Chemosphere 210 (2018) 1029–1034

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Heavy metals accumulation in soil after 4 years of continuous land application of swine manure: A field-scale monitoring and modeling estimation

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## HIGHLIGHTS

- We performed field-scale monitoring on heavy metal accumulation after 4 years of continuous land application of swine manure.
- A dynamic mass balance model was employed to estimate heavy metal accumulation.
- Accumulation occurrence of As, Hg, Cr, Cu, Zn and Mn were observed in surface soil.
- Environmental risk of Cd, Cu and Zn in surface soil were simulated in the next 10–50 years.

## ARTICLE INFO

*Article history:*
Received 5 June 2018
Received in revised form
17 July 2018
Accepted 18 July 2018
Available online 19 July 2018

Handling Editor: Willie Peijnenburg

*Keywords:*
Heavy metals
Accumulation
Land application
Swine manure
Risk assessment

## ABSTRACT

Land application of animal manure has been encouraged widely in China. This presents a risk of heavy metals (HMs) accumulation in the soil due to their high contents in the feeds and additives. A 4-year field-scale study was conducted to monitor and estimate HMs accumulation in the soil with land application of swine manure. The results show a clear tendency for As, Hg, Cr, Cu, Zn and Mn to increase gradually with the application duration, yielding an average annual increase of 0.57, 0.011, 6.20, 5.64, 22.58, and 23.45 mg $kg^{-1}$, respectively, at the annual application rate of about 250 t $ha^{-1}$ of swine manure. The estimation from the mass balance modeling indicates the environmental risk of Cd, Cu and Zn will exceed the threshold levels for agricultural soils in China in the next 10–50 years. Determination of a suitable application rate of animal manure would be the first consideration for mitigating the environmental risk of HMs currently.

## 1. Introduction

The intensive animal production is increasing in China during the past decades and the numbers of pigs and cattle exceeded 0.68 billion and 0.10 billion in 2016 (NBSC, 2017). The resultant animal manure can be an economical source of plant nutrients and a valuable soil amendment to improve soil quality and maintain soil pH (Qian et al., 2018). Land application of animal manure at agronomic rates and based on environmental concerns is thought be a suitable practice in the guidelines of pollution control for animal manure treatment (Mallmann et al., 2012), and there were many studied focusing on the nutrient balance and pollutant loss after animal manure application (Penha et al., 2015; Fan et al., 2017). Since 2011, for the purpose of reducing nutrients loss and water pollution from animal husbandry, the emission reduction of major pollutants from intensive livestock and poultry breeding farms has been firstly brought into the plan, and the application of animal manure to agricultural land is encouraged in China nationwidely (Qian et al., 2012).

While addressing the pollution control and nutrients recycling for animal manure utilization through land application, the risk of HMs accumulation should also be considered since to the application of animal manure to farmland is regarded as an important

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https://doi.org/10.1016/j.chemosphere.2018.07.107
0045-6535/

source of HMs in China and other regions in the world (Wang et al., 2013; Alvarenga et al., 2015). Commercial feeds and additives are often enriched with essential elements such as Cu, Zn, Mn and As to achieve optimum growth rate and antimicrobial properties, while some feeds and additives may also contain other non-essential elements such as Cd, Pb, Cr due to their presence in concentrates and supplements, abrasion with iron cages or tools, or environmental pollution (McBride and Spiers, 2001; Sager, 2007; Moral et al., 2008). Previous studies have shown that application of animal manure or manure composts containing high levels of HMs can result in their excessive accumulation in soil, leading to adverse effects on soil quality (Hang et al., 2009; Paradelo et al., 2011; Wang et al., 2013). HMs are nondegradable during the aerobic composting or anaerobic digestion and persist in the final composts or residues (Lopes et al., 2011; Moller and Schultheiss, 2015).

Reduction in HMs inputs in agricultural soils is an important strategy aiming to protect farmland and ensure food safety in China. A recent nationwide survey showed that 19% of agricultural soils in China already exceeded the Chinese thresholds for agricultural soils according to the report released by the Ministry of Environmental Protection of China in 2014. The control for the feeds and additives of livestock and poultry has been included to the Action Plan for Soil Pollution Prevention and Control issued by the State Council of China in 2016. Furthermore, an assessment of the impacts of land application of animal manure on soil HMs content is needed to develop sound management practices and policies, and more detailed information on their assessment and estimation is demanded. Although some previous studies reported HMs content in the soil after animal manure application (Hang et al., 2009; Paradelo et al., 2011; Wang et al., 2013), little information is available regarding all the main HMs in the soil, and few studies have implemented a field-scale monitoring and then modeling prediction.

In the present study, a field-scale experiment was conducted to monitor the accumulation patterns of the main HMs (As, Hg, Cr, Cd, Pb, Cu, Zn and Mn) in the soil with land application of swine manure for 4 years. The purpose of this work was to estimate the incremental risk of these HMs by means of an accumulation and fate model based theoretical estimation.

## 2. Materials and methods

### 2.1. Site description

The field study was carried out from 2014 to 2017 on a swine farm in Shanghai suburbs, China, on a flood plain located in Yangtze River Estuary. The farm breeds about 10,000 pigs, surrounded by around 100 ha of paddy field with shallow tillage. The solid swine manure (SSM) was dry-cleaned and squeezed by solid-liquid separator to reach a moisture of 50–60%, then applied to the paddy field after at least 1 month's composting as basic fertilizer for rice and wheat, while the liquid swine manure (LSM, including the liquid part from solid-liquid separator) was applied to the paddy field after at least 3 weeks anaerobic digestion. The annual application amounts of SSM, LSM and chemical fertilizer (CF) were 30.50, 225, 0.30 t $ha^{-1}$, respectively, which could totally provide the nutrients of around 400 kg $ha^{-1}$ of nitrogen (N), 300 kg $ha^{-1}$ of phosphorus ($P_2O_5$) and 300 kg $ha^{-1}$ of potassium ($K_2O$). The SSM and CF was evenly spread to every plot manually, while the LSM was equally delivered to every plot through irrigation network consisted of main and branch channels all over the field. This area is within a subtropical monsoon climate zone and has a mean annual temperature of 17.1 °C and precipitation of 1123.7 mm. The land is flat (slope <5°) and intensively cultivated. The soil classification is grey alluvial soil and the soil texture is sandy in the paddy field. The starting pH, density and organic matter content of the topsoil (0–20 cm) were 7.43, 1.38 g $cm^{-3}$ and 1.10%.

### 2.2. Field-scale monitoring

Samples of composted SSM, digested LSM and compound CF (3 replicates) were taken before application. Samples of plough layer soils to the depth of 20 cm (5 replicates with mixed soil) and crops (5 replicates) were taken after crop harvesting to determine the concentrations of the HMs (As, Hg, Cr, Cd, Pb, Cu, Zn and Mn). As, Cr, Cd, Pb, Cu, Zn and Mn were quantified by inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer NexION 300X) after being digested with $HNO_3$-$HClO_4$, while As and Hg were determined by hydrogen atomic fluorescence spectroscopy (HG-AFS, AF630, Beijing Ruili, China) after being digested with $HNO_3$-$H_2SO_4$-$HClO_4$. Method blanks, duplicate samples and plant standard samples were added in the analytical process of each batch samples for quality assurance and control.

### 2.3. Modeling estimation

In order to predict HMs accumulation in the soil based on theoretical estimation, a dynamic mass balance model between input and output was employed (Moolenaar et al., 1997; Franco et al., 2006).

$$d(C_s)/dt = R_i - R_l - R_p \tag{1}$$

where $C_s$ is the concentration of HM in soil, $R_i$ is the input rate of HM, $R_l$ is the leaching rate of HM to groundwater, and $R_p$ is the uptake rate of HM by crops. The input rate of HMs to the agricultural soil surface includes: total atmospheric deposition, and applications of animal manure and chemical fertilizer.

Since the output rates (leaching and crop uptake) are dependent on the concentration of HM in the soil, the integrated expression of Eq. (1) after some transformations for compatibility of units (de Meeûs et al., 2002), yields:

$$C_s(t) = C_s(0)e^{-(R_l+R_p)t} + \frac{R_i\left(1 - e^{-(R_l+R_p)t}\right)}{(10\rho d_p)(R_l + R_p)} \tag{2}$$

where $C_s(0)$ is the initial concentration of HM in the soil (mg $kg^{-1}$), $C_s(t)$ is the forecast concentration of HM in the soil at $t$ years (mg $kg^{-1}$), $d_p$ is depth of the plough layer (m) and $\rho$ is the soil bulk density (kg $m^{-3}$). In Eq. (2), the units of the input rate $R_i$ are g $ha^{-1}$ $y^{-1}$, while the leaching rate $R_l$ and the crop uptake rate $R_p$ are in $y^{-1}$. As the changes in the balance generally require long time scales, intraseasonal variations in crops uptake, leaching to groundwater and composition of the soil plough-layer are reduced by averaging of many growing seasons (Moolenaar et al., 1997).

In this study, application of swine manure supplemented with chemical fertilizer was considered as the only input rate. Aerial deposition was considered negligible because neither industrial plants nor important roads were present in the vicinity of the farm. Therefore, $R_i$ is the product of the application rate of swine manure and chemical fertilizer ($R_a$) in t $ha^{-1}$ $y^{-1}$ by the HM concentration in swine manure and chemical fertilizer ($C_m$) in g $t^{-1}$.

The leaching behavior of HMs from soil plough layer mainly depends on the soil characteristics and the precipitation rate. The following equation describes the leaching rate of HMs (de Meeûs et al., 2002):

$$R_l = 1000F/(k_d \rho d_p) \tag{3}$$

where $F$ is the precipitation excess (m $y^{-1}$), calculated as the