Investigation of Volatilization and Chemical Speciation Transformation of Arsenic in Paddy Soil under Temperature Conditions

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INTRODUCTION

Arsenic (As) is naturally occurring but can accumulate in the environment due to anthropogenic factors such as industrial activities, agricultural waste, and mining development. As exists in both inorganic (iAs) and organic (oAs) forms, and its toxicity varies depending on the chemical species. Generally, inorganic As is known to be highly toxic, and it can be transformed through biological and chemical processes in the environment. In reduced environments, such as paddy fields, As can be methylated by microbial activity, leading to the formation of volatile As compounds that may be released into the atmosphere and transported over long distances. The volatilization and mobility of these volatile As compounds can vary greatly with climate change and environmental conditions, making it an important area of research. This study aims to analyze the chemical speciation transformation characteristics of As in As-contaminated paddy soil under different temperature conditions and identify the volatilization mechanisms of As.

MATERIALS AND METHODS

Experimental Setup

The soil was collected from Sinwha-ri, Yeonmu-eup, Nonsan-si, Chungcheongnam-do, South Korea, and artificially contaminated with arsenate (iAs(V)) and dimethylarsinic acid (DMA(V)). The As-contaminated soil was treated in a glove box, where standard solutions were prepared and injected to achieve a concentration of 100 mg/kg, ensuring uniform mixing. The soil was conditioned for one week to ensure uniformity in As concentration. The experiment was conducted at two temperature conditions, 25°C and 35°C, using 200 mL serum vials containing 100 g of contaminated soil. To simulate flooding conditions, 100 mL of paddy water, filtered through HM filter paper, was added to the vials. Additionally, Rhizon samplers (MOM, 19.21.22F, 5 cm, 0.15 µm) were installed to collect porewater. The soil part was wrapped in foil to simulate the underground environment, and an LED light (PS102-10W) was used to simulate a 12-hour day/night cycle. The experiment was conducted over 91 days.

Analysis Methods

Volatile As was collected weekly using Silica gel Tubes, which were pretreated by soaking in 1% $AgNO_3$ solution and drying at 70°C. The tubes were connected to the experimental setup's outlet, and air (20.8% O_2, N_2) was injected at 100 kPa for 10 minutes to volatilize and collect the As. The collected samples were stored in the dark to prevent exposure to air. The volatilized As was extracted using 1% HNO_3 and heated at 90°C for 3 hours. The extracted samples were filtered through a 0.22 µm filter and stored at 4°C. Before As species analysis, the volatile As compounds were oxidized to the pentavalent state using 30% H_2O_2 and analyzed as stable pentavalent methylated As derivatives. Porewater As concentrations were sampled weekly (1.5 mL) using Rhizon samplers and filtered through 0.22 µm syringe filters. Total As was measured using ICP-MS (inductively coupled plasma-mass spectrometry), and As species were analyzed using HPLC-ICP-MS (high-performance liquid chromatography-inductively coupled plasma mass spectrometry).

RESULTS AND DISCUSSION

Analysis of Total Volatile Arsenic

Volatile As was collected from each batch at 7-day intervals. In the DMA(V)-contaminated soil, the total volatile As peaked at 33.6 µg on day 21 in the 35°C batch and at 17.75 µg on day 14 in the 25°C batch. For the iAs(V)-contaminated soil, the maximum volatile As production occurred at 17.91 µg on day 21 in the 35°C batch and at 18.31 µg on day 14 in the 25°C batch. These findings indicate that DMA(V)-contaminated soil produced a higher amount of volatile As compared to iAs(V)-contaminated soil with equivalent As concentrations. Additionally, the temperature-related variation in volatile As production was more pronounced in the DMA(V)-contaminated soil.

Analysis of Total Arsenic in Porewater

During the 91-day experiment, the concentration of total As in the porewater of DMA(V)-contaminated soil showed a decreasing trend, with the highest concentrations observed on day 1 (7.68 mg/L) in the 35°C batch and on day 7 (4.60 mg/L) in the 25°C batch. In contrast, the total As concentration in iAs(V)-contaminated soil was consistently lower than that in DMA(V)-contaminated batches. In the iAs(V)-contaminated soil, As levels gradually increased, peaking at 2.90 mg/L on day 63 in the 35°C batch, followed by a decline. In the 25°C batch, the concentration also increased steadily, reaching a peak of 0.51 mg/L on day 84. These results suggest that higher temperatures increase the mobility of As in both chemical forms, likely due to enhanced microbial activity, which facilitates As release from soil into the aqueous phase.

CONCLUSIONS

The results of this study provide important baseline data on the effects of extreme temperature increases due to climate change on As mobility and chemical speciation transformation. Additionally, the findings offer significant insights into the volatilization characteristics of As. Understanding how temperature conditions affect the environmental behavior of As will be crucial for developing future environmental management and climate change adaptation strategies in As-contaminated areas.

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