Heavy metal concentrations and arsenic speciation in animal manure composts in China

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ARTICLE INFO

ABSTRACT

A nationwide survey of animal manure-based composts was carried out in China. Two hundred and twelve samples were collected and analyzed for the concentrations of 9 heavy metals or metalloids and arsenic (As) speciation. The concentrations of heavy metals vary widely (Zn 11.8–3692, Cu 3.6–916, Cr 0.7–6603, Ni 0.7–73, Pb 0.05–189, As 0.4–72, Co 0.1–94, Cd 0.01–8.7 and Hg 0.01–1.9 mg kg^{-1} dry weight). Compared with the maximum permissible values of the Chinese standard for organic fertilizers, 13.7% and 2.4% of the composts exceeded the limits for As (15 mg kg^{-1}) and Cd (3 mg kg^{-1}), respectively. Some samples contained very high concentrations of Zn and Cu, although no limits have been set for these two metals in China. Further analysis showed that As was present mainly as arsenate (As^{V}), with dimethylarsenate (DMA) and monomethylarsenate (MMA) as the minor species in composts. There were significant correlations between the concentrations of Zn, Cu and As, suggesting co-contamination of these elements in some composts. Monte Carlo simulations based on the distributions of metal concentrations and application rate showed that repeated applications of compost likely increase the concentrations of Zn, Cu, Cd and Hg in soil significantly compared with the soil background levels. This study highlights a need to minimize the concentrations of Zn, Cu, Cd, Hg and As in animal manures to ensure their safe recycling to agricultural soils.

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1. Introduction

There are more than 100 million large livestock animals in China, producing approximately 250 million tons of manure annually (China EPD, 2010; China NBS, 2014). Intensive livestock production generates large amounts of manure that pose serious environmental problems, such as odor and eutrophication of freshwater. Composting is one of the best-known processes to solve these environmental problems by transforming manures into a safer and more stabilized material, which can be applied to agricultural land to recycle the valuable nutrients and improve soil physical properties (Bernal et al., 2009; Makan, 2015; Moral et al., 2009; Posmanik et al., 2013).

One of the main limiting factors in the use of manure compost is the concentrations of heavy metals (Alvarenga et al., 2015). It has been reported that the concentrations of some heavy metals or metalloids in manure have increased during the last few decades due to the additions of metals to animal feed in intensive animal production systems (Paradelo et al., 2011; Wang et al., 2013). Heavy metals are non-degradable during the composting process and persist in the final composts (Lopes et al., 2011; Moller and Schultheiss, 2015). Some studies have shown that applications of animal manures or manure composts containing high levels of heavy metals can result in excessive accumulation in soil, leading to adverse effects on soil quality (Hang et al., 2009; Zhejazkova and Warman, 2003). For instance, an 18-fold increase in the soil Cd concentration was observed when pig manure had been applied to soil for 17 years (Wu et al., 2012). Long-term (>160 years) applications of farmyard manures have increased soil Zn and Cu concentrations by approximately 60% in the Broadbalk classical experiment at Rothamsted, UK (Fan et al., 2008). Soil contamination by heavy metals is a critical issue in China. A recent nationwide survey showed that 19% of agricultural soils in China already exceed the Chinese environmental quality standards on heavy metals (China MEP, 2014). Moreover, the concentrations of heavy metals such as Cd in soil have increased considerably over the last 3 decades (Zhao et al., 2015). Therefore, there is an urgent need to monitor and minimize the inputs of heavy metals to agricultural soils.

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Composts produced in China are mainly animal manure based. However, little information is available on the ranges of heavy metal concentrations in commercial composts produced nation-wide (Guo et al., 2012; Luo et al., 2009). There are guidelines of compost quality standards in different countries, including maximum permissible limits of total concentrations of some potential toxic metals or metalloids. For As, it is also important to identify chemical species in composts, because different As species differ greatly in the chemical behavior and toxicity. Many As species have been reported in different environmental matrices, with inorganic As (arsenate As^V and arsenite As^{III}) and methylated As compounds (e.g. DMA and MMA) being commonly found in the environment (Huang et al., 2012; Liu et al., 2013). Although Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) as an animal feed additive has been banned in Europe and the USA (Huang et al., 2014), it is still in use to promote growth and treat coccidiosis in poultry, and to prevent gastrointestinal tract infections in China.

In this context, the objectives of the present study were: (1) to determine the concentrations of 9 heavy metals and metalloids (Zn, Cu, Cr, Ni, Pb, As, Cd, Co, and Hg) in manure composts collected in a nationwide survey in China; (2) to determine different As species in selected manure composts with high levels of As and fresh manures; and (3) to evaluate the potential risk of heavy metals and metalloids of manure composts in terms of heavy metal accumulation in soil.

2. Material and methods

2.1. Sample collection and pre-treatment

Samples were obtained from 212 composting factories in 10 provinces of China with dense population and high livestock densities (Fig. A.1). These factories collect animal manures, mainly cattle, swine and chicken manures from local livestock farms and produce composts in commercial operation. The composts produced are usually used as organic amendment of agricultural soils in the local areas. In the present study, mature composts were collected in October and November 2014. Five subsamples were collected from a single composting factory, mixed thoroughly into a 2.5 kg sample and transported to the laboratory. Compost samples were air-dried and ground to pass through a 100 mesh sieve and stored in labeled plastic bottles prior to analysis.

In addition, fresh cattle, swine and chicken manures were collected from the raw material pool of three commercial composting factories in Jiangsu province. Each sample was placed in a plastic container, chilled to near freezing, transported to the laboratory, and immediately lyophilized (Alpha4-LSC-16, Christ, German). The manure samples were grinded using an agate mortar and passed a 100 mesh sieve for determinations of heavy metal concentrations and As species. Manure samples were kept in −20 °C refrigerator to assure the stabilization of As species before extraction.

2.2. Reagents

The standard stock solutions of Zn, Cu, As, Cr, Cd, Ni, Pb, Hg and Co were purchased from Chinese National Standard Materials Center for measurement of nonferrous metals and electronic materials (Beijing, China). Mixed internal standard solution containing indium (for heavy metal total concentration analysis) and germanium (for arsenic species analysis) was obtained from Perkin Elmer (Waltham, USA). Roxarsone with a purity of 99% was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Analytical standards of sodium arsenite (As^{III}), sodium arsenate (As^V), sodium dimethylarsinic acid (DMA), and disodium monomethylarsonic acid (MMA) were obtained from the Xiya Chemical Reagent Ltd. (Chengdu, China) and J&K Chemical Ltd. (Shanghai, China). Optima grade methanol was purchased from Sigma-Aldrich Reagent Co., Ltd. (St. Louis, USA). All other reagents used in this study were of analytical reagent grade or better and were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ultrapure water (>18 MΩ cm^{-1}) was produced by a Millipore ultrapure water equipment with Milli-Q Synergy UV system (Bedford, USA).

2.3. Analysis of total heavy metal concentrations

All glassware and plastic-ware were soaked in a 5% (v/v) nitric acid solution for 24 h and rinsed with ultrapure water before use. All data were expressed on the dry weight (DW) basis. The total concentrations of 8 elements (total Zn, Cu, As, Cr, Cd, Ni, Pb and Co) in the compost samples (0.10 g) were determined by inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer NexION 300X) following digestion with HNO_3-$HClO_4$ (85/15, V/V). Indium supplied from Perkin Elmer (USA) was added to the samples as the internal standard. A certified reference soil material (GBW07428, obtained from the Institute of Geophysical and Geochemical Exploration, China) was included in the analysis. Blank samples, duplicate samples, and reference material were included in every batch of 20 samples for quality assurance. Repeated analysis of GBW07428 gave a recovery of 69.2–119% compared with the certified value (Zn 115 ± 5.4%, Cu 94.8 ± 1.5%, As 104 ± 1.1%, Cr 69.2 ± 3.2%, Cd 119 ± 4.9%, Ni 108 ± 2.9%, Pb 75.9 ± 0.9% and Co 98.5 ± 2.0%).

For the analysis of total Hg, 0.20 g sample was digested with HCl-HNO_3 (4/1, V/V) and diluted with ultrapure water. The concentration of Hg was measured with an atomic fluorescence spectrometer (Haiguang 230E, Beijing, China). Calibration solutions of Hg were prepared daily by appropriate dilution from the stock solution with 5% HCl (V/V) solution.

2.4. Analysis of arsenic species

Eleven compost samples which exceed the Chinese limit for As and 3 fresh manure samples (cattle, swine and chicken manure) were analyzed for arsenic species. Arsenic species were separated using a PRP – X100 anion exchange column (Hamilton, USA) in a Flexar high-performance liquid chromatography (HPLC, Perkin Elmer, USA). Concentrations of arsenic species were determined by a NexION 300X ICP-MS coupled to HPLC.

To extract As species, 0.20 g sample was weighed into a 10 mL plastic centrifuge tube, to which 5 mL 0.5 M H_3PO_4 was added. All tubes were shaken on a rotatory shaker for 16 h (200 r mim^{-1}, 25 ± 1 °C) and then centrifuged at 4000g for 10 min (Liu et al., 2013). The supernatant was filtered through a 0.22 μm membrane filter to obtain the final extracts. The mobile phase consisted of 50 mM $(NH_4)_2HPO_4$ (pH = 6.0) (A) and ultrapure water (B) using the following gradient elution program: 0–7 min: 0–20% A, 7–8 min: 20% A, 8–11 min: 20–0% A, 11–12 min: 0–100% A, 12–32 min: 100% A, 32–34 min: 100–0% A, 34–37 min: 0% A. The flow rate was 1.5 mL min^{-1} and the sample injection volume was 50 μL. Roxarsone, As^{III}, As^V, DMA and MMA could be efficiently separated by the method (Fig. A.2). Procedure blanks and duplicates of 15% samples were also included for analysis. Germanium was added to the post-column solution and measured by ICP-MS as the internal standard. There was a good agreement between the sum of As species (x) and the total As concentration (y) determined by ICP-MS following digestion with HNO_3-$HClO_4$ (y = 1.12 x + 1.52, r^2 = 0.93, n = 20, P < 0.001).