Chemosphere 173 (2017) 380–386

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The influence of sample drying and storage conditions on methylmercury determination in soils and sediments

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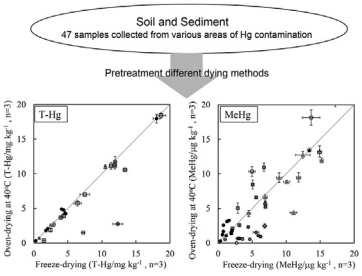
HIGHLIGHTS

- The influences of drying and storage for MeHg concentration have been investigated.
- MeHg production and decomposition process occur during drying and storage.
- The main factor of these phenomenon would be bacterial activity.
- Freeze-drying and then storage in dark and cool is best way to preserve MeHg.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form
10 January 2017
Accepted 10 January 2017
Available online 12 January 2017

Handling Editor: Petra Krystek

Keywords:
Methylmercury
Soil
Sediment
Freeze-drying
Oven-drying
Storage

ABSTRACT

The separate influences of drying and storage conditions on methylmercury (MeHg) concentrations in soil and sediment samples were investigated. Concentrations of MeHg and total Hg were determined in various soil and sediment samples that had been stored or dried under differing conditions. The influence of drying conditions (oven-drying (40 °C) versus freeze-drying) on MeHg concentrations in marine sediments, river sediments, soils, and paddy field soils was investigated (n = 43). The ratio of the MeHg concentration in oven-dried sub-samples divided by the concentration in freeze-dried sub-samples ranged from 0 to 336%. In order to confirm the production of MeHg during storage in some samples, Hg^{2+} was added at 15 mg kg^{-1} to a paddy soil, and the sample was then stored at 30 °C. The concentrations of MeHg at 1-h, 1-day, 4-days and 7-days after Hg^{2+} spiking were 2.0 ± 0.1, 13.8 ± 1.0, 36.0 ± 5.0, and 24.9 ± 1.6 μg kg^{-1} (n = 3), respectively. The concentration of MeHg at 4-days after Hg spiking and sterilizing (121 °C, 30 min) was 1.8 μg kg^{-1}, similar to the original value. These results indicate that bacterial Hg methylation and MeHg demethylation occurred within days in the soil. In addition, tests of the stability of MeHg in wet and dry samples during storage were also performed. Overall, our results indicate that the best way to preserve MeHg in soil and sediment samples is to freeze the samples immediately after collection, followed subsequently by freeze-drying, grinding, homogenization, and storage of the dry material in cool, dark conditions until analysis.

Abbreviations: MeHg, methylmercury; CL, chemiluminescence; AFS, atomic fluorescence spectrophotometry; T-Hg, total-mercury; ASGM, artisanal small-scale gold mining.

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http://dx.doi.org/10.1016/j.chemosphere.2017.01.053
0045-6535/

1. Introduction

Although mercury (Hg) is well known as a toxic metal, the toxicity is highly dependent on its chemical form. Methylmercury (MeHg) is one of the most toxic mercury species in the environment. The main MeHg exposure pathway for humans is the consumption of marine fish. In general, the contamination source of coastal marine fish is considered to be bioaccumulation through the food chain, where the primary producers of MeHg are bacteria in sediments. Recently, it was also reported that rice is the major pathway for MeHg exposure in residents of a Hg-contaminated mining area in China (Feng et al., 2008). It is known that rice paddies are active sites for Hg(II)-methylation. Flooded rice paddy soils are typically in an anaerobic condition, and MeHg is generated there by anaerobic bacteria (Rothenberg et al., 2014). Qiu et al. reported that MeHg levels in rice were most correlated with soil MeHg levels (Qiu et al., 2013). Therefore, the accurate determination of MeHg in soils and sediments is critical to understanding the Hg cycle in the environment and MeHg exposure pathways for humans.

The accurate analysis of MeHg in soil and sediment samples is sometimes difficult because MeHg concentrations in these samples are typically 100–1000 times lower than that of inorganic Hg. In addition, different soil and sediment samples can have widely varying chemical compositions, which potentially affect the determination of MeHg. The formation of artifact MeHg from inorganic Hg and the decomposition of MeHg to inorganic Hg can also occur during some analytical procedures. As a result of this complex situation, a number of different methods for the measurement of MeHg in soil and sediment have been utilized (Canario et al., 2004; Jagtap and Maher, 2015). Recently, we conducted an inter-laboratory study to compare the results of MeHg concentrations in 17 dried and powderized soil and sediment samples obtained by four different analytical methods (Kodamatani et al., 2017). Although the values obtained by four laboratories showed good agreement for most soil and sediment samples, some differences were observed. We think these differences were caused by the different conditions imposed by the analytical methods, including sample treatment and storage.

Appropriate sample storage and preparation procedures are important for obtaining meaningful analytical results. In the case of soils and sediments, sample preparation procedures such as drying and grinding are necessary prior to analysis because these samples contain water at various levels and are inhomogeneous. Hg methylation and methylmercury (MeHg) demethylation occur primarily through the activity of bacteria in soils and sediments, and MeHg concentrations in such samples can change even during storage and drying. Although there are some reports indicating that MeHg concentrations in soil and sediment samples can change during storage and drying processes (Horvat et al., 1993; Muhaya et al., 1998; Qian et al., 2000; Leermakers et al., 2005; Jagtap and Maher, 2015), the limited results could not be generalized to all kinds of soils and sediments. In recent studies of Hg analysis in soils and sediments, different sample preparation techniques such as air-drying at room temperature (Nevado et al., 2008), oven-drying (Maggi et al., 2009; Fernandez-Martinez and Rucandio, 2013), freeze-drying (Rolfhus et al., 2015), and frozen storage or chilled storage without drying (Tomiyasu et al., 2012; Pietila et al., 2015) have all been used. There is, as yet, no standard method for soil and sediment preparation prior to Hg analysis.

In this study, the influences of drying and storage conditions on MeHg concentrations in various soil and sediment samples were investigated. In particular, the effects of drying temperature and storage temperature and duration were examined. Based on the results of these experiments, we offer some recommendations for appropriate drying and storage procedures to minimize changes in the MeHg concentrations in soil and sediment samples.

2. Experimental

2.1. Reagents

A 10 mg L^{-1} standard solution of mixed MeHg and ethylmercury was purchased from Wako (Osaka, Japan). A 0.1 mg L^{-1} MeHg and ethylmercury solution was prepared in acetonitrile and stored in amber glass vials in a refrigerator at −15 °C; it showed no apparent loss or degradation over a period greater than 6 months. Emetine-CS_2 was prepared according to a published procedure (Kodamatani et al., 2011). All the other chemicals were of analytical reagent grade and were used without further purification. Water for all the solutions was purified using an Elix 5 UV (Millipore, Tokyo, Japan) and a Milli-Q Advantage system (Millipore). A 2 mM emetine-CS_2 stock solution was prepared in methanol containing 1% NH_3 and stored in the freezer; this stock solution was diluted to 0.1 mM with acetonitrile before use. A 2 mM EDTA solution was prepared in a 20 mM borate buffer (pH 9.1).

2.2. Sample collection

Soil and sediment samples were collected from seven sites near Hg contamination sources. Soil and sediment samples were collected near the Idrija mercury mine in Slovenia (Tomiyasu et al., 2012). In Indonesia, river sediments and flooded paddy field soils were collected at an artisanal small-scale gold mining (ASGM) area where metallic Hg is used to extract gold from ore (Tomiyasu et al., 2013). Soil and flooded paddy field soils were collected at abandoned gold mines in Kagoshima, Japan; the source of Hg contamination in these soils is not clear. A soil sample was collected near a chemical plant in Niigata prefecture, Japan, and river sediment samples were collected from an area affected by volcanic releases (Minamigigokudani, Mt Myoko), also in Niigata prefecture. Marine sediment core samples were collected from Minamata Bay (Tomiyasu et al., 2014) and Kagoshima Bay (Ruiz and Tomiyasu, 2015). These samples were obtained by a gravity core sampler, and individual samples were sub-sections taken along the length of the core.

2.3. Sample preparation and drying methods

Soil and sediment samples were carefully divided to provide subsamples for the various treatments. All drying and storage procedures were conducted under dark conditions to avoid any photo-induced reactions (Gustin et al., 1999). For oven-drying, samples were dried at given temperatures for ~5 days, to constant weight. Before freeze-drying, wet samples were refrigerated in a freezer and then placed in the freeze dryer (DRW240DA, Advantec, Japan). Drying was complete after three days. The dried samples were sieved through a 2-mm sieve prior to grinding. The dried, sieved samples were finely ground with an agate planetary ball mill (PM200, Verder Scientific, Germany) and stored in a freezer until analysis. The MeHg and T-Hg results for all samples were additionally corrected for moisture content because even the dried samples contained very small amounts of water. The moisture content was measured with an electronic moisture analyzer, MA 355 (Sartorius, Germany).

Sample properties were also characterized as follows: (1) Total organic carbon (TOC) and inorganic carbon (IC) were measured using a TOC-V analyzer, equipped with a SSM-5000A module (Shimadzu, Kyoto, Japan); (2) The mineral composition was measured by X-ray fluorescence (XRF, ZSX-mini II, Rigaku Co.,