Environmental Engineering and Management Journal

July 2018, Vol.17, No. 7, 1563-1573 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



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CHANGES OF ARSENIC SPECIATION DURING SWINE MANURE WINDROW COMPOSTING AT FULL SCALE

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Abstract

Organoarsenic compounds are used extensively as swine feed-additives to promote animal growth and control diseases, e.g. roxarsone (4-hydroxy-3-nitrobenzenearsonic acid) and arsanilic acid (4-aminophenylarsonic acid) are usually overused in swine industry in China. As a cost-effective technology for animal manure treatment and reuse, composting is widely used for swine manure treatment. Therefore, the purpose of this study was to investigate changes of arsenic species and fractions during a full scale swine manure windrow composting. Results showed that four arsenic species, arsenite (As (III)), arsenate (As (V)), monomethylarsonate (MMA) and dimethylarsinate (DMA), were detected and varied differently which arsenate was on a slightly increasing trend and arsenite presented a decreasing trend throughout the composting process. The percentages of arsenite, arsenate and DMA were 24.10%, 29.68%, 4.87% of total arsenic in the beginning of the composting and 8.19%, 34.13%, 4.75% of total arsenic respectively at the end of the composting. Arsenate had the similar trend to Fe/Mn oxides arsenic fraction, which decreased dramatically in the first 10 days and then was on increasing trends during the rest of the composting. The percentages of Fe/Mn oxides, residual, carbonates, organic arsenic fractions were 55.3%, 25.9%, 18.6%, 0% in the beginning and 46.6%, 22.7%, 19.1%, 11.5% at the end of the composting process, and composting was a suitable method for detoxification of arsenic by changing their forms.

Key words: arsenic fraction, arsenic species, composting, swine manure

Received: March, 2014; Revised final: August, 2014; Accepted: September, 2014; Published in final edited form: July 2018

1. Introduction

In the last several decades, along with the rapid development of intensive livestock and poultry industry in China, a great amount of animal manure was produced, e.g., 243 million metric-tons in 2007 (The first national source census bulletin of China), and may pose environmental problems, such as odor, pollution of ground and surface waters due to leaching and run-off of organics and nutrients, and soil accumulation of heavy metals (Hsu and Lo, 2001; Yan

(4-hydroxy-3et al.. 2017). Roxarsone nitrophenylarsonic acid, C₆H₆NO₆As, 28.5% As) and arsanilic acid (*p*-aminophenylarsonic acid, C₆H₈NO₃As, 34.6% As) are aromatic organoarsenic compounds widely used as feed additives in the livestock and poultry industry for improving feed efficiency, promoting growth, and controlling diseases (Chapman and Johnson, 2002). Generally, roxarsone is incorporated in the feed at levels of 25-50 mg·kg⁻¹, and arsanilic acid is at 50-100 mg·kg⁻¹ (Sierra-Alvarez et al., 2010). Several studies reported that arsenic

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concentrations in pig feeds ranged from $0.02 \sim 13.03$ mg·kg⁻¹ (Zhang et al., 2012), and average contents of roxarsone and arsanilic acid were at 7.0 and 21.2 As mg·kg⁻¹, respectively (Yao et al., 2013). Additionally, arsenite (As(III)) and monomethylarsonate (MMA) were frequently detected due to arsenic impurities in feeds bearing organoarsenic (Yao et al., 2013).

As a low bioaccumulation potential, roxarsone and arsanilic acid are largely excreted unchanged in animal manure (Garbarino et al., 2003). For example, the distribution of arsenic species in fresh poultry litter was 91% roxarsone, 1.5% dimethylarsinate (DMA), 1.1% arsenate (As(V)), 0.8% arsenite (As(III)) and 5.6% of other unknown arsenic compounds (Garbarino et al., 2003). Based on broiler production and roxarsone feed dosage, it is estimated that approximately 900 metric tons of roxarsone are released into environment in the U.S. annually by the poultry industry alone, an amount that is equivalent to 250 metric tons of arsenic (Rutherford et al., 2003). Several literatures reported that livestock and poultry manure contained a great amount of arsenic, e.g. arsenic concentration in swine manure in different regions of China varied significantly from 0.004 mg·kg⁻¹ DW (dry weight) to 194.50 mg·kg⁻¹ DW (Dong et al., 2008; Li and Chen, 2005; Long et al., 2004; Zhang et al., 2012; Zhang et al., 2005). Additionally, other investigation demonstrated that the annual amount of arsenic input to the soil applied with swine manures as organic fertilizers was 340.60 $g \cdot hm^{-2}$, and the increasing concentrations of arsenic in a able soils was $0.15 \text{ mg} \cdot \text{kg}^{-1}$ (DW) annually (Dong et al., 2008). With long-term application of swine manure as organic fertilizers on agricultural lands, organic arsenic could be converted into its inorganic form, making it water-soluble and allowing it to seep into the surface and groundwater (Garbarino et al., 2003; Rutherford et al., 2003), which ultimately had a great influence on plants, soil organisms and human health (Carbonell-Barrachina et al., 1999).

As the bioavailability and toxicity of arsenic compounds vary dramatically, the investigation of degradation, transformation, migration, arsenic environmental impact and human health risk should be based on measurement of arsenic speciation as well as total arsenic concentration (Al-Assaf et al., 2009). Although the toxicity of organic arsenics, such as arsanilic acid and roxarsone, is relatively low, their degradation and transformation can happen and thus form the more toxic metabolites, such as arsenic acid, arsenous acid and monomethylarsonous acid during their exposure to environment (Garbarino et al., 2003). The toxicity of different arsenic species varies in the order as following: As (III) > As (V) >> MMA > DMA (Jain & Ali, 2000). Additionally, the bioavailability of arsenic associated with different fractions have dissimilar impacts on the environment and their phytotoxicity connects to some forms rather the total content (Hanc et al., 2011). The sequential chemical extraction of elements can provide an understanding of chemical fractions and a predicting mobility, bioavailability and leaching rate (Tessier et al., 1979). Hanc et al., (2011) demonstrated that bioavailability arsenic fractions, such as exchangeable arsenic, decreased during the kitchen waste composting, and the order of arsenic fractions in the final compost was as follows: residual > oxidizable > exchangeable > reducible. Although there were several researches related to arsenic species (such as arsenite, arsenate and so on) and arsenic fractions (exchangeable, carbonates and so on) during the composting, the relationship between them is not clear and needs further study.

Composting, one of the most suitable technologies for treating livestock manures can reduce the mass, degrade the organic matter, provide sufficient sanitation effect and produce valuable end products (Jiang et al., 2011). In general, the chemical speciation of As is particularly important in waste management (Carbonell-Barrachina et al., 2000). Garbarino et al., (2003) studied the degradation of roxarsone in a lab-scale composting experiment, which demonstrated that roxarsone degraded easily and could enter into the environment in other form of arsenic, such as arsenate. Arsenate is the thermodynamically stable form under aerobic conditions, of which one or two protons are dissociated at natural soil/sediment pH value, and arsenate is a chemical analogue of phosphate and may interfere with oxidative phosphorylation (Ter Welle and Slater, 1967). Additionally, arsenite is a neutral species at natural pH value and inhibits the activity of enzymes by binding to thiol groups. MMA and DMA also form anions in soil/sediment (Carbonell-Barrachina et al., 2000). Arsenic is subject to chemically and/or microbiologically mediated oxidation-reduction and methylation reactions in soils, sediments or other medium (Masscheleyn et al., 1991)

Once the residual arsenic in animal manure is released into the environment with land application of animal manure as fertilizer, arsenic may pose great threat potential to food safety and environment quality. There are growing interests about the arsenic residues accumulation in animal manure and the soil (Luo et al., 2009; Zeng et al., 2007; Zhang et al., 2012), however, little work has been done to investigate the different arsenic species and fractions changed in the process of full scale swine manure composting. The objective of this study was thus to investigate different arsenic species and fractions variation during the full scale swine manure windrow composting to provide support for arsenic pollution control in animal wastes treatment and disposal.

2. Material and methods

2.1. Full-scale swine manure composting

A full scale of swine manure composting was carried out from May 22 to July 16, 2011 in a windrow composting plant located in the suburb of Beijing (N 39°42', E 116°38'), to investigate degradation of organic arsenic compounds and its metabolic products. Raw materials for composting were mixed of swine manure and mushroom residues at the ratio of 2: 3 (v/v). Fresh swine manure and mushroom residues were sampled and stored at 4°C before composting for analysis. Parameters of all composting materials, including pH, moisture content, organic matter (OM), TC, TN, and TP, were determined according to the methods (Bao, 2000) and the results were shown in Table 1. The size of the windrow pile was about 75 m³, at the length of 85 m, the height of 0.9 m and the width of 2 m at the bottom of the pile. The full scale windrow composting was operated in the open air and turned by a turner (BACKHUS 15.30, Germany) once a week in the thermophilic stage, and then the pile was moved and stored in a simple shed in the mature stage in which there was no turning. During the composting process, water was added irregularly (almost once a week) to maintain stable moisture content of the composting materials. The pile temperature, including upper, central and lower part, was recorded daily. The composting materials was sampled by mixing the upper, central and lower sites of the pile on day 1, 3, 7, 10, 23, 38 and 53, respectively. All the samples collected were stored at 4°C before analysis.

 Table. 1. Characteristics of raw materials in the full scale swine manure windrow composting

Characteristics	Materials		
	Swine manure	Mushroom	Mixture
pН	7.69	7.64	7.39
Moisture (%)	72.15	46	47.28
OM ^a (%)	68.9	87.0	78.9
TC ^b (g/kg)	331.42	395.28	223.62
TN ^c (g/kg)	25.98	22.55	15.05
TP ^d (g/kg)	12.01	4.69	16.77
C:N ratio	12.75	17.53	14.86

a. OM: organic matter; b. TC: total carbon; c. TN: total nitrogen; d. TP: total phosphorus

2.2. Reagents and standards

Six high purity chemicals, including sodium arsenite (NaAsO₂ 99.8%, Fluka, Switzerland), sodium arsenate (Na₃AsO₄·7H₂O 98.5%, Fluka, Switzerland), methyl disodium arsenate (MMA, (CH₃)AsO₃Na₂·6H₂O 99.5%, Sigma-aldrich, USA), cacodylic acid (DMA, (CH₃)₂AsO(OH) 99.4%, Sigma-aldrich, USA), aminophenyl arsenic acid (4arsanilic acid, C₆H₄AsO(OH)₂NH₂ 99%, Dr. Ehrenstorfer Gambh, Germany) and 4-Hydroxy-3nitrobenzenearsonic acid (roxarsone, $C_6H_3AsO(OH)_2(OH)NO_2$ 97.5%, Dr. Ehrenstorfer Gambh, Germany) were purchased and used as standard substances for determining 6 arsenic species (arsenate, arsenite, DMA, MMA, roxarsone and arsanilic acid) in this study. All of the following chemicals, including phosphoric acid (H₃PO₄), sodium hydroxide (NaOH) used as arsenic species extraction buffers, ammonium hydroxide (NH₄OH), ammonium dihydrogen phosphate (NH₄H₂PO₄),

ammonium nitrate (NH₄NO₃) used as mobile phases of liquid chromatogram, magnesium chloride (MgCl₂), sodium acetate (NaOAc), acetic acid (HOAc), nitric acid (HNO₃), hydrogen peroxide (H₂O₂), perchloric acid (HCIO₄), hydrofluoric acid (HF), hydroxylamine hydrochloride (NH₂OH·HCl) used as arsenic fraction extraction buffers were of analytical pure grade and purchased from Sinopharm Chemical Reagent Co. Ltd., China. All solutions were prepared in ultra-pure water from a Millipore Milli-Q system (Millipore, USA).

Phosphoric acid and ammonium hydroxide were used for pH adjustment. Phosphate buffer solution (PBS) was prepared from ammonium dihydrogen phosphate and phosphoric acid. The daily working standards for arsenic species were made from standard stock solutions (1000 mg·L⁻¹) prepared from the six arsenic chemicals dissolved in ultra-pure water. All these stock solutions of these 6 standards above were kept in the dark at 4 °C.

All mobile phases, standards and samples were filtered through 0.45 μm polyethersulfone membrane filters prior to analysis.

2.3. Analytical procedures

To determine different arsenic species, all of composting samples stored at -20 °C were firstly freeze-dried (ALPHA1-2LD PLUS, Christ, Germany) and then sieved by nylon screen with mesh size of 100, and finally analyzed by using an improved method described by Al-Assaf et al. (2009) and Garbarino et al. (2006). Each sample at 1.0 g was extracted with 5 mL 0.10 mol·L⁻¹ phosphoric acid solution (H_3PO_4) and 5 mL 0.10 mol·L⁻¹ sodium hydroxide solution (NaOH) followed by shaking for 24 hours, centrifugation at 7000 r·min⁻¹ for 10 min and filtration with 0.45µm filter. The extraction solution of arsenic was used for speciation analysis by high-performance liquid chromatography (HPLC) to inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700x, Agilent Technologies, Japan).

To determine the total arsenic concentrations of compost materials, 1.0 g sample was digested with 5mL HNO₃ (69%) and 5mL HClO₄ for 24 hours and filtered through 0.45 μ m polyether sulfone membrane filters for ICP-MS analysis.

In order to determine the extraction efficiency of the method mentioned above, samples were spiked with the standard mixture solutions of arsenite, arsenate, DMA, MMA, roxarsone and arsanilic acid at three levels: 0.01 mg·kg⁻¹ DW, 0.1mg·kg⁻¹ DW and $5.0 \text{ mg} \cdot \text{kg}^{-1}$ DW, respectively. Samples were extracted and analyzed, and the results showed that recoveries of all target compounds varied from $89\% \pm 3.27\%$ to $93.25\% \pm 2.38\%$, which suggested that it is an efficient procedure for extracting arsenic species from compost materials.

For better understanding the phytotoxicity, bioavailability and mobility of arsenic, five different arsenic fractions were analyzed during the swine manure windrow composting. The sequential chemical extraction of arsenic was applied according to Tessier et al. (1979) for the assessment of different arsenic fractions including exchangeable (1M MgCl₂, pH=7), bound to carbonates (1M NaOAc, pH=5), bound to Fe/Mn oxides (0.04 M NH₂OH·HCl in 25% (v/v) HOAc), bound to organic matter (0.02 M HNO₃ + 30% H₂O₂, pH=2), residual (digested with HF-HClO₄) in the swine manure windrow composting samples. All of the arsenic extraction solutions were stored at 4 °C and arsenic concentrations were determined by ICP-MS (Agilent 7700x, Agilent Technologies, Japan).

2.4. Instrumentation

The arsenic speciation analysis was determined by a coupling of HPLC with ICP-MS. In order to meet the separation object, an ion exchange columns $(4.6\times250 \text{ mm})$ manufactured by Agilent was selected and isocratic elution using 10 mmol·L⁻¹ ammonium dihydrogen phosphate (pH=6.2) and 10 mmol·L⁻¹ ammonium nitrate as mobile phase was applied. The mobile phase was set at a flow rate of 1.0 mL·min⁻¹ and the injection volume was 20 µL.

The ICP-MS has been used to determine elements in natural-water, biota, sediment, soil samples and other mediums since the early 1990s (Garbarino et al., 2003). In this study, samples were analyzed using an Agilent 7700x (Agilent Technologies, Japan) at ambient temperature. The Agilent 7700x is fitted with quartz, low-volume, peltier-cooled, scott-type double-pass spray chamber and a concentric MicroMist (borosilicate glass) nebulizer.

The ICP-MS was tuned daily using a 1 μ g·L⁻¹ tuning solution containing 7Li, 89Y, 205Tl (Agilent Technologies, Japan). The ICP-MS was used to quantify the arsenic species at m/z 75. A helium gas

collision cell was utilized for the removal of polyatomic interferences of ⁴⁰Ar³⁵Cl⁺, which usually affect the determination of ⁷⁵As when using ICP-MS. The method separated the arsenic species within 13 min and the limits of detection for different arsenic species ranged from 0.1 to 0.2 μ g·L⁻¹.

3. Results and discussion

3.1. Pile temperature

During 53 days composting, including 23 days of the thermophilic stage and 30 days of the mature stage, the pile temperature increased to approximately 55°C rapidly in the first 10 days (Fig. 1), and then sustained above 55 °C for more than 7 days, which met with the requirements of sanitary standard for the nonhazardous treatment of night soil in China (GB-7959-87). Generally, the pile temperature in the central layer was much higher than those in the bottom and the top. The pile temperature increased successively up to over 60 °C in the thermophilic stage then kept increasing to 70 °C in the mature stage and decreased slightly but still around 60 °C at the end of the composting.

The pile temperature is an important factor of affecting composting performance due to its influence on the activity and diversity of microorganisms (Finstein et al., 1986). In general, high pile temperatures are consequences of biological activity and have been considered a necessary condition for good composting (de Bertoldi et al., 1983). In the beginning of composting, mesophilic microorganisms are initially present, and their activity raises the pile temperature (Poincelot, 1975). As the pile temperature kept climbing, thermophilic microorganisms predominated gradually during the thermophilic stage and parts of organic matter were decomposed in this process.



Fig. 1. Changes of pile temperature during the full scale swine manure windrow composting

In the mature stage, the pile temperature decreased, and mesophilic microorganisms kept decomposing complex organic matter and the composting was in an anaerobic condition because of no turning (Miyatake and Iwabuchi, 2006). In this study, due to low turning frequency of composting pile and high ambient temperature in summer, the pile temperature kept increasing and sustained highly during the thermophilic stage and the mature stage which was up to 70°C. However, high pile temperatures in fact inhibit growth of the majority of microorganisms, thus slow down decomposition of organic matter. Only a few species of thermophilic sporigenous bacteria show a metabolic activity above 70°C (de Bertoldi et al., 1983).

3.2. pH value, moisture content and organic matter

The pH values went up from 5.3 to 8.1, increasing by more than two pH units during the composting process (Fig. 2). This is attributed to ammonia nitrogen generation from the organic matter degradation. During the first 7 days, the pH values fluctuated a little, e.g., it rose in the first 3 days and then fell rapidly on the 7th day. This was a consequence of the activity of acid-forming bacteria which break down complex carbonaceous material into organic acid intermediates (de Bertoldi et al., 1983) in the early stage of swine manure windrow composting. Organic matter and moisture contents decreased 7.8% and 23.3%, respectively, as shown in Fig. 2. In the process of composting, complex physical, chemical, and biological reactions occurred, i.e., organic matter was degraded while metals and metalloids, such as arsenic, could potentially be transferred to other forms (Pinel-Raffaitin et al., 2007).

3.3. Arsenic species and fractions

To determine changes of arsenic species during the swine manure windrow composting, 6 forms of arsenic compounds were investigated, including arsenite, arsenate, MMA, DMA, arsanilic acid and roxarsone. The results showed that neither arsanilic acid nor roxarsone was detected in the composting process, which demonstrated that these organoarsenic compounds were degraded before the swine manure composting in accordance with results of Garbarino et al., (2003). Garbarino et al., (2003) studied that the rate of roxarsone degradation increased with the temperature. When the temperature was up to 40 °C, 60% of roxarsone had degraded within 40 hours. In the present study, raw material of composting was stored in the open air for a few days before composting and the pile temperature was up to 40 °C. Therefore, roxarsone and arsanilic acid had already degraded before composting. The secondary metabolite was arsenite that decreased from 24% (on the first day) to 8% (on the 53th day) of total arsenic. The organic arsenic forms, including MMA and DMA, fluctuated a little but maintained a stable low level at approximately 5% of total arsenic. Furthermore, unidentified arsenic compounds accounted for approximately 27% to 60% in this process and need further study in the future.

As shown in Fig. 3a, the main arsenic metabolite was arsenate that varied drastically from about 30% to 60% of total arsenic throughout the full scale swine manure windrow composting.



Fig. 2. Changes of moisture content, organic matter and pH value during the full scale swine manure windrow composting

As shown in Fig. 3b, arsenate concentration declined roughly from about 400 $\mu g \cdot k g^{-1}$ to almost below the limit of detection during the first 7 days, however, it went up dramatically to 727 μ g·kg⁻¹ from the 7th day to the 10th day and then increased slowly until the 40th day and finally dropped a little at the end of the swine manure windrow composting. It was interesting that the variation of arsenite was totally opposite to that of arsenate, in other words, concentration of arsenite went up when that of arsenate went down obviously, vice versa. These results showed that concentrations of arsenite reached to the maximum (437 μ g·kg⁻¹) on the 7th day of the swine manure windrow composting, while concentration of arsenate dropped down to the minimum (below the limit of detection).

Composting is an aerobic process which uses naturally occurring microorganisms to convert biodegradable organic matter into a humus-like product (Georgacakis et al., 1996). Arsenic species variation depended on many factors, including temperature, pH value, moisture content, redox potential and microorganism activity.

Additionally, the dominant form of arsenic in oxygenated situation is arsenate (Byrd, 1990; Neff, 1997). This might explain why arsenate was the primary arsenic species in the full scale swine manure windrow composting process (Fig. 3a.).



Fig. 3. Changes of different arsenic species during the full-scale swine manure windrow composting: (a) Percentage, (b) Concentration

Moreover, the other inorganic arsenic form, arsenite, appeared in all of the compost samples. With alteration of some composting factors, including temperature, pH value and moisture content, both inorganic arsenic forms, arsenate and arsenite, transformed mutually in the composting process (Fig. 3b.). Garbarino studied that the moisture content and the temperature influenced the rate of arsenic transformation (Garbarino et al., 2003). In this study, the full scale windrow composting was operated in the open air and turned once a week during the thermophilic stage. Pile turning increased the air flow which could bring more oxygen through the pile and its porosity. Jiang et al. reported that the pile temperature risings were observed after turning and these risings were caused by the degradation of partially decomposed materials which were transferred from the anaerobic areas to the aerobic areas (Jiang et al., 2011).

In this study, the first turning happened on the first day and the second turning happened on the 8th day. Therefore, oxygen content might be deficiency due to the activity of a great amount of aerobic microorganisms and decomposition of organic matter in the end of the first week, the pile might probably be under anaerobic or anoxic condition. Additionally, relatively high moisture content (approximately 50%) in the beginning of composting might impede oxygen internal diffusion, causing partial anaerobic condition. The presence of microorganisms in the composting pile combined to anaerobic condition might enhance transformation of arsenic from As (V) to As (III). These might well explain that the oxidation state arsenic (arsenate) decreased to a low level and reduction state arsenic (arsenite) increased up to a relatively high level on the 7th day of composting (Fig. 3b). The mobility of five different arsenic fractions changed in the order as following: exchangeable > carbonates > Fe/Mn oxides > organic > residual. The exchangeable fraction was the most toxic and highly mobility arsenic form. However, the surprising result

of this study was that the exchangeable fraction of arsenic kept in a really low level ($0 \sim 84.9 \ \mu g \cdot kg^{-1} DW$) during the composting (Fig. 4). The carbonates fraction of arsenic varied from 18.6% to 45.3%, and its average value was 30% in the composting process. The mobility and bioavailability of Fe/Mn oxides fraction of arsenic highly depended on Eh and pH values, and changed dramatically during the swine manure windrow composting process.

The organic and residual fractions of arsenic were relatively low mobility arsenic forms which accounted averagely for approximately 10% and 29% respectively during the whole composting process. Their concentrations at the end of composting were not much difference (arsenate at 576.53 μ g·kg⁻¹DW and arsenic bound to Fe/Mn oxides at 637.46 µg·kg⁻ ¹DW). In general, arsenic presenting as arsenate under oxic conditions is often adsorbed into organic matter, iron and manganese oxides and oxyhydroxides (Newton et al., 2006). According to this conclusion, arsenic bound to Fe/Mn oxides to some extent ought to be a part of arsenate during most of the time of composting in this study. Furthermore, because arsenate was the main species and arsenic bound to Fe/Mn oxides was the main fraction, it seemed they were linked. The low frequency of pile turning in the thermophilic stage and a relatively low pH value (around 5.0) at the start of composting might explain both of arsenate and arsenic bound to Fe/Mn oxides decreasing roughly in the first 10 days. As shown in Fig. 5, it is interestingly found that variation of arsenate had the similar trend to arsenic bound to Fe/Mn oxides in the first 10 days of composting. In the environment, As (V) and As (III) are the dominant forms of inorganic arsenic, which As (III) is much more toxic than As (V) (Jain and Ali, 2000). In this study, the variation of the ratio of As (V) to As (III) reflected their mutual transformation to some extent. The point on the 7th day was extremely low and might be due to low frequency pile turning in the first week of composting.



Fig. 4. Changes of five arsenic fractions during the full scale swine manure windrow composting process: (a) Percentage, (b) Concentration

In this study, it seemed that the influence of the pile turning on the ratio of As (V) to As (III) was obvious. It was thrilling to notice that the ratio of As (V) to As (III) kept increasing along with the composting, which indicated that the proportion of the more toxic As (III) decreased. In the thermophilic stage, the pile was turned thoroughly once a week and the composting was almost under aerobic condition.

This might be the main reason that the ratio of As (V) to As (III) kept increasing in the first 38 days. Nevertheless, there was no pile turning in the mature stage and the composting was almost under partial anaerobic condition, which might result in the ratio of As (V) to As (III) dropping dramatically in the last several days. Therefore, one pile turning should be added in the mature stage to better control the proportion of As (III) for improving detoxification on arsenic. Moreover, some reports indicated that under near-neutral conditions (pH=6.5) and different Eh conditions (Eh=450, 325, 100 and 0mV), the major inorganic arsenic species was always arsenate (Carbonell-Barrachina et al., 2000).

There were some reports on the variation of the ratio of As (V) to As (III) in other medium, like the ocean, coastal waters and estuary (Neff, 1997), however, little works have been done about the ratio of As (V) to As (III) during the composting process. For example, in open ocean seawater, the ratio of As (V) to As (III) may exceed 300 (Li, 1991), and coastal water was influenced by freshwater runoff and high primary production, the ratio may be much lower (Andreae and Andreae, 1989). Different from ocean, coastal waters and estuary, high level activity of microorganisms in the composting process might contribute a lot to the variation of aerobic/anaerobic condition, temperature, pH value and so on, therefore

the actual true reason about the ratio of As (V) to As (III) variation in the composting process needs further studies. Compared with As (III) and As (V), the concentrations of organic arsenics such as MMA and DMA were relatively lower, in the range of 0~150 µg·kg⁻¹ DW. Methylation theoretically will not occur abiotically even if there is a supply of Carbon source, such as protein and other organic compounds because the C-C, C-N and C-O bonds are more stable than C-As bonds (Williams, 1988). Biomethylation of metals and metalloids occurs extensively in the environment and methylated compounds show different properties in mobility, bioavailability and toxicity in comparison to their inorganic precursors (Sigel, 2010). Fig. 6 showed that the ratio of As (V) to As (III) kept increasing in the first 38 days and then decreased in the last several days of the composting.

It is interesting to point out that the ratio of As (V) to As (III) in this study achieved maximum value at pH of about 6.5, and stayed at a very low level at pH of around 5.5 (Fig. 7). The process of biomethylation was regarded as a detoxification process for many years; however, more recent research has indicated that the reverse is in fact the case (Sigel, 2010). Fig. 3b showed that the tendency of DMA was similar to that of arsenate, which both declined in the beginning and then climbed smoothly until the 40th day and decreased a little in the last days of the composting. The level of MMA was always the lowest, even lower than the limit of detection in the full-scale swine manure windrow composting process.

The methylated arsenic accounted for 1% to 9% of total arsenic in the composting process. Recently, Diaz-Bone et al. (2010) indicated that metalloids, such as arsenic, could undergo intensive biomethylation during composting.



Fig. 5. Correlation between arsenate and Fe/Mn oxides arsenic concentrations during the full scale swine manure windrow composting process



Fig. 6. The ratio of As (V) to As (III) variation with time during the full scale swine manure windrow composting process



Fig. 7. The relationship between pH value and the ratio of As (V) to As (III) during the full scale swine manure windrow composting process

Extraordinary high concentrations of up to 150 mg·kg⁻¹ methylated arsenic species as well as conversion rates up to 50% were observed. In this study, the percentages of methylated arsenic were not so high because of a relatively low level of total arsenic in the compost materials. The other reason might be that DMA and MMA were only a small part of methylated arsenic species and other forms of methylated arsenic species were not detected in this study. The total arsenic concentrations kept relatively

stable and showed a slightly increasing trend from 1.35 mg·kg⁻¹ DW to 1.69 mg·kg⁻¹ DW (Fig. 3b) due to the decomposition of organic matter and the reduction of bio-mass during the swine manure windrow composting process. The primary arsenic species was As (V), increasing from 29.6% of total arsenic on the first day to 34.1% of total arsenic on the 53th day. A very promising result was that the most toxic arsenic species, arsenite, reduced a lot from 24.1% to 8.1% of total arsenic (Fig. 3a). Additionally, organic arsenic

(MMA and DMA) accounted for 4.7% at the end of composting.

4. Conclusions

During 53 days composting, arsenite decreased from 325.71 to 138.35 μ g·kg⁻¹ DW and arsenate increased from 401.19 to 576.53 μ g·kg⁻¹ DW. The percentages of arsenite, arsenate and DMA were 24.10%, 29.68%, 4.87% of total arsenic in the beginning and 8.19%, 34.13%, 4.75% of total arsenic respectively at the end of the composting. Arsenate had the similar trend to Fe/Mn oxides arsenic fraction.

During this composting process, the most toxic arsenic, arsenite, decreased about 16%. It was proven that composting was a suitable method for detoxification of arsenic by changing their forms.

Acknowledgements

This work is financially supported by Special Fund for Agro-scientific Research in the Public Interest (No. 201303091), the National Natural Science Foundation of China (No. 50578156 and No.21077122) and the National Key Technology R&D Program (2012BAC25B00).

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