Zhou *et al*. 2005), but also promote metal transport through leaching and runoff (L'Herroux *et al*. 1997; Aldrich *et al*. 2002). For example, manure-borne heavy metals were readily adsorbed on soil particles. These particles may be transported via water runoff to surface water. As reported by Römkens *et al*. (2002), the contribution of arable soils to the total load of Cu, Cd and Zn in Dutch surface waters could be as high as 60%. Xue *et al*. (2003) found that manure-borne Cu

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and Zn inputs to soils resulted in concentrations in the waters of the associated catchments that often exceeded the surface water quality criteria. However, agricultural runoff as a source of surface water contamination by heavy metals has not previously received sufficient attention.

Northeast China, including Liaoning, Jilin and Heilongjiang provinces, is an important grain-production region. Unfortunately, elevated concentrations of heavy metals in farmlands pose a high potential risk for agricultural products (Guo and Zhou 2004). In particular, wastewater irrigation has historically contaminated farmlands in the middle of Liaoning Province, including Shenyang, Fushun, Jinzhou, Liaoyang, Anshan and Yingkou cities. Heavy metals had accumulated in soils in irrigation areas, a total area of approximately 28 000 ha (Chen *et al.* 1980). The area in which wastewater is used for irrigation has recently been reduced significantly. However, manure loading of Cu was almost 33 times as high in irrigation water as in the average Cu inputs found in irrigation water in China (Luo *et al*. 2009). The application of manure may also enhance the risk of Cu contamination in this area. For this study, we selected northeast China, including Liaoning, Jilin and Heilongjiang provinces, as a representative research area. Cu content of a range of farm manures was measured to determine average concentrations for each manure type. Moreover, we estimated the potential pollution risk from Cu resulting from animal manure application in the wastewater irrigation area, and we also estimated the quantitative role of adsorptive Cu losses into rivers through runoff.

2 Materials and methods

2.1 Sampling and analysis

In all, 224 poultry and livestock feeds and manures were sampled in Northeast China. The study included analysis of 104 feed samples and 120 manure samples. Detailed sampling information is given in Table 1. The fresh feed and manure samples were air-dried in the shade, then ground and passed through a 0.25-mm mesh PVC sieve. A 0.5-g subsample of the dry powder was weighed and digested in heated, concentrated HNO_3 and H_2O_2 (USEPA 1996). The Cu concentration in the filtered supernatant was determined by graphite furnace atomic absorption spectrometry (AAS, Vario6, JenaCo.Ltd., Germany).

The accuracy of the analysis was checked by using samples of wheat and soil with certified concentrations (GSS-1, GBW-08501, respectively, China National Center for Standard Materials). Recovery of Cu was 97.8% and 98.1% in GSS-1 and GBW-08501, respectively. A 15% parallel replication of samples was also used as a quality control procedure.

2.2 Data collection and preprocessing

Datasets based on 1:100 000, 1:250 000 and 1:1 000 000 digitized maps were acquired from the Data Center for Resources and Environmental Sciences, CAS. The land slope was determined using a digital elevation model (DEM) map. The town coverage was extracted from the digital land use/cover map. All data sets were preprocessed using ArcGIS 9.2 to create raster grids with a 50m×50m cell resolution. Data regarding animal production were obtained from the Statistical Yearbook of Liaoning, Jilin and Heilongjiang provinces and from investigations by our research group.

3 Results and discussion

3.1 Concentrations of Cu in the feeds and manures

All feed samples contained Cu in a wide range of Cu concentrations. This result indicated that Cu additives were applied widely in intensive animal production (Table 2). The mean concentrations of Cu were 179.8, 16.6 and 20.8 mg kg^{-1} in pig, chicken, and cattle feeds, respectively, with concentration ranges of 2.3–1137.1, 2.9–98.1 and 2.7–114.7 mg kg^{-1}, respectively. The mean concentration of Cu in pig feeds was 8–11 times that found in chicken and cattle feeds. The highest Cu concentration found was 1137.1 mg kg^{-1}. The pig, cattle and chicken feeds from animal farms in Jiangsu Province in China contained levels of Cu similar to those found in the feeds investigated by our research. However, Dong *et al*. (2008) found a much higher mean Cu concentration of 294.1 mg kg^{-1} in pig feeds from the pig farms of Hangzhou, a large city in the Yangtze River Delta. This result suggests that farmers tend to use more Cu additives to promote the growth of pigs.

Table 1 Sampling information for poultry and livestock feeds and manure samples.

Province	Feed samples			Manure samples		
	Pig	Chicken	Cattle	Pig	Chicken	Cattle
Jiling	13	18	21	10	14	18
Heilongjiang	8	8	21	7	8	9
Liaoning	15	9	17	17	9	12
Total	34	31	39	36	35	49

Table 2 Concentrations of Cu in animal feed and manure (mg kg^{-1} dm^{-1}).

Samples		Pig	Chicken	Cattle
Feed	Range	2.3–1137.1	2.9–98.1	2.7–114.7
	Median	113.8	10.6	11.5
	Mean±S.D.	179.8±261.1	16.6±19.1	20.8±24.2
Manure	Range	77.6-1521.2	1.5-487.4	10.3-112.9
	Median	639.3	51.8	29.5
	Mean±S.D.	642.1±383.6	65.6±78.6	31.1±16.2

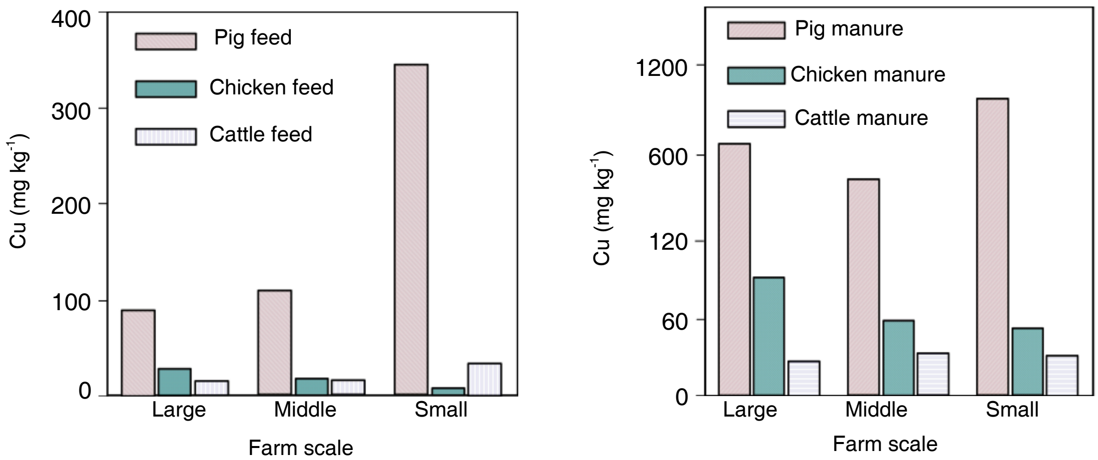

Fig. 1 Cu concentration in feeds and manures for three size scales of animal farms.

Indeed, previous research has shown that Cu additives are more effective in promoting the feed conversion rate and the growth of weaner pigs than that of grower-finishers and sows (Cang *et al*. 2004).

Like animal feeds, all animal manures contained Cu (Table 2). Average concentrations of Cu in pig, cattle, and chicken manure were 642.1, 65.6, and 31.1 mg kg^{-1}, with wide ranges of 77.6–1521.2, 1.5–487.4 and 10.3–112.9 mg kg^{-1}, respectively. An extremely high Cu concentration of 1521.2 mg kg^{-1} was detected in the pig manure. Likewise, 913 mg Cu kg^{-1} in pig manure was reported in other research in Jilin Province (Zhang *et al*. 2005). The wide range and wide dispersion of values found in the manure Cu dataset in this survey differ substantially from the results given in international reports such as Nicholson *et al*. (1999) in England and Wales and Sager (2007) in Austria. This comparison reveals a unique aspect of metal Cu concentrations in animal production in China. Nicholson *et al*. (1999) reported a range of Cu concentrations in pig slurry from less than 1.0 to 807.0 mg kg^{-1}, and Sager (2007) measured a range of manure Cu concentrations similar to that reported in the study of Nicholson *et al*. (1999).

In our study, the average Cu concentrations found in manures had the following rank order: pig manure>chicken manure>cattle manure. This result agrees with the results of a study of manure Cu in Beijing and Fuxin (Xiong *et al*. 2010). Our previous study indicated that Cu concentration in manure has a significantly positive relationship to that in animal feeds (Li *et al*. 2007). Therefore, the dietary strategy used in pig farming might result in more Cu in the manure. The limit of Cu content for animal manure land application should follow the GB18918-2002 standard (Cu<800 mg kg^{-1} dm^{-1}). According to this standard, Cu concentrations in all chicken and cattle manures were lower than the limit; however, 11 of 36 pig manure samples exceeded the limit in this study. Pig manure could pose a higher risk of Cu pollution on farmlands than chicken and cattle manures.

All farms investigated in this survey were classified into three groups according to animal population (Table 3). The feed and manure concentration of Cu for different sizes of farms is shown in Fig. 1. The Cu concentration of manures showed a good relation with animal feeds. For example, the small pig farms displayed the highest Cu concentrations in pig feeds, the Cu in manures showed the same tendency as those of feeds. Small farms are widely distributed in rural areas, where misuse of heavy metal additives in feeds may result from less supervision by the government and less professional knowledge. For these reasons, the small farms should receive more attention regarding the high levels of Cu in manures.

Table 3 Animal numbers in small, middle and large farms.

Farm scale	Animal population		
	pig	chicken	cattle
Small	<200	<2000	<100
Middle	200–800	2000–20000	100–300
Large	>800	>20000	>300

3.2 Potential Cu pollution risk in soil of wastewater irrigation areas

As an effective organic fertilizer, animal manure is widely applied to arable land in order to improve soil quality and crop productivity. In order to understand the potential risk of manure Cu in a worst-case situation (assuming that 30% of all animal manure will be evenly applied to farmlands in the wastewater irrigation area), the loading rates of Cu in wastewater irrigation area farmlands were estimated using Eq. (1)

$$L_t = \frac{B\sum_j N_{jt} P_j (1-F_j) C_j}{A_t} \qquad (1)$$

where L_t is the loading rate of Cu in city t (kg km^{-2}); C_j is the mean concentration of Cu in animal manure j (mg kg^{-1}); N_{jt} is the production of animal j in city t; P_j is animal j's excretive coefficient (Li *et al*. 2007); F_j is the moisture content of j's animal manure (pig manure, 85%; cattle manure, 75%; chicken manure, 52%); B is the proportion of animal manure applied to farmlands (30%); and A_t is the farmland area in city t (km^2).

Fig. 2 illustrates the Cu loading rates for animal manure use in the farmlands of wastewater irrigation areas. The total input of manure Cu to farmlands of six cities was 436.1 t, with Cu loading rate ranging from 12.3 to 35.4 kg km^{-2}. Specifically, the highest loading rates, ranging from 21.8 to 35.4 kg km^{-2}, were found in Xiaolinghe Area, located in Jinzhou city. The lowest loading rate was in Liuhao area of Liaoyang city. Compared with the results reported by Nicholson *et al*. (2003), the Cu loading rate in this study was lower than the corresponding value of 453.4 kg km^{-2} in England and Wales. However, long-term irrigation using wastewater in the irrigation area in six cities has produced high accumulations of heavy metals (Li *et al*. 2008). Based on the present load of wastewater, the time to increase topsoil concentrations from the present value to the maximum permissible limit (GB15618-1995, Cu<100 mg kg^{-1}) was estimated to 113 years (Jiang *et al*. 2004). The manure Cu loading rate was found to be 10%–30% of that for wastewater. In fact, Cu inputs will include other sources such as atmospheric deposition, sewage sludge and other inorganic fertilizers. However, the input of animal manure may be an important source in six cities in addition to wastewater.

3.3 The loss of manure-borne Cu to rivers

Liao River, located in Northeast China, has a higher pollution risk from heavy metals than other rivers in China. In particular, the extent of Cu pollution was found to be serious in the Liao River Estuary (Ma and Wang 2003). Zhang *et al*. (2008) have suggested that industrial and human population wastewaters are two main sources of heavy metal contamination. However, few reports have addressed non-point agricultural resources. Based on the principle of the universal soil loss equation (USLE), Yang *et al*. (2006) developed a new model to estimate the loss loads of absorbed nitrogen and phosphorus input to rivers over a large scale. In the present study, the loss of Cu in wastewater irrigation area farmlands was estimated using this model, as shown by Eqs. (2), Eqs. (3) and (4):

$$C_a = A \times Q_a \times \eta \times 10^{-3} \qquad (2)$$

$$\eta = \frac{B_t}{B_l} \qquad (3)$$

$$Q_a = \frac{L_t \times 10^6}{\delta \times h \times 10^7} \qquad (4)$$

where Ca is Cu loss in kg km^{-2}, A is the rate of water soil erosion (t km^{-2}), estimated according to the study of Yang *et al*. (2006); Qa is the load rate of manure Cu on farmlands of wastewater irrigation areas (mg kg^{-1}); η is the enrichment coefficient, 0.74; B_1 is the background concentration of Cu in soil of Liaoning Province, 19.8 mg kg^{-1} (China Environmental Monitoring Station 1990); B_t

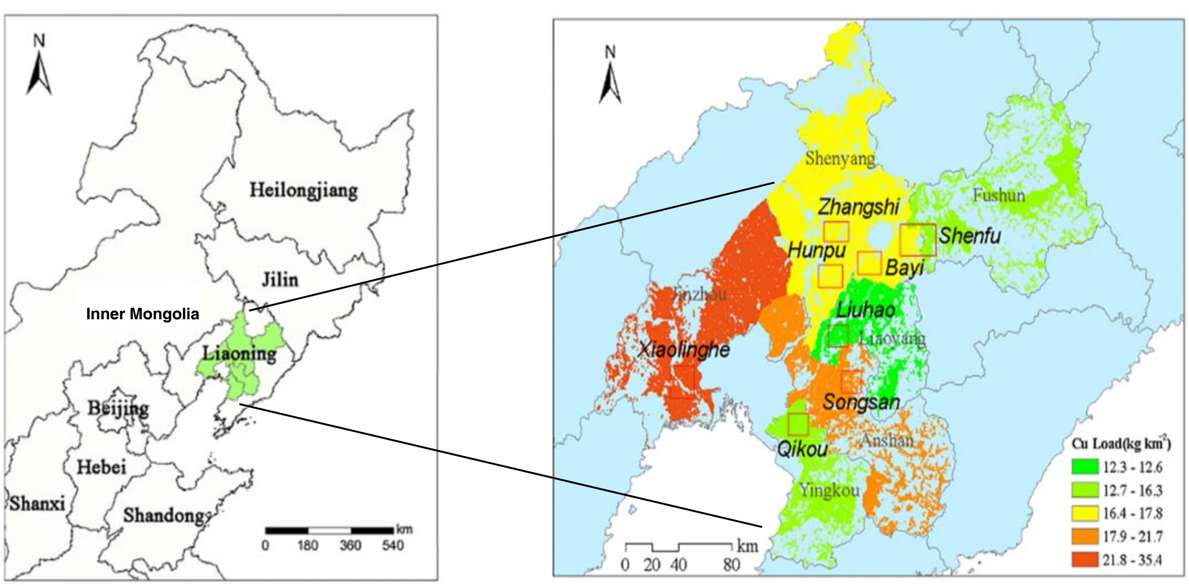

Fig. 2 Cu load of animal manures in the wastewater irrigation areas of Liaoning Province (Irrigation areas were marked by squares).

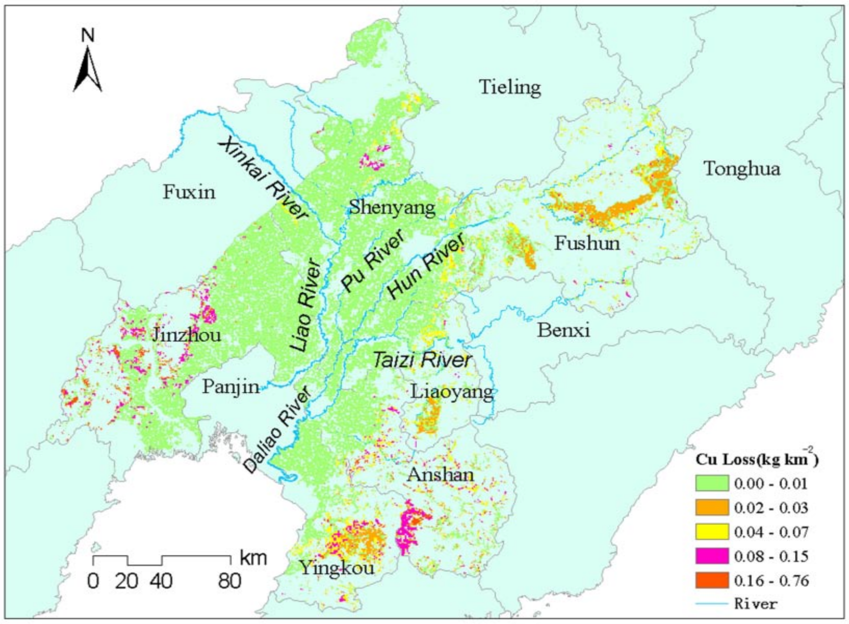

Fig. 3 The loss load of animal manure Cu in the wastewater irrigation areas of Liaoning Province.

is the background concentration of Cu in the sediment of Liao River, 14.6 mg kg^{-1} (Bao 1988). Calculations assume a soil density (δ) of 1.3 g cm^{-3} and a plough depth (h) of 20 cm.

The distribution of loss rates of manure-borne Cu in six cities is shown in Fig. 3. The amount of adsorbed Cu input to rivers in six cities was 226 kg y^{-1}. Shenyang city has the lowest Cu loss rate of the six cities, lower than 0.01 kg km^{-2}. Fushun and Yingkou have higher loss rates than Shengyang, with most values in a range of 0.02–0.07 kg km^{-2}. The highest loss rates were found in the south of Anshan and the west of Jinzhou. According to Zhang *et al*. (2008), Cu concentrations in the sediments of Hun River in Fushun city were higher than those in the Liao River. This result was in agreement with the distribution of loss rates of manure-borne Cu. Therefore, agricultural non-point-source pollution from Cu may be one of the important sources for the impairment of surface water.

4 Conclusions

The concentrations of Cu in animal manures clearly exhibited a wide range, from 1.5 to 1521.2 mg kg^{-1} dm^{-1}. The rank order of average Cu concentration in manures was pig manure>chicken manure>cattle manure. Pig manure could pose a higher risk of Cu pollution to farmlands than chicken and cattle manures. The Cu loading rates of six cities ranged from 12.3 to 35.4 kg km^{-2}. The highest Cu loading rate was found in Jinzhou city. The amount of adsorbed Cu input to rivers in six cities was 226 kg y^{-1}. Non-point contribution of manure Cu may be one of the important inputs affecting surface water.

References

Aldrich A P, D Kistler, L Sigg. 2002. Speciation of Cu and Zn in Drainage Water from Agricultural Soils. *Environmental Science and Technology*, 36: 4824–4830.

Bao Y E. 1988. Relationship between the sediments of Liao River estuary and backgroud of heavy metals. *Marine Environmental Science*, 7: 20–27. (in Chinese)

Cang L, Wang Y J, Zhou D M, Dong Y H. 2004. Heavy metals pollution in poultry and livestock feeds and manures under intensive farming in Jiangsu Province, China. *Journal of Environmental Science*, 16: 371–374.

Chen T, Wu Y Y, Zhang X X. 1980. The mend of Cd soils and prevention an ation in ripe in zhangshi irrigation area. *Environmental Science Sinica*, l: 7–11. (in Chinese)

China Environmental Monitoring Station. Background value of soil elements in China. Beijing: China Environmental Science Press, 1990.

Dong Z R, Cheng Y D, Lin X Y, Zhang Y S, Li D H. 2008. Investigation on the contents and fractionation of heavy metals in swine manures from intensive livestock farms in the suburb of Hangzhou. *Acta Agriculturae Zhejiangensis*, 20: 35–39. (in Chinese)

GB 15618-1995. Environmental quality standard for soils. State environmental protection administration of China.

GB 18918-2002. Discharge standard of pollutants for municipal wastewater treatment plant. State environmental protection administration of China.

Guo G L, Zhou Q X. 2004. Contaminative Trends of Heavy Metals in Phaiozem of Northeast China. *Journal of the Graduate School of the Chinese Academy of Sciences*, 21: 386–392. (in Chinese)

Jiang Y, Liang W J, Zhang Y G, Xu Y F. 2004. influence of wastewater irrigation on environmental capacity of soil heavy metals and rice growth. *Chinese Journal of Eco-Agriculture*, 12: 124–127. (in Chinese)

L'Herroux L, S Le Roux, P Appriou, J Martinez. 1997. Behaviour of metals following intensive pig slurry applicatons to a natural field treatment process in Brittany(France). *Environmental Pollution*, 97: 119–130.

Li M S, Tong L J. 2008. Specificity and ecological risk of heavy metal pollution in Liaoning sewage irrigation district. *Chinese Journal of Eco-Agriculture*, 16: 1517–1522. (in Chinese)

Li W, Li Y X, Zhang F S, Lin C Y, Xiong X, *et al*. 2007. The special and temporal distribution features of anmimal production in three northeast provinces and the impacts of manure nutrients on the local environment. *Journal of Agro-Environment Science*, 26: 2350–2357. (in Chinese)

Li Y X, Li W, Wu J, Xu L, Su Q H, Xiong X. 2007. Contribution of additive Cu to its accummlation in pig feces: study in Beijing and Fuxin of China.

Journal of Environmental Sciences, 19: 610–615.

Luo L, Ma Y B, Zhang S Z, Wei D P, Zhu Y G. 2009. An inventory of trace element inputs to agricultural soils in China. *Journal of Environmental Management*, 90: 2524–2530.

Ma D Y, Wang J Y. 2003. Evaluation on potential ecological risk of sediment pollution in main estuaries of China. *China Environmental Science*, 23: 521–525. (in Chinese)

Nicholson F A, S R Smith, B J Alloway, C Carlton-Smith, B J Chambersa. 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *The Science of the Total Environment*, 311: 205–219.

Nicholson F A, B J Chambers, J R Williams, R J Unwin. 1999. Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresource Technology*, 70: 23–31.

Römkens P F A M, A C C Plette, G G C Verstappen. 2002. Contribution of agriculture to the heavy metal loads of Dutch surface water. In: Steenvoorden J, F Iaessen (Eds.). Agricultural Effects on Groundand Surface Waters: Research at the Edge of Science and Society. *IAHS Publication*, 273: 337–342.

Sager M. 2007. Trace and nutrient elements in manure,dung and compost samples in Austria. *Soil Biology and Biochemistry*, 39: 1383–1390.

USEPA. 1996. Acid digestion of sediments, sludge and soils (Method 3050B).2nd. United States Environmental Protection Agency.

Wang F H, Ma W Q, Dou Z X, Ma L, Liu X L, *et al*. 2006. The estimation of the production amount of animal manure and its environmental effect in China. *China Environment Science*, 26: 614–617.

Xiong X, Li Y X, Li W, Lin C Y, Han W. 2010. Copper content in animal manures and potential risk of soil copper pollution with animal manure use in agriculture. *Resources, Conservation, and Recycling*, 54: 985–990.

Xue H, P H Nhat, R Gachter, P S Hooda. 2003. The transport of Cu and Zn from agricultural soils to surface water in a small catchment. *Advances in Environmental Research*, 8: 69–76.

Yang S T, Cheng H G, Bu Q S, Zhang J Y, Shi X X. 2006. Estimation of soil erosion and its application in assessmentof the absorbed nitrogen and phosphorus load in China. *Acta ScientiaeCircumstantia*, 26: 366–374. (in Chinese)

Yao L X, Li G L, Dang Z. 2006. Major chemical components of poultry and livestock manures under intensive breeding. *Chinese Journal of Applied Ecology*, 17: 1989–1992. (in Chinese)

Zhang J, Wang S Q, Xie Y, Wang X F, Shen X J, *et al*. 2008. Distribution and pollution character of heavy metals in the surface sediments of Liao River. *Environmental Science*, 29: 2413–2418.(in Chinese)

Zhang S Q, Zhang F D, Liu X M, Wang Y J, Zou S W, *et al*. 2005. Determination and analysis on main harmful composition in excrement of scae livestock and poultry feedlots. *Plant Nutrition and Fertilizer Science*, 11: 822–829. (in Chinese)

Zhou D M, Hao X Z, Wang Y J, Dong Y H, Cang L. 2005. Copper and Zn uptake by radish and pakchoi as affected by application of livestock and poultry manures. *Chemospher*, 59: 167–175.

东北畜禽粪便铜残留及潜在污染风险

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摘要：采集东北三省224个不同规模畜禽养殖场饲料和粪便样本，并测定其中铜含量，在此基础上估算了辽宁省主要污灌区农田畜禽粪便铜负荷以及畜禽粪便铜的流失量。研究结果显示，猪、鸡和牛饲料中铜含量分别为179.8、16.6和20.8 mg kg^{-1}。粪便样品中铜含量介于1.5−1521.2 mg kg^{-1}。猪粪中铜含量平均为642.1mg kg^{-1}，高于鸡粪(65.6 mg kg^{-1})和牛粪(31.1 mg kg^{-1})。污灌区农田畜禽粪便铜负荷介于12.3−35.4 kg km^{-2}，以小凌河污灌区负荷水平最高。污灌区畜禽粪便铜随土壤输入河流的流失量均低于0.76 kg km^{-2}，其中锦州市西部和鞍山市南部流失量较大。研究认为，东北三省畜禽粪便中铜残留浓度较高，长期农用将导致区域土壤和地表水体铜潜在污染风险增加。

关键词：畜禽粪便；铜；污灌区；农用