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Article

Insight into Mercury (Hg) Species, Transformation, and Release in Plants Through Temperature-programmed Thermal Desorption

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ABSTRACT: The pivotal role of vegetation uptake in the global biogeochemical cycle of mercury (Hg) necessitates investigation on Hg species and transformation within plants, which have been limited by methodological constraints. This study established a temperature-programmed thermal desorption method to provide well-resolved thermal release profiles of Hg complexes with various biomolecules and Hg in plant tissues, showing significant differences from those of inorganic Hg compounds. Wild plant tissues and Hg(0)-exposed poplar leaves in the laboratory demonstrated consistency with Hg complexes with biomolecules at 180°C, 220°C, and 280°C. Besides, thermal release profiles revealed that a proportion of plant Hg is more thermally stable compared to Hg-biomolecule complexes. Specifically, for wild plants, 13%-42% of Hg in leaves was released above 300°C, and 61%-76% of Hg in roots was released between 280°C and 450°C, likely caused by different matrices, Hg sources, and transformation processes. Results also revealed a complete transformation of Hg(0) into oxidized Hg after foliar Hg(0) uptake. The notable Hg release from 180°C to 450°C raises concerns about Hg emissions during various biomass thermal processes, beyond biomass burning. Therefore, controlling Hg release in these processes is promising for reducing emissions and producing low-Hg biofuels.

INTRODUCTION

Mercury (Hg) poses a significant global hazard due to its long-distance transport and severe biological toxicity. Vegetation plays a pivotal role in the Hg biogeochemical cycle by substantially taking up Hg from the atmosphere, soil and aquatic systems. Approximately 2100–3200 Mg and 1200–1950 Mg of Hg are stored in underground and aboveground woody tissues,[1] with Hg mainly derived from surrounding soil [2-5] and atmosphere,[6-9] respectively. Vegetation uptake of atmospheric Hg profoundly influences atmospheric Hg(0) levels and transport.[10-12] Subsequently, incorporation of Hg into vegetation has a significant impact on regional and global Hg cycles through processes like

deposition to soil via litterfall and throughfall, re-emission to the atmosphere after photoreduction, and transfer into food chains.[1, 13] Moreover, biomass burning contributes to ~600 Mg yr^{-1} of Hg release to the atmosphere, including 300 Mg yr^{-1} from forest fires and 151 Mg yr^{-1} from fires in woody savannas/shrublands.[14-16]

Consequently, Hg species and transformation within plants are crucial for their subsequent environmental behaviors and risks, yet substantial methodological constraints remain for plant Hg speciation analysis. Presently, the analysis approach for methylmercury (MeHg) is well-established, but MeHg represents only a small fraction of the total Hg (THg) (tree leaves: 0.04%-2.3%; rice leaves: ≤ 5%).[17-22] Hg-thiol complexes identified via liquid chromatography coupled with mass spectrometry also constitute a minor proportion, with the soluble fraction available for analysis accounting for less than 1% of root THg.[23] Therefore, a comprehensive understanding of Hg species in plants is necessary, with X-ray absorption techniques and thermal desorption being promising approaches. X-ray absorption techniques, including X-ray absorption near edge spectroscopy and extended X-ray absorption fine structure, provide information on chemical coordination environments of Hg without sample treatment.[23-27] However, this technique faces challenges in distinguishing spectra of different Hg compounds, and it requires samples with high concentrations of Hg (> μg/g).[23,28,29] Comparatively, thermal desorption is more sensitive for Hg speciation analysis, as Hg in samples is totally released during pyrolysis and detected by inductively coupled plasma-mass spectrometry,[30] atomic absorption spectrometry (AAS),[31] or atomic fluorescence spectrometry (AFS).[32] Hg compounds undergo physical changes and chemical reactions, reflected in the thermal release profiles.[33-36] This technique has been successfully applied in solid matrices like soil,[31, 37-40] sediment,[34, 41] tailings,[40] fly ashes,[38, 39] coals,[42, 43] atmospheric samples,[30, 32, 44] and gypsums,[38] yet its performance in biological samples remains unknown.

Therefore, this study established a temperature-programmed thermal desorption method coupled with AFS to obtain well-resolved thermal desorption curves for Hg complexes with various biomolecules and Hg in plant tissues. These thermal desorption curves were compared with those of inorganic Hg compounds. Thermal release profiles of Hg in plant tissues from wild and laboratory were characterized to provide more insights into Hg species, transformation and thermal stability in plants. Additionally, thermal release profiles would shed light on Hg release behaviors and associated risks during biomass burning and other thermochemical processes.

EXPERIMENTAL

Chemicals and reagents. Inorganic Hg compounds included mercuric sulfide (*α*-HgS, *β*-HgS), mercuric chloride ($HgCl_2$), mercuric sulfate ($HgSO_4$), and mercurous sulfate (Hg_2SO_4). *α*-HgS was purchased from Aladdin (Shanghai, China). *β*-HgS and $HgCl_2$ were obtained from Sinopharm Chemical Reagent (Shanghai, China). $HgSO_4$ and Hg_2SO_4 were purchased from Macklin (Shanghai, China). Small biomolecules included cysteine (Cys) (97%, Sigma-Aldrich, St Louis, MO), glutathione (GSH) (99%, Macklin, Shanghai, China), glutathione disulfide (GSSG) (98%, Macklin, Shanghai, China), $(\gamma Clu\text{-}Cys)_2$-Cly ($PC_2$) (95%, Kangbei Biochemical, Ningbo, China), and $(\gamma Clu\text{-}Cys)_3$-Cly ($PC_3$) (95%, Kangbei Biochemical, Ningbo, China). Biomacromolecules included soybean isolate protein (≥ 85%, Solarbio, Beijing, China), lecithin from soybean (14%-23%, Solarbio, Beijing, China), human albumin (99%, Xiya Reagent, Linyi, China), horseradish peroxidase (Solarbio, Beijing, China), and pUC 19 plasmid (TransGen Biotech, Beijing, China). Certificated reference materials of stream sediment (GBW07301a, GSD-1a) and citrus leaf (GBW10020, GSB-11) were obtained from Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences (Langfang, China). Ultrapure water (≥ 18.2 MΩ·cm) was obtained using a Milli-Q Element system (IQ 7000, Millipore, Billerica, MA). All other reagents were of analytical grade or higher.

Preparation of inorganic Hg compounds and Hg complexes with biomolecules. Inorganic Hg compounds (*α*-HgS, *β*-HgS, $HgCl_2$, $HgSO_4$, and Hg_2SO_4) at the Hg concentration of 1 mg/kg were separately prepared by successive dry dilution using silica sand (200-250 mesh) previously heated at 650°C for 2 h. Biologically relevant molecules, including small biomolecules (Cys, GSH, GSSG, PC_2, and PC_3) and macromolecules (soybean isolate protein, soybean lecithin, human albumin, horseradish peroxidase, and DNA), were selected to prepare Hg complexes with biomolecules. Stock solution (1:99, *m/v*) of soybean isolate protein and soybean lecithin was prepared in ultrapure water and then mixed with $HgCl_2$ solution diluted in ultrapure water at a mass concentration ratio of 2:1. Stock solution (2 mM) of other biological molecules prepared in ultrapure water was mixed with $HgCl_2$ solution at a molar concentration ratio of 2:1. The mixtures were then incubated on ice for 30 min before analysis, with a final Hg concentration of 100 μg/L.

Preparation of wild plant samples and chamber-grown poplar leaves exposed to Hg(0). Wild plant samples were collected from Wanshan Hg mining areas, Guizhou Province, China, with *Mentha canadensis* and *Oenanthe javanica* collected in May, 2017 and *Aster indicus* in October, 2018. After transport to the laboratory at 4°C, aboveground parts (consisting of stems and leaves) and roots were separated, rinsed with tap water and deionized water, freeze-dried and ground to powder.

Poplar cuttings (around 10 cm in length) of *Populus* × *euramericana* cv. '74/76' were cultured in 40 mL brown bottles

Fig. 1 Schematic diagram of the temperature-programmed thermal desorption apparatus. This apparatus consisted of five units: gas control (unit A), temperature-programmed desorption (unit B), purification (unit C), atomization (unit D), and AFS detection (unit E).

Fig. 2 Thermal desorption profiles of $HgCl_2$ standard solution (A) and the standard curve of $HgCl_2$ ranging from 0.01 to 5 mg/L (B).

Fig. 3 Thermal desorption profiles of certificated reference materials of stream sediment (GBW07301a) (A) and citrus leaf (GBW10020) (B). Three measurements were shown for each certificated reference material. The grey dotted line represented the temperature gradient.

Table 1. The temperature programming procedure for temperature-programmed thermal desorption

Time (min)	Temperature (°C)	Holding (min)
0	80	0
2	150	5
9	200	5
16	300	5
22	400	2
26	500	2
30	650	8

containing 1/2 Hoagland nutrient solution in an artificial light incubator (light: 14 h, 27°C; dark: 10 h, 25°C). Poplar seedlings with 8-10 leaves were exposed to Hg(0) vapor for 12 hours in a Tedlar bag (40 cm × 45 cm) with an open glass vial containing 20 μL liquid Hg(0). Hg(0) vapor concentrations in the Tedlar bag were 520 ± 34 μg m^{-3} at 6 hours and 477 ± 88 μg m^{-3} at 12 hours. Upon removal of liquid Hg(0) from the Tedlar bag following a 12-hour exposure, thermal desorption analysis of poplar leaves was conducted immediately (0 day) and at 1, 2, 5, 10, and 28 days thereafter.

Temperature-programmed thermal desorption analysis. Inorganic Hg compounds, Hg complexes with biomolecules, plant tissues and certificated reference materials were subjected to temperature-programmed thermal desorption using the apparatus depicted in Fig. 1. This apparatus comprised five units: gas control (unit A), temperature-programmed desorption (unit B), purification (unit C), atomization (unit D), and AFS detection (unit E).

Solid samples (10–20 mg) or liquid samples (10 μL) were loaded into a quartz boat placed in the quartz tube (25 mm (Φ) × 48 cm (L)) of a Lindberg/Blue M furnace (Thermo Scientific, Waltham, MA), which constituted the temperature-programmed desorption unit (unit B). The quartz tube and quartz boat were previously heated (650°C, 2 h) to eliminate any residual Hg. Prior to thermal desorption, the apparatus was purged with argon for 5 min at 400 mL/min by the gas control unit (unit A). The polytetrafluoroethylene gas tubing (1/8 inch diameter) was used to minimize potential adsorption of Hg vapor. Subsequently, Hg vapor generated in the temperature-programmed desorption unit (unit B) was carried into the purification unit (unit C) by argon at 100 mL/min. The purification unit consisted of glass tubes (12 mm (Φ) × 100 mm (L)) filled with soda lime and quartz wool to eliminate interfering substances such as moisture and organic compounds. Sequentially, Hg vapor was introduced into the atomization unit (unit D) to convert other potential Hg compounds into Hg(0) and minimize interference at 700°C utilizing a Delixi Electric heating apparatus (Leqing, China).[37] Following this step, the Hg vapor was analyzed by AFS (Brooks Rand Laboratories, Seattle, WA) (unit E). The optimized temperature programming procedure of unit B is provided in Table 1, and real-time temperatures displayed by the furnace were also recorded.

Quality assurance and quality control. The Hg stock solution (1000 mg/L) was prepared by dissolving $HgCl_2$ in 5% (*v/v*) nitric acid. The standard curve of the temperature-programmed thermal desorption method was constructed using Hg standard solution at 0.01, 0.02, 0.05, 0.2, 0.5, 1, 2, and 5 mg/L. The small peak prior to the major peak is likely due to the sublimation of $HgCl_2$.[45] The major Hg peak of $HgCl_2$ around 180°C was selected for peak area integration (Fig. 2), exhibiting good linearity (R^2 = 0.9986). This affirms the use of peak area integration for semi-quantitative analysis of Hg compounds during thermal desorption. Therefore, the proportion of Hg contents in different peaks was calculated based on peak area integration using Origin 2022 software. The thermal Hg release profiles of certificated reference materials of stream sediment and citrus leaves, as depicted in Fig. 3, exhibited consistence across different injections, with better measurement

Fig. 4 Thermal desorption profiles of inorganic Hg compounds (α-HgS, β-HgS, $HgCl_2$, $HgSO_4$, and Hg_2SO_4). Inorganic Hg compounds, at a final concentration of 1 mg/kg, were individually prepared through successive dry dilution using silica sand. Expect for $HgSO_4$, other compounds showed no Hg peak after 20 min. The grey dotted line represented the temperature gradient.

Fig. 5 Thermal desorption profiles of Hg complexes with biological small molecules (A) and macromolecules (B). Biological small biomolecules included cysteine (Cys), glutathione (GSH), glutathione disulfide (GSSG), (γClu-Cys)$_2$-Cly (PC_2), and (γClu-Cys)$_3$-Cly (PC_3). Biological macromolecules included DNA, soybean isolate protein, soybean lecithin, human albumin, and horseradish peroxidase. The Hg-biomolecule complex solution had a final Hg concentration of 100 μg/L. The mass concentration ratio between soybean isolate protein/soybean lecithin and Hg was 2:1, while the molar concentration ratio between other biological molecules and Hg was 2:1. The grey dotted line represented the temperature gradient.

reproducibility observed for citrus leaves. This suggests that the method is reproducible and applicable to analysis of biological samples. During thermal desorption analysis, each sample was measured at least three times and the certificated reference material of stream sediment was measured daily.

RESULTS AND DISCUSSION

Thermal release profiles of inorganic Hg compounds. Thermal desorption profiles of α-HgS, β-HgS, $HgCl_2$, $HgSO_4$ and Hg_2SO_4 are shown in Fig. 4. The release temperatures of major peaks followed the order: $HgCl_2$ (~150°C) < β-HgS (~180°C) < α-HgS (~300°C), Hg_2SO_4 (~150°C and 300°C) and $HgSO_4$ (150°C-450°C). Except for $HgSO_4$, the thermal release temperatures of inorganic Hg compounds were no more than 300°C. These findings closely align with literature findings for $HgCl_2$, β-HgS, α-HgS, and $HgSO_4$.[31,43,46] The characteristic thermal release profiles reflect the binding environment and stability of Hg species,[31] and both physical processes and chemical decomposition occur during thermal desorption.[32] The release temperature of $HgCl_2$ is the lowest (~150°C) owing to its volatile nature (vapor pressure at 25°C: 1.60×10^{-4} mbar) [30] and its propensity for pyrolysis into Hg(0) and Cl_2.[33,43] Besides, multistep chemical reactions occur during the pyrolysis of Hg compounds.[43] For example, $HgCl_2$ and Hg(0) are generated from Hg_2Cl_2 at relatively low temperatures, and $HgCl_2$ was further decomposed into Hg(0).[33,43] The different thermal desorption temperatures of trigonal α-HgS (~300°C) and cubic β-HgS (~180°C) are primarily attributed to their distinct crystalline structures.[46] As noted in some literature,[43,47] multiple peaks have been observed during the pyrolysis process of $HgSO_4$, with the formation of HgO being an important factor.[43] $HgSO_4$ exhibited thermal release temperatures ranging from 150°C to 450°C, different from earlier literature documenting the major release temperatures of 250°C,[31] 400°C [46] and 550°C.[42,43] Such considerable variability in the thermal release behaviors of same Hg compounds has been reported across different studies, which is attributed to various factors such as the dry dilution procedures, matrices, diluents, temperature programs, carrier gases, and flow rates.[30-32,43,46] Therefore, experimental conditions and methodologies need to be considered when interpreting the thermal release profiles for Hg compounds.

Thermal release profiles of Hg complexes with biomolecules. Hg in organisms primarily binds to a variety of biomolecules, such as small molecules (*e.g.*, Cys, PCs),[21,23,29,48,49] proteins,[50] and DNA.[51,52] Thermal desorption profiles of Hg complexes with small biomolecules and macromolecules were investigated in this study. Through optimization of ramp rates and holding temperatures, the temperature-programmed thermal desorption method yielded well-resolved thermal desorption profiles for these Hg complexes. The proportion of Hg contents in each peak was determined via peak area integration of the pyrolysis curves.

The thermal release profiles of Hg complexes with small thiol-containing biomolecules (Cys, GSH, GSSG, PC_2 and PC_3) exhibited similarities, as depicted in Fig. 5A. Two prominent peaks were observed at 180°C and 280°C, along with a less abundant peak at 220°C. Through semi-quantification, it was determined that 68%, 57%, 50%, 35%, and 40% of Hg was released at 180°C for Hg complexes with Cys, GSH, GSSG, PC_2, and PC_3, respectively. Besides, a smaller proportion of Hg was released at 280°C, with 17% for Cys, 29% for GSH, 26% for GSSG, 30% for PC_2, and 36% for PC_3.

Fig. 5B presents the thermal release profiles of Hg complexes with biological macromolecules, revealing both similarities and differences compared to small thiol-containing molecules. Consistent with Hg complexes with small thiol-containing molecules, complexes with horseradish peroxidase and DNA exhibited three Hg peaks at 180°C, 220°C, and 280°C. However, the distribution of different Hg peaks varied with these complexes.

Fig. 6 Thermal desorption profiles of poplar leaves exposed to Hg(0) for 12 hours in laboratory (A) and wild plant samples collected from Hg mining areas, including *Aster indicus* (B), *Mentha canadensis* (C) and *Oenanthe javanica* (D). Poplar leaves were sampled at different sampling time (0, 1, 2, 5, 10 and 28 days) after 12-hour Hg(0) exposure. The grey dotted line represented the temperature gradient.

Hg complexes with horseradish peroxidase released 77% of Hg at 180°C, while Hg complexes with DNA released comparable amounts of Hg at 180°C (24%), 220°C (24%), and 280°C (23%). For Hg complexes with soybean lecithin, soybean isolate protein, and human albumin, significant Hg release occurred at 180°C (47%-77%) and 280°C (9%-46%), with no detectable Hg at 220°C. The majority of Hg was released at 180°C for Hg complexes with soybean lecithin (74%) and human albumin (76%), while Hg complexes with soybean isolate protein released comparable amounts of Hg at 180°C (47%) and 280°C (46%).

The characteristics of thermal desorption profiles among these Hg-biomolecule complexes may arise from the specific binding sites and coordination environments of Hg, though interpreting these observations remains challenging. The presence of multiple peaks during pyrolysis suggests the potential formation of additional Hg compounds, necessitating further investigation. Hg can bind with various functional groups in biota, with thiol groups showing a particularly strong affinity. Surprisingly, even in the absence of thiol groups, Hg complexes with DNA and soybean lecithin displayed comparable thermal release behaviors to Hg complexes with thiol-containing biomolecules. Unlike inorganic compounds, Hg complexes with biomolecules possessed similar thermal release patterns (Fig. 5), suggesting that thermal desorption cannot effectively distinguish different Hg-biomolecule complexes.

Thermal release profiles of Hg in chamber-grown poplar leaves and wild samples. The temperature-programmed thermal desorption method was applied to analyze poplar leaves exposed to Hg(0) in laboratory and wild plant samples collected from Hg mining areas, aiming to elucidate Hg species and transformation in plant samples, as depicted in Fig. 6.

The thermal release profiles of Hg in poplar leaves, determined at intervals of 0, 1, 2, 5, 10, and 28 days following a 12-hour Hg(0) exposure, are depicted in Fig. 6A, with an average Hg concentration of 1.58 mg/kg after exposure. Three prominent Hg peaks were observed at 180°C, 220°C, and 280°C, consistent with those observed for most Hg-biomolecule complexes (Fig. 5). However, the proportion of Hg peaks at different temperatures varied, with the majority occurring at 220°C (49%-68%) and 280°C (28%-51%) except for 28 days (180°C: 24%; 220°C: 76%). It is commonly reported that Hg(0) is released from the solid phase

within the temperature range from 50°C to 150°C,[30, 31, 34, 35] but no discernible peak was observed within this temperature range for poplar leaves following Hg(0) exposure, implying complete Hg(0) oxidation within leaves after foliar Hg(0) uptake.

Figs. 6B, 6C, and 6D illustrate the thermal release profiles of Hg in aboveground parts and roots of wild plants, including *Aster indicus* ($THg_{aboveground\ parts}$: 6.09 mg/kg; THg_{root}: 6.77 mg/kg), *Mentha canadensis* ($THg_{aboveground\ parts}$: 1.85 mg/kg; THg_{root}: 9.66 mg/kg), and *Oenanthe javanica* ($THg_{aboveground\ parts}$: 2.31 mg/kg; THg_{root}: 18.8 mg/kg). These three plant species exhibited similar thermal release patterns. Typically, the aboveground parts displayed five peaks at 180°C, 220°C, 280°C, 320°C, and 400°C. The most significant Hg release was observed at 220°C (*Aster indicus*: 42%-48%; *Mentha canadensis*: 32%-43%; *Oenanthe javanica*: 36%-41%), and Hg release was also observed at temperatures above 300°C (*Aster indicus*: 17%-37%; *Mentha canadensis*: 26%-42%; *Oenanthe javanica*: 13%-37%). Whereas the Hg peaks between 280°C and 450°C were not well resolved for roots, with significant release observed for *Aster indicus* (64%-69%), *Mentha canadensis* (61%-71%), and *Oenanthe javanica* (67%-76%). Additionally, compared with aboveground parts, the proportion of Hg released at 220°C was significantly lower in roots (*Aster indicus*: 22%-26%; *Mentha canadensis*: 26%-31%; *Oenanthe javanica*: 14%-27%). Thus, compared with aboveground parts, Hg in roots exhibited greater thermal stability, likely attributed to their different Hg sources and transformation processes. In aboveground parts, atmospheric Hg(0) is the main contributor to Hg accumulation and undergoes oxidation.[6-9] While dissolved Hg(II) in soil pore water significantly contributes to root Hg accumulation, and soil particles may also be absorbed or internalized by roots.[2-5, 53]

Consistent with thermal desorption profiles of Hg-biomolecule complexes, Hg(0)-exposed poplar leaves and wild plants exhibited Hg peaks at 180°C, 220°C, and 280°C, revealing the importance of Hg-biomolecule complexes in plants. However, it is hard to distinguish the exact Hg-biomolecule complex dominating in plants due to the similar thermal release profiles of various Hg-biomolecule complexes. Besides, Hg(0)-exposed poplar leaves and wild plants showed a smaller proportion of the Hg peak at 180°C compared to Hg-biomolecule complexes, which may be related to Hg transformation processes or differences in matrices. Wild plants released more Hg above 300°C compared to chamber-grown poplar leaves, indicating more thermally stable Hg species in wild plants, possibly due to the aging process of Hg. For example, it was suggested that the formation of β-HgS_{NP}-type in plants required time as a secondary Hg species, and that soil Hg particles may be incorporated into wild plants.[26, 28, 29] Additionally, the proportion of leachable Hg in foliage by aqua regia/UV digestion decreased with foliage aged,[54] suggesting that Hg species in plants become less reactive over time.

CONCLUSION

In this study, Hg-biomolecule complexes demonstrated significant Hg release at 180°C (35%-77%) and 280°C (9%-46%) but lesser Hg release at 220°C (0%-33%), differing from inorganic Hg compounds. Although accurately discerning Hg-biomolecule complexes based on thermal release characteristics remains challenging, temperature-programmed thermal desorption provides insight into the transformation and thermal stability of plant Hg. Hg(0) was found completely transformed into oxidized Hg after foliar uptake. Plant Hg was released at 180°C, 220°C, and 280°C, similar to Hg-biomolecule complexes. However, a portion of Hg in plant tissues exhibited greater thermal stability, with 13%-42% released from wild plant leaves above 300°C and 61%-76% released from roots between 280°C and 450°C. Therefore, Hg binding forms in plants are more complex than inorganic Hg compounds and Hg-biomolecule complexes investigated in this study, which requires further research.

Given that the release temperatures of plant Hg (180°C to 450°C) align with biomass burning[55,56] and thermal treatment processes,[57-59] it underscores the need for effective control over Hg emissions during these processes. Furthermore, incorporating thermal treatments such as torrefaction and pyrolysis will facilitate the production of biofuels with reduced Hg contents and minimize overall Hg emissions.

AUTHOR INFORMATION

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Notes

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