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# Effects of combined composting and vermicomposting of waste sludge on arsenic fate and bioavailability

Blanka Maňáková, Jan Kuta, Markéta Svobodová, Jakub Hofman*

*Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kamenice 753/5, CZ-62500, Czech Republic*

## HIGHLIGHTS

- Industrial sludge with high As content was treated by composting and vermicomposting.
- The volume of compost decreased, which led to an increase in total As content.
- The labile arsenic fraction was significantly decreased.
- $As^V$ was the predominant arsenic species formed.
- The mobile fraction was not directly related to bioavailability to earthworms.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Composting and vermicomposting are traditional processes for the treatment of sludge. During these processes, the humification of organic matter has a significant effect on the physicochemical form and distribution of heavy metals. In this study, industrial sludge (groundwater treatment waste) contaminated by arsenic ($396 \pm 1\ mg\ kg^{-1}$) was used. Such sludge poses a significant challenge with respect to effective treatment. Composting, vermicomposting (with *Eisenia fetida*), and the combined approach of composting and vermicomposting were performed to determine the evolution of arsenic speciation, mobility and bioavailability. The composting/vermicomposting was done with sludge, horse manure, and grass in the ratios of 3:6:1. A solution of 0.1 M $NH_4COOCH_3$ was used as a single extraction solvent for determination of the mobile arsenic pool and targeted arsenic species ($As^{III}$, $As^V$, monomethylarsenic acid – $MMA^V$, dimethylarsenic acid – $DMA^V$). The analysis of arsenic in the extracts was carried out by means of HPLC–ICP-MS spectrometry. In addition, the earthworm species *E. fetida* was used for bioaccumulation tests that followed the compost and vermicompost processes. The obtained results indicate a reduction in arsenic mobility and bioavailability in all matured composts and vermicomposts. The combined process exhibited a greater effect than compost or vermicompost alone.



## 1. Introduction

The overproduction of anthropogenic waste sludge has led to the use of inappropriate disposal practices and caused the introduction of metals into the environment. Nowadays, composting and vermicomposting are two of the best-known processes for the biological stabilization of sludge [1]. During these processes, heavy metals are redistributed to a newly formed matrix and the level of metal contamination generally grows [2–4]. From another point of view, the role of composting could be considered as an important environmental sink for the elimination of metals.

Arsenic bioavailability and toxicity is strongly dependent on arsenic species. The mobility of sludge-born arsenic entering into composting/vermicomposting processes is strongly related to

* Corresponding author. Tel.: +420 549 494 267; fax: +420 549 492 840.
*E-mail address:* hofman@recetox.muni.cz (J. Hofman).

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**Table 1**
Selected properties of sludge used in the study.

| As (mg kg$^{-1}$) | $As^{III}$ (mg kg$^{-1}$) | DMA (mg kg$^{-1}$) | MMA (mg kg$^{-1}$) | $As^{V}$ (mg kg$^{-1}$) |
|---|---|---|---|---|
| 396 ± 1 | <0.004 | <0.003 | <0.003 | 1.26 ± 0.04 |
| pH | TC (%) | TOC (%) | TIC (%) | Dry mass (%) |
| 8.5 | 1.03 ± 0.01 | 0.23 ± 0.03 | 0.80 ± 0.03 | 63 ± 1 |

redox processes, microbial activity, and the degradation of organic matter [5]. Arsenic interaction with organic matter may include redox reaction, complexation, colloid formation, and sorption competition; however, the direct chemical effect of organic matter on the redox speciation of arsenic has not yet been proven. Beside $As^{III}$ oxidation and various methylation reactions [6], microbial processes are a potential cause of high variability in $As^{V}$ reduction, during which microorganisms use $As^{V}$ as an electron acceptor and mediate transformation to the more toxic and mobile $As^{III}$ species [7]; however, chemical reactions may also contribute to this process. $As^{V}$ usually remains bound to iron, alumina and manganese oxides, which limit its mobility and bioavailability [8]. The toxicity and behavior of arsenic and its compounds in the environment is summarized in many reviews [6,9].

The aim of this work was to understand the influence of composting, vermicomposting, and both processes combined (following vermicomposting of composted material) on the concentration, mobility, and chemical speciation of arsenic. The main emphasis included assessment of the mobile As fraction, targeted arsenic species, and arsenic bioavailability. Chemical studies were undertaken using bioaccumulation tests with earthworms performed before and after composting and vermicomposting.

## 2. Materials and methods

### 2.1. Materials

Dewatered sludge with a high arsenic concentration (396 ± 1 mg kg$^{-1}$ dry weight) was used as the initial material for the study. The sludge was produced by a groundwater treatment plant, which cleans groundwater seriously contaminated by arsenic from phosphogypsum (PG) deposits in Fosfa Postorna (Breclav, Czech Republic). PG is a by-product from processing fluorapatite by the "wet acid" method for phosphoric acid production in fertilizer plants [10]. The cleaning process of contaminated water consisted of the addition of slaked lime ($Ca(OH)_2$) to adjust pH and also precipitation by means of the addition of ferric sulfate ($Fe_2(SO_4)_3$). Metal precipitates were removed from the water by filtration and a yellow sludge was the final waste product of the remediation. Immediately after sampling, the sludge sample was air-dried for 25 days on a plastic tarp. The dried sludge was pulverized to a grain size <8 mm and ground. The basic properties of the sludge and metal content are shown in Tables 1 and 2. On the basis of the total arsenic content, this sludge is considered to be a highly hazardous waste material, according to EPA [11].

Horse manure mixed with sawdust was taken from a small horse farm which does not extensively use chemistry, pesticides or pharmaceuticals. The horse manure was spread for 20 days on a plastic tarp for air-drying. Grass was acquired from a meadow covered mostly by *Trifolium pratense*, *Festuca pratensis*, *Lolium perenne*, *Poa pratensis*, and *Festuca rubra*. The grass was cut into 25–30 cm long pieces. The basic chemical characteristics of the horse manure and grass clippings are shown in Table 2.

### 2.2. Composting

A container for home compost production was used and filled with approximately 290 l of the following materials: sewage sludge, horse manure with sawdust, and grass clippings. The components were mixed in a dry state (except for the fresh grass) in the volumetric ratio of 3:6:1 (sludge/manure/grass). After that, water was added equivalent to 50% of the dry material weight. Composting was allowed to run for 90 days outside the laboratory at ambient temperature. The container was placed under the roof to avoid contamination by rain. Turning was done weekly to ensure aeration. The moisture content was maintained at approximately 50% of water holding capacity (WHC) by the squeeze-test and periodic addition of water. Changes in temperature were automatically monitored daily in the middle of the compost with a digital temperature probe. In addition, the pH value and bulk density of the compost was monitored monthly in collected representative samples. 5 kg sample (composites of five sub-samples taken randomly) was collected before composting (C-0) and similar samples taken after 30, 60 and 90 days of composting (C-30, C-60 and C-90). Each sample was air-dried, thoroughly homogenized by hand (the sludge particle size was not maintained), and stored at laboratory temperature before analysis. The pH value (of a suspension of 1 g of sample in 10 ml of water) and dry bulk density were determined for each sample.

### 2.3. Vermicomposting

An earthworm culture (*Eisenia fetida*) was cultured at the laboratories of the Research Centre for Toxic Compounds in the Environment (Brno, Czech Republic) in a mixture of garden substrate (50%), granulated cattle manure (40%), and Sphagnum peat (10%). The water content of the substrate was approximately 80% WHC (water holding capacity) and the pH was adjusted to 6–7 with $CaCO_3$. The earthworms were fed with granulated cattle manure and the culture was maintained at 20 ± 1 °C in darkness. The vermicomposting experiments were carried out in the laboratory using plastic vermicomposting boxes of 10 l capacity. Two vermicomposts were carried out with different substrates: (a) for vermicompost $VC_1$, the material C-0 was used (C-0 is hereinafter called $VC_1$-0), (b) for vermicompost $VC_2$, the material C-90 was used (C-90 is hereinafter called $VC_2$-0). Eight liters of dry substrate were placed in vermicomposting box and water was added to reach 50% of the dry material weight. Then, 200 earthworms *E. fetida* per 1 l of dry matter (i.e. 1600 individuals per box) were added. Each vermicompost was established in duplicate to ensure a sufficient amount of material for analysis. The mean weight of adult earthworms was approximately 200 mg at the beginning of the experiment. All vermicomposts were kept in the dark at a laboratory temperature of 22 °C for a period of 90 days. The moisture content was maintained at approximately 50% WHC by the squeeze-test and by the periodic sprinkling of water on filter paper, which covered the substrates in the box. The mixtures were turned over manually every 30 days. During the process of vermicomposting no extra feed was added. Samples were collected at the beginning of the experiment ($VC_1$-0 and $VC_2$-0) and after 30, 60 and 90 days of vermicomposting