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Occurrence of trace elements and antibiotics in manure-based fertilizers from the Zhejiang Province of China

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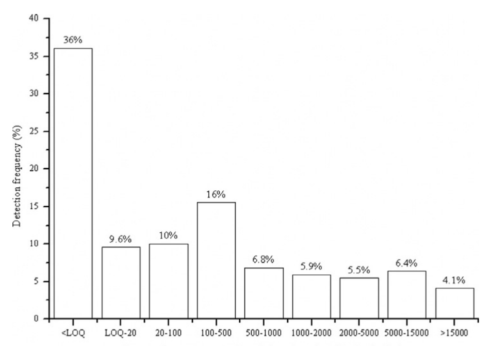
HIGHLIGHT

- Antibiotics and trace elements were investigated in manure-based fertilizers.
- 64% of manure-based fertilizers were positively detected with at least one drug.
- Enrofloxacin was the most frequently detected compound with detection ratio at 39%.
- 10% fertilizers might pose a high potential ecological risk after application on soil.

GRAPHICAL ABSTRACT



Occurrence of seven trace elements and forty three antibiotics was investigated in manure-based fertilizers in Zhejiang province of China. The trace elements included copper, zinc, arsenic, chromium, mercury, lead and cadmium; the targeted antibiotics included four groups: sulfonamides, tetracyclines, fluoroquinolones and chloramphenicols. The medium values of copper, zinc, arsenic, chromium, mercury, lead and cadmium in the analyzed samples were 160, 465, 7.9, 21.2, 0.3, 8.1 and 0.6 $mg \cdot kg^{-1}$, respectively. Seventeen antibiotics were detected. Enrofloxacin was the most frequently detected compound with the detection rate of 39.3% and the concentrations ranged from 6.7 $\mu g \cdot kg^{-1}$ to 4091 $\mu g \cdot kg^{-1}$. Based on the referred loading rates, 10% of the collected manure-based fertilizers might pose a high potential ecological risk after their application onto agriculture soil due to the presence of antibiotics.

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ABSTRACT

The occurrence of seven trace elements and forty three antibiotics was investigated in manure-based fertilizers from the Zhejiang province of China. These trace elements included copper, zinc, arsenic, chromium, mercury, lead and cadmium. The targeted antibiotics included four groups: sulfonamides, tetracyclines, fluoroquinolones and chloramphenicols. The median amounts of copper, zinc, arsenic, chromium, mercury, lead and cadmium in the analyzed samples were 160, 465, 7.9, 21.2, 0.3, 8.1 and 0.6 $mg \cdot kg^{-1}$, respectively. Seventeen antibiotics were detected. Enrofloxacin was the most frequently detected compound, with a detection rate of 39.3% and concentrations ranging from 6.7 $\mu g \cdot kg^{-1}$ to 4091 $\mu g \cdot kg^{-1}$. Based on the referred loading rates in agricultural soil, 10% of the collected manure-based fertilizer samples might pose a high potential ecological risk due to the presence of antibiotics.

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1. Introduction

Livestock and poultry manure has been used as land fertilizer, as it is rich in nitrogen, phosphorus and organic matter that can improve the physical and chemical properties of soil and provide nutrients essential to agriculture (Qureshi et al., 2008). For intensive cultivation of livestock and poultry in China, some feed additives, such as trace elements and veterinary antibiotics, have been used to promote growth, improve productivity or control animal diseases (Hou et al., 2015; Wu et al., 2013). Of the common trace elements in animal diets, approximately 90% of copper (Cu) is lost in the feces (Kornegay et al., 1976), and most of the antibiotics are expelled in the feces and urine (Zhao et al., 2010). Both trace elements and antibiotics have therefore become important sources of pollution as this manure has been continuously applied to agricultural land (Wang et al., 2013).

Recent results showed that the use of pig manure led to accumulation of cadmium (Cd) in both exchangeable and reducible soil fractions (Wu et al., 2012). The use of swine compost led to an increase in the total metal content of Cu and zinc (Zn) in agricultural land (Zhao et al., 2005). The accumulated trace elements in soil can affect soil fertility and product quality, and they may also migrate from agricultural soil to water resources during run-off or through leaching (Kumar et al., 2013; Li et al., 2007; Zhao et al., 2005). Therefore, the residues in animal manure and manure-based fertilizer should receive scientific attention due to their potential to transfer trace elements to biota in their environment.

In addition to trace elements, the occurrence of veterinary antibiotics in the environment and their potential risks to the environment and to human health has led to increasing concerns (Du and Liu, 2011). Though certain types of antibiotics in manure could partially decline during the composting process (Arikan et al., 2009), a considerable fraction of the antibiotics excreted by animals will eventually be found in farmlands via manure or manure-based fertilizer application. Significant levels of antibiotics have been detected in animal manure in China (Pan et al., 2011; Zhao et al., 2010). The persistence of antibiotic residues may contribute to the development of antibiotic-resistant bacteria in manure and agriculture soil (Holzel et al., 2010; Peng et al., 2015). Studies have indicated that antibiotics can be taken up by vegetables from soils supplemented with animal manures (Hu et al., 2010b), which may cause potential human health risks associated with consumption of the affected vegetables. The discharge of antibiotics and trace elements from animal production-linked ecosystems to the environment may cause a combined effect of selection and co-selection toward antibiotic-resistant bacteria (Seiler and Berendonk, 2012), and positive correlations between some antibiotic resistance genes and typical heavy metals have been described (Ji et al., 2012).

Manure and manure-based fertilizers have been widely applied, especially to the cultivation of vegetables, crops and fruits in China. Many studies have examined the levels of trace elements (Cang et al., 2004; Kilic et al., 2014; Wang et al., 2013; Zhang et al., 2012), antibiotics (Ho et al., 2014; Hu et al., 2010a; Hu et al., 2010b; Huang et al., 2013; Zhang et al., 2015; Zhao et al., 2010), and both trace elements and antibiotics (Karcı and Balcıoğlu, 2009) in manure samples. However, information on trace elements or antibiotic residues in particular manure-based fertilizers is still limited (Zhao et al., 2005; Zhang et al., 2015). Indeed, according to our survey in recent years, the numbers of fattening swine and poultry being raised in Zhejiang province were approximately 11 million and 300 million per year, respectively. And more than 80% of the manure from these animals will be manufactured into fertilizers prior to being applied to the crops, vegetables and other plants. Considering the risk of residues in organic fertilizers to an agricultural environment, this study was conducted (1) to provide a profile of the levels of seven trace metals (Cu, Zn, arsenic (As), chromium (Cr), mercury (Hg), lead (Pb) and Cd) and four substance classes of antibiotics in livestock and poultry manure-based fertilizer samples collected during 2013–2014 in the Zhejiang province; (2) to characterize the occurrence, abundance, and species variation of the trace elements and antibiotics in collected organic fertilizer samples; and (3) to evaluate the possible consequences of applying organic fertilizers containing these residues to the agricultural soil environment.

2. Materials and methods

2.1. Reagents and materials

The standards of sulfonamides (SAs), tetracyclines (TCs), fluoroquinolones (FQs) and chloramphenicols (CPs) (information on these compounds is shown in Table S1) and the corresponding isotopically labeled internal standards were purchased from Dr. Ehrenstorfer GmbH (Germany) or Witega (Germany). Chromatographic grade methanol was obtained from Merck (Germany). Purified water was prepared using a Milli-Q water purification system (Millipore, USA).

2.2. Sample collection

Dried manure-based fertilizer samples are commercially available in the Zhejiang province (China) and are commonly produced according to the following procedure: (1) raw manure is mixed with organic materials, such as sawdust or straw; (2) the mixture is thermophilically composted at 65–70 °C and with 60–65% initial moisture; and (3) the compost is granulated, freeze-dried, milled and sieved. Then, the compost is applied directly to a field. From February 2013 to January 2014, 219 manure-based fertilizer samples were collected. Based on the source of the fertilizer, 38 samples were classified as being from chicken manure, 38 from cattle manure, 116 from pig manure and 27 from a mixture of pig and cattle manure or chicken and cattle manure. All of the samples were collected from the most recently produced batches, and their storage time in the plant was no more than five days. Samples were sealed in a plastic container and stored at −20 °C prior to analysis. All samples were analyzed within a week of collection.

2.3. Extraction of antibiotics from samples

SAs and FQs residues in the manure-based fertilizer samples were extracted by the aqueous-organic solvent mixture and cleaned up by solid-phase extraction using an Oasis HLB cartridge (200 mg, 6 mL), which was developed from the previous description (Li et al., 2015). Briefly, a mixed internal standards and 1.0 g of sample were added to a 50 mL centrifuge tube along with 20 mL extraction solvent (acetonitrile:Na_2EDTA-McIlvaine (pH = 4.0) at a 3:7 (v/v) for SAs; acetonitrile:Na_2EDTA-McIlvaine (pH = 7.0) at a 1:1 (v/v) for FQs). After it was subjected to ultrasonication for 20 min and centrifuged at 7000 rpm for 5 min, the supernatant was collected. With two replicates for each sample, all of the supernatant was evaporated to dryness using a rotary evaporator in a water bath at 40 °C. After that, the residual solvent was diluted to 40 mL with water, and then 20 mL of which was loaded into an Oasis HLB cartridge preconditioned with 5 mL methanol and 5 mL water. The cartridge was further washed with 5 mL water (discarded) and eluted with 10 mL methanol (collected for analysis). Under the nitrogen gas at 40 °C, the eluate was completely evaporated. Then, the residue was dissolved in 1 mL methanol: water at a ratio of 1:1 (v/v). For extraction of TCs and CPs, samples were prepared according to the method described by Hou et al. (2015) and Zhou et al. (2012) with some modifications. To 1.0 g of sample, 0.4 g Na_2EDTA was added, and the antibiotics were extracted with 10 mL acetonitrile: phosphate buffer (pH = 3) at a ratio of 1:1 (v/v). Then it was subjected to ultrasonication for 20 min and centrifuged at 7000 rpm for 5 min, the supernatant was collected. The above procedure was repeated three times, and all three supernatants were combined. A solution containing 15 mL of supernatant was diluted to 150 mL with water and then acidified to $2.8 \le pH \le 3.0$ using phosphoric acid. The resulting solution was loaded into SAX-HLB cartridges which had been preconditioned with 6 mL