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The role of relative humidity in the control of gaseous elemental mercury emissions: Insights from herbaria museum collections

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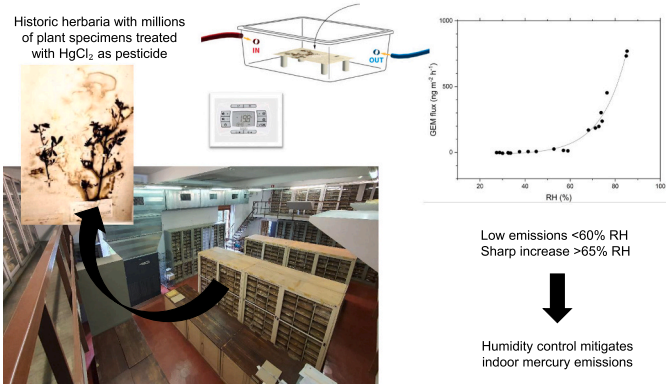
HIGHLIGHTS

- Humans are exposed to volatile Hg released by herbaria collections.
- Flux-chamber experiments quantify Hg emissions from treated samples at different RH.
- RH controls Hg emissions, with GEM fluxes increase exponentially above ~65% RH.
- Field monitoring confirms RH-driven GEM variations in indoor air.
- RH control offers a simple strategy to mitigate indoor Hg pollution..

GRAPHICAL ABSTRACT



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ABSTRACT

Natural history collections are irreplaceable archives of global biodiversity, yet many remain affected by chemical contamination originating from historical conservation practices. Among these, mercury-based pesticides extensively used in herbaria continue to pose risks to human health, indoor air quality, and the accessibility of biodiversity collections. In this paper, we investigate the role of relative humidity (RH) in regulating gaseous elemental mercury (GEM) emissions from mercury-contaminated herbarium specimens, i.e. plant samples mounted on paper supports. We combined controlled laboratory experiments, using a non-steady-state flux chamber, with in-situ monitoring of GEM, temperature, and RH in the herbaria halls of the Natural History Museum of the University of Florence (Italy), hosting one of the world's most important botanical collections. Our results demonstrated a strong, non-linear dependence of GEM emissions on RH. Mercury fluxes from

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contaminated specimens were very low in dry conditions (30–60% RH) but increased exponentially at RH above c. 65%. In-situ herbaria halls monitoring confirmed that RH increases systematically coincide with higher GEM concentrations. These findings may suggest that moisture-driven physicochemical changes in cellulose-based materials strongly enhance mercury mobilisation and volatilisation. By explicitly linking microclimatic control to contaminant emissions, this study provides actionable evidence bridging scientific understanding and risk management in indoor environments. Maintaining low and stable RH (40–60%) emerges as a cost-effective strategy to reduce GEM emissions while preserving herbarium specimens. More broadly, our results highlight how environmental controls can mitigate chemical pollution in biodiversity repositories, supporting safer access to collections essential for ecological, taxonomic, and global change research.

1. Introduction

The preservation of cultural heritage represents a critical challenge for society, as collections housed in museums, archives, and libraries are continually exposed to environmental factors that influence their physical and chemical condition [14,10]. The indoor environments of these institutions, whether historic or modern, possess an exceptionally complex atmospheric composition [43]. While for decades the primary focus of conservation has been on the influence of temperature (T), relative humidity (RH), and light [14], it is increasingly recognised that atmospheric pollutants, both gaseous and particulate, play a significant role in the deterioration of museum objects and pose a risk to human health [14,21,49].

Sources of pollution within museum environments are multiple, originating from both external and internal factors [39]. A growing concern pertains to internally generated pollutants from the off-gassing of building materials, furnishings, and the collection objects themselves [79,90]. In confined spaces, such as display cases, drawers, and cabinets, the emissions of these compounds can accumulate to high concentrations [22]. Prominent off-gassing pollutants include volatile organic compounds (VOCs), especially volatile organic acids (VOAs) such as acetic acid and formic acid, but also aldehydes [18,2,26,28,80,86]. Environmental variables significantly influence the off-gassing of pollutants [6,94] and determine their emission rate and concentration in museum environments [1,14,36,78]. Understanding and meticulously controlling these factors is essential for mitigating the risks of deterioration to museum collections and for ensuring a safe environment for staff and visitors [49,14,36].

An illustrative and particularly persistent case of indoor pollution involves mercury (Hg) contamination in specific museum collections (see [21] and reference therein): historic herbaria represent one of the most significant documented cases of indoor mercury contamination worldwide [11,13,20,21,25,45,50,60]. Herbaria are collections of dry plants mounted on paper sheets, representing unique repositories for taxonomic and biodiversity studies [16,52,62,91]. For nearly two centuries, mercuric chloride ($HgCl_2$) has been widely used as a pesticide and fungicide to treat herbarium specimens against insect and fungal infestations [85,88]. Although its use was discontinued by the mid-1980s, treated specimens continue to pose a hazard for collection samples, staff and researchers, due to the presence of high levels of gaseous elemental Hg (GEM, Hg^0), resulting from the reduction of the Hg^{2+} in $HgCl_2$, and particulate-bound Hg (PBM) [20,21]. This scenario is further complicated by the fact that herbarium environments are generally designed as closed systems where indoor-outdoor air exchange is minimised to prevent sample infestations caused by moulds, insects, fungi, and other biological agents. As a consequence, herbaria develop a distinctive microclimate and are particularly vulnerable to the accumulation of pollutants over time [13].

Previous studies focused on the characterization of the Hg contamination in the herbaria of the Natural History Museum of the University of Florence (Florence, Italy; FI hereafter), among the most important botanical collections worldwide (see 2): GEM spatial monitoring allowed to highlight anomalous concentrations in the FI halls, which are prompted by the herbaria samples as well as by the wood and metal cabinets where they are stored [13,22,21]; the PBM pollution was also studied, characterizing its size, chemical speciation and concentration, and calculating the workers' exposure risk to this pollutant [20,21]. Based on these previous results, the present work aims to understand how environmental variables, such as T and RH, influence the GEM emissions from herbaria samples. High T conditions promote Hg volatilisation, as evidenced by the strong and significant correlation usually observed between T and GEM, both in herbaria [13,25,68] and, more generally, in contaminated environments [32,40,42,81,15,84,69]. The case of RH appears more complex. To the authors' knowledge, the influence of this parameter on GEM concentrations in herbaria was never studied, with the exception of Deering et al. [25], who just mention that the low GEM concentrations measured in the Natural History Museum in Berlin (Germany) could be due to low RH (28%) and T (19 °C) conditions. In the case of soils as well, the influence of RH has received less attention compared to that of light and T [81]. Most of the available studies suggest a weak inverse relationship, where GEM emissions tend to decrease slightly as RH increases [34,40,56,92,33]. Floreani et al. [33], attribute this behaviour to the dependence of RH on both radiation and T, rather than to a direct effect of RH on GEM. However, the effect of relative humidity on Hg fluxes is not consistent across studies. Some have reported a positive correlation [27], while others observed no clear relationship [35].

Despite this scarce attention to the effect of RH in the literature, the interaction of water vapour with surfaces is a crucial aspect to consider in materials science, particularly relevant for biopolymers such as cellulose, since water vapour can penetrate their chain network and alter their properties [7,77]. In a study on formaldehyde emissions from wood-based panels [17], it was found that emissions are also influenced by extrinsic environmental conditions, including T and RH. According to Huang et al. [47], RH is one of the main environmental factors affecting the emission behaviour of formaldehyde from building materials, with emissions increasing by a factor of 10 when RH rose from 20% to 85%. The mechanism underlying pollutant emissions from wood is commonly attributed to the swelling of wood fibres. According to Joffre et al. [48], wood fibres exhibit pronounced swelling with increasing RH due to their hydrophilic nature. This behaviour is driven by moisture uptake associated with the abundance of accessible hydrogen bonds and hydroxyl groups [97]. Paper-based materials, the predominant component of herbarium samples (composing sheets, folders, and supporting cardboards), show a similar response to RH. They are highly hygroscopic and can absorb substantial amounts of water from ambient humidity, eventually equilibrating with ambient RH and reaching their equilibrium moisture content [46,51,70,75]. Moisture diffusion through paper is a complex phenomenon, which has been studied and modelled by several authors [4,7,46,53,61,67,75,76]. Paper can be modelled, for example, as a porous, hygro-responsive material, where moisture diffuses by different pathways: within the porosity (as water vapour), within the cellulose fibres (as condensed water), and between the fibres and the pore space [4,75,76]. Continuous exchange between these domains determines the overall moisture dynamics within the paper structure that, in turn, affects the physical structure and the permeability of pollutants through cellulose fibres. Concerning the desorption behaviour of pollutants from cellulose-based materials, the study by

Wolf et al. [93], who investigated the effect of different RH conditions on the desorption of VOCs from paper and board, indicated an exponential increase of VOCs emissions at about 60% RH for a temperature of 23°C. This evidence suggests that, if the same behaviour is verified for GEM emissions from herbaria samples, maintaining indoor RH at low levels would be a simple and cost-effective strategy to minimise the GEM release and human exposure, while ensuring the samples' preservation.

Starting from the reassessment of data previously acquired in the FI [13,21] and integrating it with new in-situ measurements and lab experiments, the broader aim of this paper is to deepen our understanding of the effect of humidity on GEM emissions to adopt informed conservation strategies in natural history museums and, possibly, other Hg-polluted indoor environments.

2. Study site and background studies

The FI, founded in Florence in 1842, constitutes the most important part of the Botanical Collection of the Natural History Museum of the University of Florence (Italy). Hosting millions of plant samples, it is considered one of the most relevant herbaria in the world for its history and collections (Moggi 2009; Thiers 2018). $HgCl_2$ was employed to protect samples from infestations from the herbarium's founding until the early 20th century [71,72].

The *exsiccata* collections of the FI are divided into historical herbaria (i.e., closed collections not increased by new samples, such as the Herbarium Webb) and open herbaria (i.e., collections continuously increased by new plant samples, such as the Herbarium Centrale Italicum). Historical herbaria represent the most ancient and the most $HgCl_2$-treated group, considering that they are dated before 1920, when likely all herbarium samples were treated with $HgCl_2$; differently, open herbaria contain both treated and non-treated samples, the latter including the most recent botanical samples.

The herbarium is hosted in 13 halls on two floors of the same building (close to Piazza San Marco in the centre of the city of Florence), which are characterised by different indoor climatic conditions [22]. Both floors have several windows that remain permanently closed to protect the collection from microorganisms that could cause infestations. Some windows are fitted with small openings (typically 30 × 30 cm^2) covered with non-woven fabric that acts as a filter. Some of the openings are equipped with fans that draw in the air from outside, which is then expelled through the openings without fans. This is the only system in the herbarium halls that ensures air exchange. On the first floor, almost all the rooms have an air-cooling system (hereafter ACS), not exchanging air with the outside, which is activated at night to regulate the T of the halls. On the second floor, there is no ACS.

The herbarium represents a complex indoor microenvironment characterized by spatially heterogeneous microclimatic conditions. Dishomogeneous GEM concentrations were detected in different halls, especially between the first and second floor, mainly depending on the type of collections present and the air conditioning and ventilation systems, as highlighted in previous studies [13,21]. Information about risk assessments at the FI and comparisons with national and international regulatory limits can be found in Cabassi et al. [13] and Ciani et al. [20,21]. A strong seasonality was identified, with GEM concentrations in the herbaria halls increasing in summer when T is higher, especially at the second floor [13]. In particular, Ciani et al. [22,21] illustrated the unexpected effect of the ACS on GEM concentrations in the halls on the first floor: GEM concentrations significantly increase when the ACS is turned on and reduces the T. Ciani et al. [21] suggested that this anomaly could be hypothetically attributed to the formation of an alloy between Hg^0 and the steel of the conditioner, while other studies [38,8] on different sites tentatively proposed that air conditioning filters could condense Hg vapour and then reevaporate it. Although these hypotheses do not seem sufficient to fully explain the unexpected increase in GEM following the ACS activation, since ACS filters are periodically replaced and do not exhibit significant Hg content even at the end of their service life, they could be one of the contributing factors. Another relevant parameter may be RH. Even though the latter is not actively controlled by the ACS, a decrease in T leads indeed to an increase in RH in herbarium halls [21], since T and RH are inversely correlated in closed systems. Therefore, we conducted a dedicated study on Hg^0 emissions from paper as a function of RH in order to assess the impact of humidity on Hg release and, if any, to identify the optimal climatic conditions to minimise emissions.

3. Materials and methods

3.1. GEM fluxes from the FI botanical samples

To evaluate the effect of RH variations on GEM emissions from herbarium samples in a simplified, controlled environment, a non-steady-state flux chamber was set up following Floreani et al. [33]. The flux chamber was used to record the GEM fluxes emitted by four FI herbarium samples, i.e. dry plants fixed onto a sheet of paper (Fig. 1, Table 1). Three samples (Camp2, Camp3, and Camp4) belong to the open herbarium, and are dated between 1842 and 1869; their paper supports bear the stamp "*poisoned with sublimate*" (Fig. 1), which testifies that they have been treated with $HgCl_2$. Furthermore, a recent sample (Camp1), dated 1984, was chosen as a reference blank, since the treatments with $HgCl_2$ of the FI samples had already ceased at that date. Although the number of analysed samples was limited, relative to the

Fig. 1. Herbarium samples of the Natural History Museum of the University of Florence from which the GEM fluxes were recorded in the non-steady state flux chamber. Top left: Camp1; top right: Camp2 with zoom up of the stamp "AVVELENATA CON SUBLIMATO" (i.e., poisoned with sublimate); bottom left: Camp3; bottom right: Camp4.

Table 1
Herbarium samples of the Natural History Museum of the University of Florence from which the GEM fluxes were recorded in the non-steady state flux chamber.

Sample name	Museum n.	Botanical species	Date	Treated with $HgCl_2$
Camp1	not present	*Trifolium*	1984	No
Camp2	FI071379	*Trifolium spumosum* L.	1856	Yes
Camp3	FI090808	*Sempervivum* sp.	1869	Yes
Camp4	I090807	*Cirsium spinosissimus* L.	1842	Yes

entire collection, it was considered adequate, given the comparable $HgCl_2$ treatment and conservation environment of all the FI herbarium samples. The sample size was kept small to minimize the number of historical specimens exposed to extreme RH conditions, as well as to account for time constraints.

The GEM concentrations were measured using a Lumex® RA-915M analyser (hereafter Lumex), a real-time Hg^0 detector based on differential atomic absorption spectrometry with Zeeman background correction [83]. This instrument allows a direct GEM determination with high selectivity, a wide dynamic range (2–50,000 ng m^{-3}), and low detection limit (2 ng m^{-3}) [83]. Relative intrinsic error of measurement is not more than ±20% according to the instrument producer. GEM fluxes were recorded in a plexiglass chamber, which was sealed and connected to the Lumex through two polyethylene tubes (Fig. 2). The tests were always carried out protecting the chamber from solar or artificial irradiation in order to replicate the normal condition of the samples, which are preserved in closed cabinets, and to exclude the possible effect of Hg photolytic reduction. Moreover, the flux chamber experiments were carried out in a room below ground level to minimise T variations. T (C°) and RH (%) inside the chamber were measured by an Onset Hobo U12–013 datalogger (accuracy ± 0.35 °C and ± 2.5%).

The GEM flux (F, ng m^{-2} h^{-1}) inside the chamber was calculated as follows:

$$F = \left(\frac{dC}{dt}\right) \times \frac{V}{A}$$

where dC/dt is the variation of GEM concentration over time inside the chamber, V is the volume of the chamber (0.055 m^3), and A is the surface of the herbarium sample placed inside the chamber (about 27 cm^2). The GEM increase over time (dC/dt) was calculated using the ProFit v.7.0.19 software (Quantum Soft) as the slope of the line fitting the GEM concentrations versus time, assuming an acceptable linear regression if $R^2 \geq 0.8$.

The GEM fluxes from each FI sample were measured at three different RH conditions, as reported in Table 2. First of all, GEM fluxes were recorded in background environmental conditions (start test); then, the RH inside the flux chamber was varied by inserting silica gel (dry test) or water-filled containers (wet test). Each test was replicated three times. For each test, the GEM concentration inside the chamber was recorded six times, each for a 5-min period (frame time 1 s) at regular time intervals of 25 min, for a total duration of 2.5 h. In the case of Camp3 and Camp4, GEM concentrations higher than the upper detection limit of the Lumex (50,000 ng m^{-3}) were reached before the end of the wet tests. Therefore, in order to measure the GEM flux, a single, uninterrupted, 15-minute measurement of GEM concentration was performed (fast-wet test, Fig. 2) and, similarly to the other tests, repeated three times for each sample.

Before the start of each test, the chamber was cleaned with an alcohol solution, and a blank measurement was performed by recording the GEM concentration inside the empty chamber for 5 min. The flux values obtained from these blank measurements were subtracted from those calculated for the individual tests.

Table 2
Protocol employed to measure GEM fluxes from the herbarium samples at different relative humidity (RH) conditions in the non-steady state flux chamber.

Test name	RH conditions
start test	Environmental RH (50–75%)
dry test	Low RH (≤ 40%)
wet test	High RH (≥ 80%)
fast-wet test	

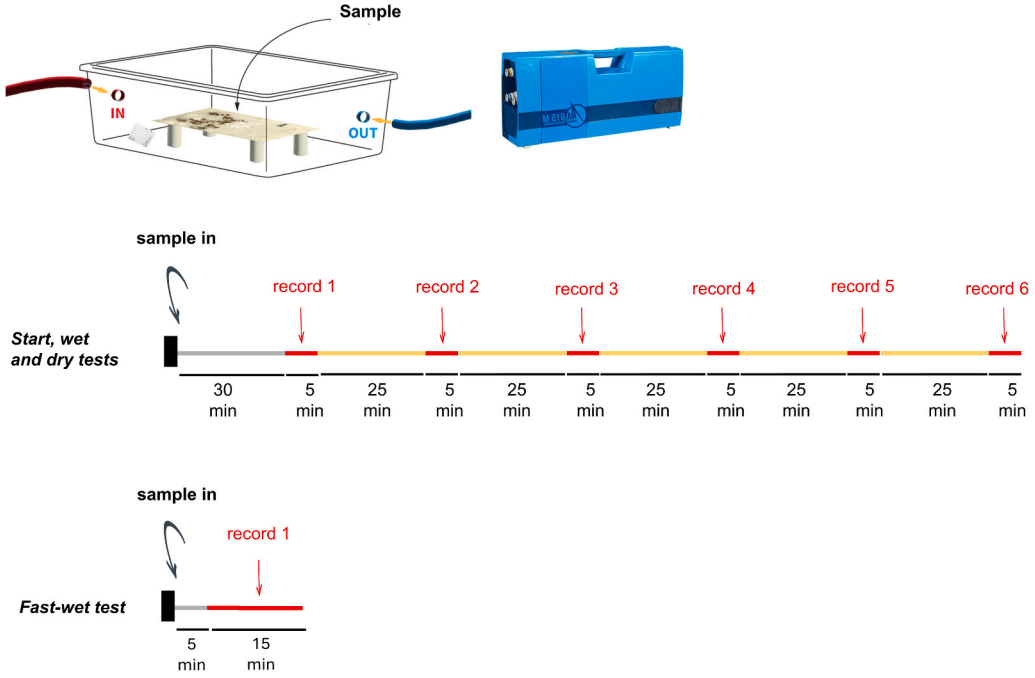

Fig. 2. Sketch of the experimental set-up for the flux chamber measurements (top) and scheme of the start, dry, wet (centre) and fast-wet tests (bottom) used to measure the GEM fluxes from the herbaria samples.

In all the experimental tests, T was not completely stable, having an average value of 20 °C with a standard deviation of 1.2 °C. Therefore, to better compare the results, GEM fluxes were normalised to 20 °C following the Arrhenius equation as proposed by Song and Van Heyst [87] for a similar experiment:

$$F = F_T \times \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{293}\right)\right],$$

where F is the GEM flux normalized to 20 °C (293 K), F_T is the measured GEM flux, T is the mean experimental T measured during the test, R is the gas constant (8.314 J $mol^{-1}K^{-1}$), and E_a is the Arrhenius activation energy; the latter was set to 58,576 J mol^{-1}, i.e. the enthalpy of vaporization of Hg^0, as proposed by Scholtz et al. [82]. The data prior to normalization, as well as the plot of non-normalized GEM fluxes versus temperature, are reported in Table S1 and Figure S1 of the Supplementary Information.

3.1.1. Flux calculation and uncertainty

As previously discussed in 3.1, for each test type, which was replicated for three times, six independent 5-minutes GEM measurements were performed every 25 min using the Lumex analyser, with an acquisition frequency of 1 s, resulting in 300 data points per run. The mean GEM concentration and the corresponding standard deviation were calculated from the 5-minute dataset using Microsoft Excel. The same procedure was applied to all six measurements for each test, thus resulting in six mean GEM concentration values and standard deviation values per test replica. The resulting values were then imported into the ProFit v.7.0.19 software package (Quantum Soft) for data analysis. A linear regression was performed using the Levenberg-Marquardt algorithm, a damped least-squares optimization method which minimizes the sum of squared residuals between experimental data and the fitted model. The fitting procedure provided the best-fit straight line together with its slope, a, and the associated uncertainty, Δa. The slope was subsequently used as the concentration rate term (dC/dt) in the flux calculation. Assuming negligible uncertainties in the chamber volume and the sample surface area measurements, the uncertainty associated with the calculated flux was taken to be equal to the uncertainty of the fitted slope, Δa. The RH-GEM relationship was modelled using the ProFit software. Finally, data of the three replicates of each test (start, dry, and wet) were averaged, and the relative standard deviation was calculated. Plots in Figs. 3, 4 and 5 were generated using the OriginPro 2020 software (OriginLab Corporation).

3.2. GEM, T, and RH monitoring in the Herbarium halls

GEM concentrations were recorded continuously along with T and RH values on the first floor of the FI, in order to compare the data obtained in the non-steady state flux chamber with the real system of the herbarium. On the first floor, Hg concentrations among halls are almost homogeneous [21].

Acquisitions were performed in different seasons with the Lumex operating continuously, taking a measurement per minute, for a time span of at least 24 h while the ACS was first off (by night) and then on (during the day). Shorter records of 4 h with the ACS on were also acquired. T (°C) and RH (%) values were recorded using the T and RH datalogger described in 3.1. During all these acquisitions, the ventilation rate system was switched off.

GEM (ng m^{-3}), T (C°), and RH (%) recordings are reported as average values ± standard deviation, min - max throughout the text: these data are reported for the time intervals with the ACS both on and off. The data recorded in the Herbarium halls were plotted using OriginPro 2023 software (OriginLab Corporation). The effect of ACS on Hg concentrations and RH was investigated using the non-parametric Mann–Whitney test, due to the non-normal distribution of data. The test was performed by comparing GEM concentrations and RH values recorded when the ACS was turned on with those recorded when the ACS was off. The analysis was carried out using R-Studio software [74], with a significance level equal to 0.05.

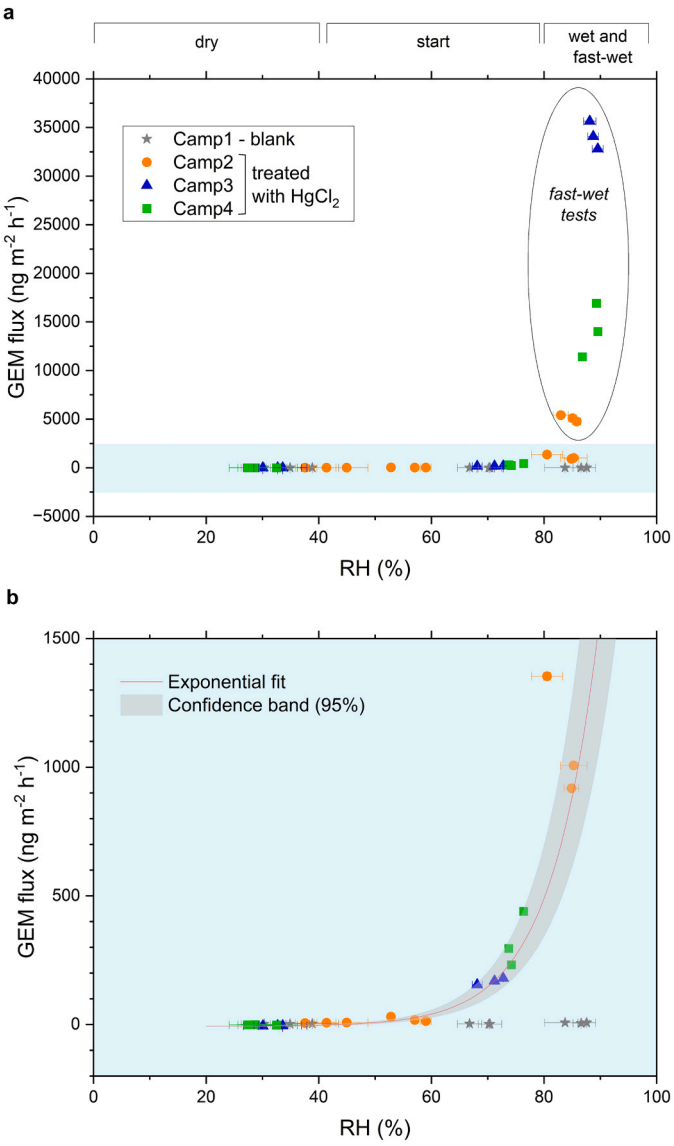

Fig. 3. Gaseous elemental mercury (GEM) fluxes as a function of relative humidity (RH). (a) GEM fluxes measured under dry, wet, and fast-wet conditions for different samples. The error bars associated with the GEM fluxes are smaller than the plotted symbols. (b) Zoom of panel (a) excluding the fast-wet tests; the red line represents an exponential fit to the data from the samples treated with $HgCl_2$.

Moreover, selected time series, which presented clear oscillations in T, RH and GEM induced by the ACS, were subjected to spectral analysis to identify possible common characteristic frequencies between the three parameters. The GEM concentration time series were first regularized to a uniform temporal resolution of 1 Hz. Missing and invalid values (e.g. values ≤ 0) were identified and grouped into consecutive gaps of varying duration (which were never longer than 40 s). Single-sample gaps were treated by calculation of the nearest neighbours mean, while gaps longer than one second were reconstructed using a stochastic modelling approach. To preserve the properties of the GEM signal, including variance and temporal dependence, missing data were reconstructed using a conditional stochastic simulation based on the AutoRegressive Integrated Moving Average (ARIMA) model [55]. For each gap exceeding one second, a local temporal window containing

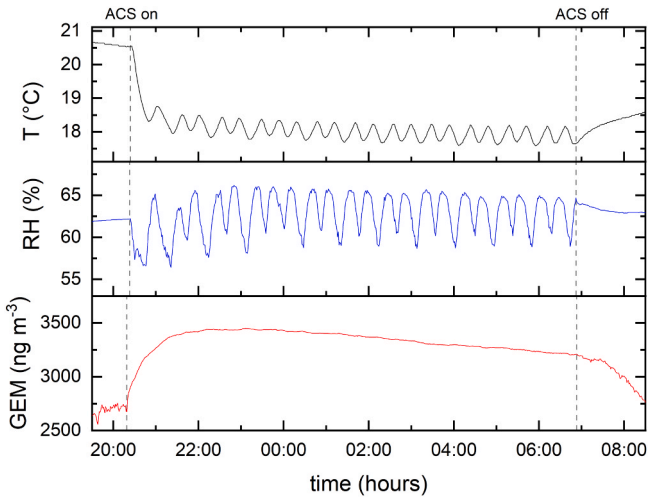

Fig. 4. Example of a 24-hour monitoring of GEM (ng m^{-3}), RH (%) and T (°C) at the first floor of the herbarium of the University of Florence (FI) during summer, showing the effect of the air conditioning system (ACS).

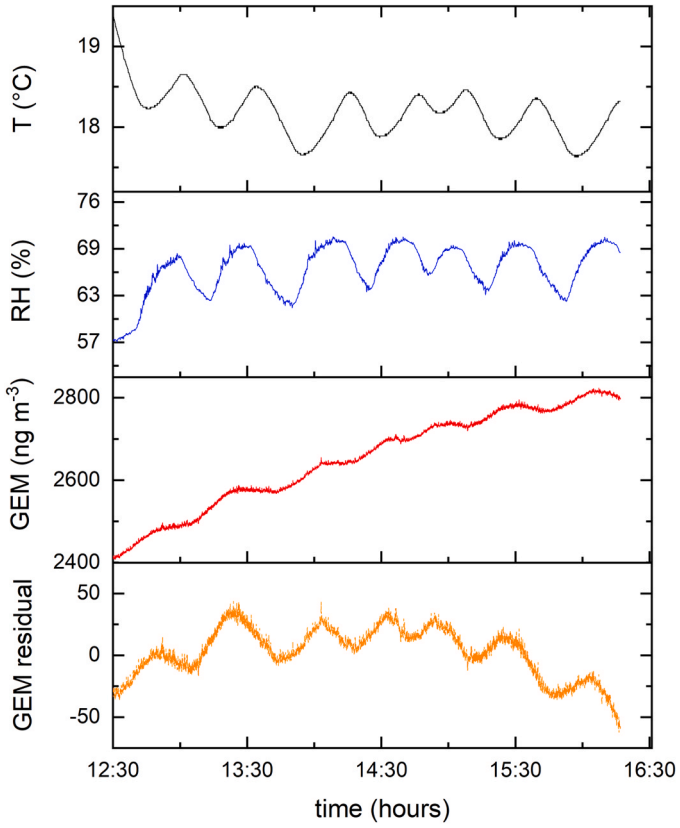

Fig. 5. Example of a 4-hour monitoring of GEM (ng m^{-3}), RH (%) and T (°C) with the air conditioning system (ACS) on at the first floor of the herbarium of the University of Florence (FI). GEM residuals (ng m^{-3}) are shown in the bottom panel.

valid observations before and after the gap was defined. Within this window, a non-seasonal ARIMA model was fitted. This approach is well-suited for high-frequency environmental measurements where preserving variability is essential [9]. This procedure was performed in RStudio environment [73] by means of multiple packages (dplyr, tidyr, ggplot2, forecast, imputeTS). Before spectral analysis, linear or polynomial fitting was performed on the corrected GEM time series to remove slow, non-stationary trends like long-term drifts of the signal [12]. Finally, spectral analysis was carried out on the time series of GEM residuals, T, and RH. Fast Fourier Transform (FFT) with Hanning windowing and amplitude correction was performed solely on the time series intervals in which the ACS was on. This method identifies the oscillation frequencies that characterize each time series [23,65,95]. Both polynomial fitting and spectral analysis were performed by means of OriginPro 2023 software (OriginLab Corporation).

4. Results

4.1. GEM fluxes from Herbarium samples and the effect of relative humidity

The results of the experiment measuring GEM fluxes from herbaria samples at different RH in the flux chamber are reported in Table 3 and Fig. 3.

The blank, non-poisoned sample (Camp1) showed a low GEM flux of 2.1 ± 0.5 ng m^{-2} h^{-1} at environmental conditions (start tests, RH = 72.3 ± 1.2%). No differences were recorded during the dry tests (2.3 ± 0.7 ng m^{-2} h^{-1}), despite that the RH inside the chamber was sensibly lower (35 ± 4%) compared to the initial conditions. The wet tests (RH = 84.4 ± 0.7%) provided slightly higher GEM fluxes but in the same order of magnitude (6.5 ± 1.2 ng m^{-2} h^{-1}).

Considering the $HgCl_2$-treated samples, GEM fluxes showed highly comparable trends. During the start tests they ranged between 21 ± 9 ng m^{-2} h^{-1} (Camp2 at RH = 50 ± 4%) and 320 ± 110 ng m^{-2} h^{-1} (Camp4 at RH = 76.2 ± 1.7%). The fluxes sensibly decreased during the dry tests, with the lowest value being slightly negative (Camp3, f = −4.9 ± 0.9 ng m^{-2} h^{-1} at RH = 34.5 ± 1.3%). On the contrary, the GEM concentrations strongly increased during the wet tests. The mean GEM flux from Camp2 at RH 71.0 ± 1.2% was 1090 ng m^{-2} h^{-1}, while GEM concentrations exceeded the Lumex upper detection limits (50,000 ng m^{-3}) in the case of Camp3 and Camp4, so that fast-wet tests (see 3.1 and Fig. 2) had to be performed. The highest flux was recorded during the fast-wet tests from Camp3 (34,000 ± 1400 ng m^{-2} h^{-1}) at RH 92.0 ± 0.8%. The GEM fluxes during the fast-wet tests were sensibly high also for the other two FI samples (5100 ± 300 ng m^{-2} h^{-1} from Camp2 and 14,000 ± 2800 ng m^{-2} h^{-1} from Camp4) compared to the start tests.

Finally, it is worth noting that the same trends described above are also evident in the unnormalized data (i.e., without correction to 20 °C), indicating that the limited temperature variations during the experiments were not significant (see Table S1 and Figure S1).

Table 3
Average GEM fluxes (ng m^{-2} h^{-1}) normalised to T = 20 °C and corresponding RH values (%) recorded in the flux chamber from Herbarium samples of the Natural History Museum of the University of Florence. Data are reported as average values ± standard deviation (σ) of three tests.

Sample	Test	F (ng m^{-2} h^{-1}) ± σ	RH (%) ± σ
Camp1	start test	2.1 ± 0.5	72.3 ± 1.2
	dry test	2.3 ± 0.7	35 ± 4
	wet test	6.5 ± 1.2	84.4 ± 0.7
Camp2	start test	21 ± 9	50 ± 4
	dry test	6.6 ± 1.1	39 ± 4
	wet test	1090 ± 230	71.0 ± 1.2
	fast-wet test	5100 ± 300	89.92 ± 0.09
Camp3	start test	168 ± 13	75.8 ± 2.5
	dry test	−4.9 ± 0.9	34.5 ± 1.3
	fast-wet test	34,000 ± 1400	92.0 ± 0.8
Camp4	start test	320 ± 110	76.2 ± 1.7
	dry test	−1.7 ± 0.8	30.3 ± 2.8
	fast-wet test	14,000 ± 2800	89.0 ± 1.4

4.2. The monitoring of GEM in the herbarium halls

The monitoring of GEM and environmental variables during all the seasons of the year on the first floor of the FI revealed GEM concentrations always higher (difference statistically significant at the $\alpha = 0.05$ level) when the ACS is turned on (Table 4, Fig. 4), confirming that the previously observed phenomenon [21] was not an isolated event.

Data from different acquisitions show high variability (Table 4), which reflects not only seasonality but also the typical complexity of the FI halls, a real environment, with movement of people and samples during the day. However, the following general trends are confirmed. The ACS-induced decrease in T is followed by an increase in both RH and GEM concentration. Higher variations in T, typical for example during summer, correspond to higher variations also in the other two parameters. The variations in T and RH are not immediately evident from the average values reported in Table 4, as these parameters do not exhibit a simple monotonic variation but rather a pronounced oscillatory behaviour induced by the ACS operation, as discussed below. However, a clearer distinction can be observed when considering the full range of values (minima and maxima), which consistently indicate that ACS operation promotes conditions associated with lower T and higher RH levels. This was further supported by the Mann–Whitney test, which yielded a p-value < 0.05.

A delay between the T decrease and the RH and GEM increases is often - but not always - observed, and it is likely to be attributed to the time needed by the materials in the FI - dry plants, herbarium sheets, cabinets, etc. - to stabilize to the new T conditions.

The highest increase in GEM concentrations, compared to the background values, i.e. when the ACS is turned off, was recorded during summer (2460 ± 140 ng m^{-3} with ACS off, and 3240 ± 160 ng m^{-3} with ACS on; see example in Fig. 4). During spring the average concentrations were 4600 ± 400 ng m^{-3} (ACS off) and 5170 ± 270 ng m^{-3} (ACS on), during autumn 2880 ± 210 ng m^{-3} (ACS off) and 3400 ± 190 (ACS on), and during winter 2940 ± 120 ng m^{-3} (ACS off) and 3200 ± 180 ng m^{-3} (ACS on) (Table 4).

Average T values ranged between 19.2 and 20.4 with the ACS off and from 17.8 and 19.2 with the ACS on, while average RH ranged from 45.3 ± 0.8 to 61.9 ± 0.9% with ACS off, and from 49 ± 3 to 62 ± 3% with the ACS on (Table 4).

Examining more in detail the herbaria hall response when the ACS is switched on, it was observed that the T decreases over time until, as expected, the ACS reaches the programmed T value (Fig. 4). Subsequently, the T begins to oscillate over time (Fig. 4). These fluctuations arise from the on-off system control: once the desired T is reached, the system switches off, allowing the T to rise again, and then switches back on (Fig. 4). The RH values show a generalised increase as T decreases, oscillating as well, most likely due to its inverse dependence to T. GEM exhibits a clear generalised increase after the ACS starting; it shows a less pronounced periodic behaviour compared to T and RH, which however can be better appreciated on shorter records and on GEM residuals series obtained after the polynomial fitting described in chapter 3.2 (Fig. 5). The periodic behaviour of T, RH and GEM residuals was investigated more in detail by Fourier spectral analysis, which showed that all the three parameters display common oscillation periods when the ACS is on (Table 5). The latter varies approximately between half an hour to one hour, with slight variations among the different time series examined, which are likely to be due to day-to-day differences in the behaviour of the ACS in response to the prevailing microclimatic conditions.

Table 4
GEM concentrations (ng m^{-3}), T (°C), and RH (%) recorded at the first floor of the Herbarium Centrale Italicum when the air-cooling system is turned off and on.

Season		air-cooling system off			air-cooling system on		
		average ± σ	min	max	average ± σ	min	max
winter	GEM (ng m^{-3})	2940 ± 110	2730	3210	3200 ± 180	2800	3500
	T (°C)	20.4 ± 0.5	19.6	21.0	19.2 ± 1.1	16.8	20.4
	RH (%)	45.3 ± 0.8	44.4	47.0	49 ± 3	45	56
spring	GEM (ng m^{-3})	4600 ± 400	4200	5200	5170 ± 270	4120	5420
	T (°C)	19.2 ± 1.2	16.3	20.6	17.8 ± 1.5	16.1	21.1
	RH (%)	59.8 ± 1.2	58.3	66.4	60 ± 3	54	68
summer	GEM (ng m^{-3})	2460 ± 140	1870	2970	3240 ± 160	2490	3450
	T (°C)	19.9 ± 0.6	18.4	24.8	18.1 ± 0.6	17.4	20.5
	RH (%)	61.9 ± 0.9	52.4	63.0	62 ± 3	54	66
autumn	GEM (ng m^{-3})	2880 ± 210	2650	3350	3400 ± 190	2920	3760
	T (°C)	19.6 ± 0.4	19.0	20.0	19.0 ± 0.3	18.5	19.7
	RH (%)	53.8 ± 0.6	51.1	56.8	54.2 ± 0.3	50.3	60.6

5. Discussion

A strong positive correlation was observed between the emission of GEM from herbarium samples and the RH of the surrounding air. This relationship was consistently highlighted by both the controlled experiments performed in the non-steady state flux chamber and the in-situ monitoring of GEM in the FI halls.

$HgCl_2$-treated samples exhibited markedly higher GEM fluxes when RH increased in the flux chamber. On the contrary, during the dry tests (RH = 30–40%) fluxes decreased to nearly zero. In two cases (Camp3 and Camp4), they even became slightly negative. Similar observations of negative GEM fluxes have been reported in the literature (cf., [19]) and are most likely attributable to a combination of instrumental uncertainty and minor sink effects, such as adsorption of GEM onto chamber surfaces, silica gel, or the sample matrix itself. At any rate, these small fluctuations around zero are not significant for the identification of the main trends, since the observed RH-induced variations in GEM fluxes are one to two orders of magnitude larger (tens to hundreds of ng m^{-2} h^{-1}).

The fluxes showed indeed a clear and consistent trend, suggesting that, although the number of samples was limited, it was sufficient to provide process-based evidence of a real effect.

In addition to this, it is noteworthy that the trend of GEM fluxes from

Table 5
Characteristic oscillation shared by T, RH and GEM time series obtained by Fourier Transform analysis of selected registrations in the herbarium of the University of Florence (FI).

Time series	Oscillation period (min)		
	T	RH	GEM
1	37	37	37
2	42	42	42
3	37	37	37
4	27	27	27
5	66	66	66
6	33	33	33
7	80	71	71
8	66	66	66

the poisoned samples as a function of RH (dry, start and wet tests) can be well described by the empirical exponential function

$$F = a_1 + a_2 \times ((RH - a_3)/a_4),$$

with fluxes starting to rise significantly around 60–65% RH (Fig. 3b). The four parameters a_{1-4} were obtained by fitting the data using the ProFit v.7.0.19 software package and resulted $a_1 = -6.5 \pm 0.4$ ng m^{-2} h^{-1}, $a_2 = 8.84 \pm 0.27$ ng m^{-2} h^{-1}, $a_3 = 40.6 \pm 0.4\%$ and $a_4 = -9.09 \pm 0.12\%$.

As no dedicated studies have specifically investigated the effect of humidity on GEM emissions from paper, a comparison with other matrices and pollutants is necessary. As discussed in the introduction, in the case of soils a weak negative correlation between RH and GEM fluxes is generally reported [34,40,56,92,33], in contrast to the observations made in this study. However, several studies highlighted that higher moisture contents in soils result in higher GEM emissions (see [89], and references therein), particularly in the case of precipitation events, which induce an immediate spike in GEM fluxes [87,54,41], while the linear correlation with T weakens [82]. Moreover, if the soil moisture content before the rain event is low, the rainfall triggers an immediate release of Hg, while this effect is attenuated if the soils are wet [41]. In the case of paper, a behaviour similar to that observed for soils is evident: a marked increase in emissions occurs when herbarium samples, initially dry, are exposed to moisture. In this context, the process does not involve direct wetting but only an increase in the air humidity, which is sufficient due to the high hygroscopicity of paper.

When considering other pollutants, it is noteworthy that the observed exponential trend is consistent with findings for VOC emissions from paper and board, which similarly exhibit a sharp increase with rising RH, following an exponential relationship [93,97,5]. Two main mechanisms have been proposed to explain this kind of response in previous studies about VOCs emissions: (i) the moisture-induced swelling of the paper matrix, which mechanically facilitates the migration of embedded pollutants, and (ii) the high polarity of water molecules, which outcompete other compounds for binding sites on the negatively-charged paper surface [93]. Mechanism (i), in particular, could well explain the release not only of VOCs but also of Hg compounds from cellulose-based materials, including both support paper and plant samples.

It is important to note that, in the case of herbaria samples, the actual oxidation state of Hg in the paper sheets and the plant samples is uncertain. Direct evidence on samples from other herbaria suggests that Hg might occur mainly as Hg^{2+}, forming Hg sulfide compounds, such as metacinnabar, also accompanied by residual $HgCl_2$ and HgO [31]. In agreement with this, particles with Hg and S in 1:1 at. ratio were observed in the deposited particulate matter recovered at the FI [20], and a good correlation between Hg and S was also highlighted on the FI herbarium plants and paper sheets by ion beam analysis techniques [63]. XANES analysis was recently performed and would provide additional insights. At any rate, a reduction process converting Hg^{2+} to Hg^0, which then volatilizes, is certainly ongoing as evidenced by the high GEM concentrations detected in air. This reduction may be further promoted by the presence of reactive functional groups, such as aldehydes and carboxylic acids, which are typical of degraded paper [44]. High moisture levels, in turn, are known to accelerate paper degradation by acid hydrolysis and oxidation [96]. This chemical mechanism could further contribute to the observed Hg^0 emission enhancement under high humidity conditions.

The observed threshold between 60% and 70% RH is also in good agreement with the literature on paper-water interaction. According to Nilsson et al. [67], the dependence of water diffusivity in paper increases strongly at RH above 60%. Similarly, the isotherms correlating RH with the equilibrium moisture content for paper show an almost linear trend for RH < 50%, which then increases more sharply at higher RH [37,76], meaning that, above this threshold, paper absorbs more water to reach equilibrium.

The monitoring in the herbarium halls confirmed that increases in RH following ACS activation were systematically accompanied by elevated GEM concentrations, despite the T decrease (Fig. 4). Temperature and RH exhibit an inverse relationship, while RH and GEM follow the same general trend. Minor delays between the latter two variables can reasonably be explained by the time required for system re-equilibration and adjustment. The strong interconnection between environmental parameters and GEM was further confirmed by the FFT analysis: the ACS on-off behaviour allowed us to verify that the GEM time series oscillates at the same frequency as T and RH.

In addition to this, other factors could contribute to the observed increase in GEM when the ACS is activated, including the potential contamination of the system components hypothesized in previous studies [21,38,8]. It is to note that GEM concentrations near the ACS air inlet and outlet were checked using the LUMEX with the system both on and off. No increase in concentration was observed at the outlet when the system was operating (Table S2), which would have indicated potential contamination and Hg emission from within the system. Therefore, although contamination of the ACS system cannot be completely excluded, it appears unlikely to be a sufficient explanation for the observed increase in GEM concentrations. Possible turbulence and changes in indoor air circulation induced by the ACS are unlikely to significantly affect the levels of GEM detected in the halls, since the system is closed and nearly homogeneous for GEM [21].

The laboratory experiment presented in this study was designed to isolate and amplify RH variations in order to clearly investigate their effect on GEM emissions and extrapolate the underlying trend. The RH fluctuations recorded in the herbarium halls (approximately 44–68%), even if smaller, fall within the broader range explored in the laboratory (approximately 30–92%). Notably, these in-situ values lie close to the threshold (~60–65% RH) at which a marked increase in GEM emissions was observed in the experiments. This supports the relevance of the laboratory findings for real-world conditions, both in the herbarium FI and in other contaminated herbaria where ACSs are absent or less effective.

The clear effect of RH on GEM emissions highlights the importance of controlling this parameter in Hg-polluted indoor environments such as herbaria, indicating that maintaining moderately low RH can be an effective strategy to reduce GEM emissions. In this scenario, the key role of RH in the preservation of the specimens must also be taken into consideration. The first and most important Italian technical standard on the topic (D.M. 10/05/2001, [24]) recommends 40–60% RH as the optimal range for the chemical and physical conservation of herbaria and botanical collections. The same document specifies 40–55% RH (with a maximum daily fluctuation of 6% RH) and 18–22 °C (with a maximum variation of 1.5 °C) to prevent microbial deterioration of paper collections. Similarly, international standards for the conservation of archives and library materials (e.g., ISO 11799:2003) generally accept 60% as the upper RH acceptable threshold [51]. Notably, these ranges appear to be also suitable for minimising GEM emissions, which increase sharply above about 65% RH according to our data (Fig. 3). Conversely, RH levels below 40% would be too dry for the preservation of herbarium specimens and do not offer significant additional benefits in reducing GEM emissions (Fig. 3, Table 3).

It is also interesting to note that the most recent literature and legislation on microclimatic control in museum buildings [3,57,58,59,29] do not provide definite T and RH ranges ideal for conservation, rather focusing attention on the need to avoid strong oscillations and taking into account the historic climate in which the samples have acclimatized [58]. In the specific case of the FI, RH values measured on the first floor (equipped with ACS) range between approximately 45% and 60%, falling within the recommended range. However, the strong fluctuations, occurring both during transitions when the ACS is switched on or off, and even while it is operating, should be avoided. Effective

microclimatic control is therefore necessary in the herbarium to minimise fluctuations in RH and T. Based on our findings, maintaining RH around 50% (40–60%) appears to be the most suitable strategy for both the conservation of samples and the reduction of GEM emissions. Any adjustments should be implemented gradually, with continuous monitoring of specimen conservation during this stabilisation process as suggested by international standards [29].

6. Conclusions

This study combined an in-lab experiment and in-situ monitoring in the museum halls of the FI to investigate the effect of humidity conditions on GEM emissions from herbarium samples contaminated with $HgCl_2$ due to past conservation treatments. Both approaches clearly highlighted a strong, direct, and positive correlation between RH and GEM levels. As evidenced by many authors (see [21] and references therein), Hg^0 pollution in herbaria worldwide represents a serious concern for both visitors and staff. Moreover, ensuring safe access to these collections is fundamental for state-of-the-art research on biodiversity and climate change as demonstrated by multiple recent studies [16,52,62,91]. A few approaches have been attempted to reduce Hg^0 emissions, but with only limited success [31,30]. The confinement of Hg^0 is particularly challenging because herbaria generally contain vast numbers of specimens (approximately 2 million samples in the case of FI), making strategies based on individual-sample treatments largely impractical. Our data suggests a potential solution to this problem through the simple control of RH and T in herbarium halls. While appropriate T values, approximately between 18 and 22 °C, are already achieved in the FI halls provided with ACS, we recommend that low RH be also maintained in the herbarium, preferably around 50%, and with minimal fluctuations. This would improve the air quality, ensuring at the same time the proper conservation of the collections as recommended by international standards and museum practice.

The flux chamber experiments provided controlled and reproducible conditions that allowed to isolate the effect of RH, offering useful insights for real-world (i.e. herbarium) conditions. It raises the RH control as a key factor in managing GEM emissions and supporting risk assessment strategies.

The highlighted behaviour of paper materials, which constitute the main sources of Hg in herbaria, is consistent with their hygroscopic nature, as their physical and chemical properties are strongly influenced by RH variations. The increase in Hg^0 release due to moisture uptake likely results from the paper fibres swelling, the preferential occupation of paper binding sites by water molecules, and possibly enhanced reduction by reactive functional groups formed during humidity-induced paper degradation.

This study focused on the behaviour of the herbarium specimens and of the paper that encloses them. However, as highlighted by Cabassi et al. [13] and Ciani et al. [22], the wood of the cabinets is impregnated with Hg^0 as well, indicating that not only the paper but also the wood contributes to the GEM contamination in the herbarium halls as a secondary source. Therefore, a study of the behaviour of wood as a function of RH and the possible treatments that the wood cabinets may undergo to minimise the Hg flux is currently ongoing and will be the subject of future publications.

Finally, the importance of RH control on indoor GEM emissions highlighted in this study may be relevant to other Hg-polluted indoor scenarios, including old dental offices [38,8], medical and educational institutions where Hg-containing instruments were stored [64], and industrial plants [66].

Environmental Implication

Herbaria represent essential infrastructures for biodiversity science but they are also a persistent and global source of indoor mercury pollution due to past $HgCl_2$ treatments. This study demonstrates that relative humidity (RH) is a key driver of gaseous elemental mercury (GEM) emissions from contaminated cellulose-based materials. Laboratory experiments and in-situ monitoring show that emissions increase sharply when RH exceeds 65%. These results identify indoor humidity as a critical control parameter. Maintaining stable RH within 40–60% can substantially reduce emissions, providing a simple and scalable mitigation strategy applicable to museums and other mercury-contaminated indoor environments, therefore limiting human exposure to GEM.

CRediT authorship contribution statement

Lorenzo Lastrucci: Writing – review & editing, Investigation. **Pilario Costagliola:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Massimo Chiari:** Writing – review & editing, Supervision, Formal analysis. **Marco Benvenuti:** Writing – review & editing, Supervision, Funding acquisition. **Gaia Marsiaj:** Writing – review & editing, Visualization, Investigation, Formal analysis. **Valentina Rimondi:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Alessia Nannoni:** Writing – review & editing, Visualization, Formal analysis, Data curation. **Rosarosa Manca:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis, Data curation. **Francesco Ciani:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2026.142990.

Data Availability

Data will be made available on request.

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