



A Simplified Drying Procedure for Analysing Hg Concentrations

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Abstract Mercury (Hg) in peatlands remains a problem of global interest. To mitigate the risks of this neurotoxin, accurate assessments of Hg in peat are needed. Treatment of peat that will be analysed for Hg is, however, not straightforward due to the volatile nature of Hg. The drying process is of particular concern since Hg evasion increases with the temperature. Samples are, therefore, often freeze-dried to limit Hg loss during the drying processes. A problem with freeze-drying is that cost and equipment resources can limit the number of samples analysed in large projects. To avoid this bottleneck, we tested if drying in a 60 °C-degree oven could be an acceptable

alternative to freeze-drying. We both freeze-dried and oven-dried (60 °C) 203 replicate pairs of peat samples, and then examined the differences in total Hg concentration. The Hg concentration differed significantly between the two drying methods with a median Hg deficit in oven-dried samples of 4.2%. Whether a 4.2% deficit of Hg depends on one's purpose. The lower median Hg concentration in oven-dried samples has to be weighed against the upside efficiently drying large sets of peat samples. By freeze-drying a subset of the samples, we fitted a function to correct for Hg loss during oven-drying ($y = 0.96x + 0.08$). By applying this correction, the freeze-drying bottleneck could oven-dry large-scale inventories of total Hg in peatlands with results equivalent to freeze-drying, but only have to freeze-dry a subset.

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1 Introduction

Mercury (Hg) is a potent neurotoxin contaminating a large portion of the soils and lakes in the world. Hg is a naturally occurring element, although anthropogenic emissions today equal three times the natural emissions to the atmosphere (Futsaeter & Wilson, 2013; Streets et al., 2019). The volatile nature of gaseous elemental mercury also enables long-range transport of Hg, making it a global

pollutant, and even remote areas are subject to Hg contamination (Åkerblom et al., 2014).

Increased awareness of Hg exposure has led to a systematic and successful international action to mitigate global Hg pollution. As a result, atmospheric Hg concentrations have been declining in recent decades (Obrist et al., 2018; Zhang et al., 2016). Hg deposition, however, continues to pose a serious environmental threat. Once introduced to an ecosystem, Hg will accumulate in the food chain, leading to possible human exposure. Hg dynamics in anoxic environments are particularly relevant to understand, because such conditions promote the formation of the toxic compound methyl mercury (MeHg) most prone to bioaccumulation (Branfireun et al., 2020; Wu et al., 2019). In the boreal biome, peatland ecosystems with high MeHg production potential constitute the major source of MeHg to the aquatic food chain (Bishop et al., 2020).

Inorganic Hg is the source for microbially mediated production of MeHg. In order to estimate and monitor potential MeHg production, it is crucial to have exact and reliable methods for quantifying Hg concentrations in peat. However, peatlands are strongly heterogeneous environments with a distinct microtopography resulting in a large variability in the accumulation of Hg, both spatially and vertically. Surveying total Hg in peatlands thus requires large sample sets. The volatile nature of elemental Hg also brings a risk of losing Hg when preparing and pre-treating samples for analysis (Martínez-Cortizas et al., 1999). A severe bottleneck for processing large Hg sample sets is drying, since high temperatures increase the risk of Hg volatilization, especially the volatile species elemental Hg (Hg(0)) (Fernández-Martínez et al., 2005; Hojdova et al. 2015). Freeze-drying of soil samples is therefore a common practice (Yang et al., 2017). Freeze-drying is done at low temperatures (i.e. $-50\text{ }^{\circ}\text{C}$) and, hence, may better preserve Hg in the sample. Despite the fact that freeze-drying prevents temperature-induced loss of Hg(0), it should be noted that also freeze-drying may cause sample processing artefacts. High vapour pressure at vacuum may result in Hg loss (Martínez-Cortizas et al., 1999). Freeze-drying is however seen as the best option available and the “gold standard” for drying soil samples, but it is at the same time an expensive and time-consuming method. Equipment resources can

thus limit the number of samples analysed in many projects.

Existing reports of Hg loss when oven-drying peat soil, as compared to freeze-drying, are few (Hojdová et al., 2015; Norton et al., 1997; Roos-Barraclough et al., 2002). The objective of this study was, therefore, to examine how well drying of peat soils at $60\text{ }^{\circ}\text{C}$ for 96 h replicates freeze-drying in terms of sample Hg concentration. If the deviation in measured Hg after drying at $60\text{ }^{\circ}\text{C}$ is insignificant, or systematic, relative to the results after freeze-drying, then oven-drying could be a faster, more affordable, and acceptable alternative to freeze-drying. Using 203 sample replicates and subsequent statistical analysis, our study constitutes a thorough investigation of the effects of oven-drying on Hg concentration. It is an important complement to the existing literature (Norton et al., 1997; Martínez-Cortizas, A., Pontevedra-Pombal, X., García-Rodeja, E., Nóvoa-Muñoz, J.C., Shoty, W. 1999; Roos-Barraclough et al., 2002; Fernández-Martínez et al., 2005; Hojdová et al., 2015; Yang et al., 2017) on sample preparation prior to Hg analysis of peat soil.

2 Methods

2.1 Sampling and Subsampling

Peat cores were sampled in June–August 2019 from eight peatlands (fens) located within a distance of 10 km near Umeå, Sweden [$63^{\circ}54'\text{N}$, $20^{\circ}36'\text{E}$]. For detailed site descriptions, see Wang et al. (2020). A cylindrical corer of 16 cm in diameter was used to extract 50-cm-deep peat cores with the mire surface as a reference level (modified from Clymo, 1988). The cores were kept in air- and watertight PVC tubes sealed with plastic caps and transported to the lab within 6 h after sampling. The samples were then placed at $-18\text{ }^{\circ}\text{C}$ and stored until subsampling.

Within 2 weeks after sampling, the cores were sliced into 2-cm (16 cm in diameter) discs using a bandsaw with a stainless-steel blade. Slicing was done in an $-18\text{ }^{\circ}\text{C}$ freeze room, both to yield undisturbed discs and also to avoid potential volatilization of Hg from the peat samples associated with thaw. The discs were then split into two half discs, generating two replicates of each sample. One was used for freeze-drying and one for oven-drying at $60\text{ }^{\circ}\text{C}$. Due

to a very high total number of samples along with equipment resource limitations, only a subset of the samples were freeze-dried. The rest of the samples were dried in a 60 °C oven for 96 h (until constant weight). To monitor the potential loss of total Hg during drying, 203 sample pairs from the same 2-cm disc (replicates) were both freeze-dried and dried at 60 °C in an oven. The oven-dried samples were placed in a desiccator for cooling immediately after drying to avoid moisture absorption during cooling.

The dry samples were homogenized by hand in a zip-lock bag to ensure a sample representative of each half disc. One gram of dry sample was then ground in a tube mill (IKA Tube Mill Control) during 10-s intervals to avoid heat generation during milling.

2.2 Analytical Methods

Analysis of total Hg was done using a Direct Mercury Analyzer (DMA 80) (Milestone, Shelton, CT, USA). Each peat sample was analysed in replicates and a certified reference sample was analysed every fifth sample for validation of the analytical precision (NIST 1515 – Apple Leaves Standard Reference Material® and ERMCD-281 – Rye Grass ERM® Certified Reference Material). The total Hg concentrations of the certified reference material had a precision within 2% of the mean total Hg concentration (95% confidence interval) of the reference value. The mean of our measurements underestimated the reported value of the standard by 5% and 4% respectively for NIST 1515 and ERMCD-281.

2.3 Statistical Methods

To test the hypothesis that Hg peat soil concentration measurements after oven-drying (60 °C) did not differ from the concentration determined after freeze-drying, we employed the Lin concordance correlation coefficient. This method is based on the assumption that one measurement technique represents “a gold standard “ (i.e. freeze-drying in our study), against which all other alternatives must be evaluated (Lin, 1989). This statistic is commonly used in medical and clinical studies for testing a new method when there is already an established methodology (King et al., 2007; Lin, 1989) (Microsoft Excel was used for statistical analysis and graphics).

In addition to a Pearson regression model, the Lin concordance correlation coefficient (CCC) also accounts for the agreement with a 45° line (Lin, 1989). To obtain the CCC, the Pearson correlation coefficient is multiplied by the deviation from the 45° line (C_b ; Eq. (2)). The CCC has values between –1 and 1, similar to the Pearson correlation coefficient, but the CCC only attains a perfect positive or negative correlation if the Pearson correlation coefficient equals unity and the absolute deviation from the 45° line is zero (Fig. 1) (King et al., 2007; Lin, 1989).

The relationship between the Lin and the Pearson correlation coefficients can be written as in Eqs. (1–4). In Eqs. (2–4), v measures the offset (Fig. 1b) in relation to the scale and ω represents the scale shift (Fig. 1c).

$$\rho_c = \frac{2\sigma_{12}}{\sigma_1^2 + \sigma_2^2 + (\mu_1 - \mu_2)^2} = \rho C_b \quad (1)$$

$$C_b = \frac{2}{\omega + \frac{1}{\omega} + v^2} \quad (2)$$

$$\omega = \frac{\sigma_x}{\sigma_y} \quad (3)$$

$$v = \frac{\mu_x - \mu_y}{\sqrt{\sigma_x \sigma_y}} \quad (4)$$

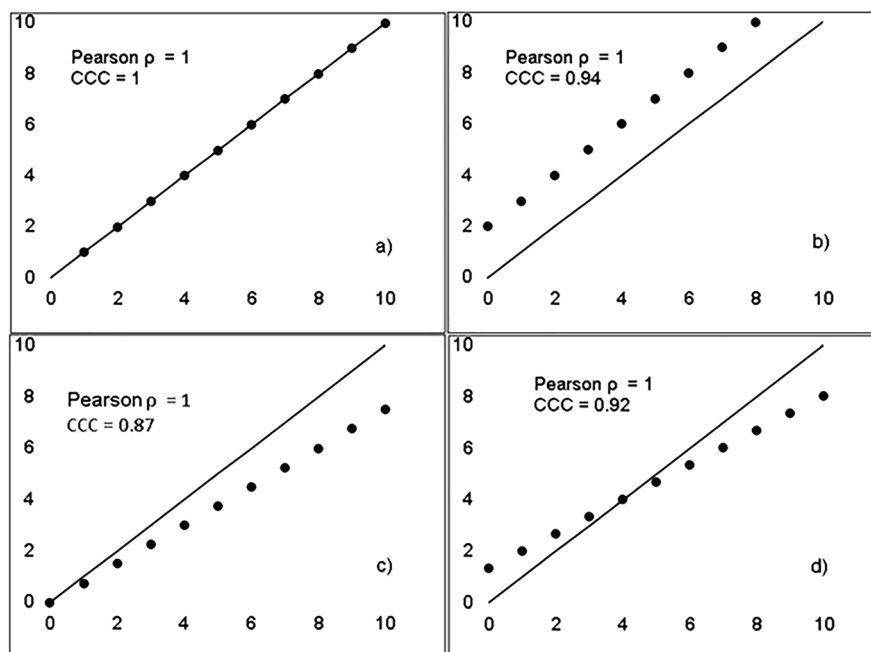
2.4 Wilcoxon’s Signed-Rank Test for Paired Samples

The data were log-transformed to attain normality. The Hg concentration in oven-dried samples was however still not normally distributed (Shapiro–Wilk test (Shapiro & Wilk, 1965)). We therefore employed the non-parametric tests equivalent to the t -test to test for a difference between the two drying methods; Wilcoxon’s signed-rank test for paired samples (Wilcoxon, 1945). The null hypothesis indicates no difference between the samples, while the alternative hypothesis is a difference with a significance level of 0.05.

2.5 Linear Regression Model and Validation

To predict Hg concentrations from freeze-dried samples using oven-dried samples, we fitted a linear function to the log-transformed Hg concentrations. The Y -value is thus freeze-dried samples and X -value oven-dried samples.

Fig. 1 a The theoretical patterns of correlation when the Lin concordance correlation coefficient (CCC) and the Pearson are both unity. b to d are examples of when the Pearson correlation coefficient is also unity but fails to detect a deviation between two methods, whereas the CCC does indicate a deviation.



To avoid over-fitting and to cross-validate our results, we employed K -fold cross-validation for our data set (Lachenbruch & Mickey, 1968). Our data set (203 sample pairs) was randomly assigned into 10 discrete groups of which seven of these groups had 20 members and three of them 21 members ($K=10$). Nine of the discrete groups were used as a training data set to fit a function to predict the 10th group for validation. The model was looped ten times until all groups had served as a validation set. By combining the predicted values from each of the ten cross-validation runs, we generated a parameter of predicted Hg concentration from freeze-dried samples. The predicted Hg concentrations were then compared to the observed Hg concentrations in freeze-dried samples to validate the model.

2.6 Moisture Content of Oven-Dried and Freeze-Dried Samples

The hygroscopic nature of peat can alter the accuracy of dry bulk density determinations, and hence the concentration of a substance, in the samples. We therefore tested for a difference in water loss between oven-dried and freeze-dried samples using a non-parametric correspondent to a pairwise t -test (Wilcoxon's signed-rank test for paired samples). The

data were not normally distributed, according to a Shapiro–Wilk test, and thus we used non-parametric statistics.

In addition to the Wilcoxon signed-rank test, we calculated the ratio between water loss during oven-drying and freeze-drying for each sample pair. Using all ratios, an average ratio was calculated to get a single quotient to compare oven-drying and freeze-drying. Identical water loss between the two drying methods would then yield an average quotient of 1.

3 Results

The Lin correlation coefficient yields a value of 0.91. The CCC uses both the offset (0.038) and scale shift (0.95) to calculate the C_b (1.0). The C_b is the correction factor that is multiplied by the Pearson correlation coefficient to obtain the CCC. While the CCC is suited for the comparison of two methods, it does not define the significance of a potential difference between the two methods. In Fig. 2, the regression line of log [Hg] from oven-dried vs. freeze-dried peat samples is not significantly different from a 1:1 line in terms of either offset (95% c.l.; $-0.02, 0.17$) or slope (0.90, 1.0).

One-tailed Wilcoxon paired signed-rank test showed a significant difference between the two drying methods at a 95% significance level ($p=0.017$). The median Hg deficit in oven-dried samples was 4.2%, with quartiles of -13% and 15%. The negative value indicates a negative Hg concentration deficit (i.e. gain). A deficit of 4.2% corresponds to a Hg loss rate of $19 \text{ ng kg}^{-1} \text{ h}^{-1}$ when drying samples in a $60 \text{ }^\circ\text{C}$ oven for 96 h.

Equation (5) stems from linear regression of Hg concentrations in freeze-dried (Y) and oven-dried (X) peat samples. Through this equation, Hg concentrations in freeze-dried samples can be predicted using oven-dried peat samples (see also Fig. 2).

$$y = 0.96x + 0.08 \tag{5}$$

By using K -fold cross-validation, we generated a dataset of predicted Hg concentrations in freeze-dried samples (Lachenbruch & Mickey, 1968). The result was an R^2 of 0.83. For reference, this R^2 value is similar to the R^2 value of the regression ‘oven-dried Hg concentration’ vs ‘freeze-dried Hg concentration’ which was also 0.83 (Fig. 3).

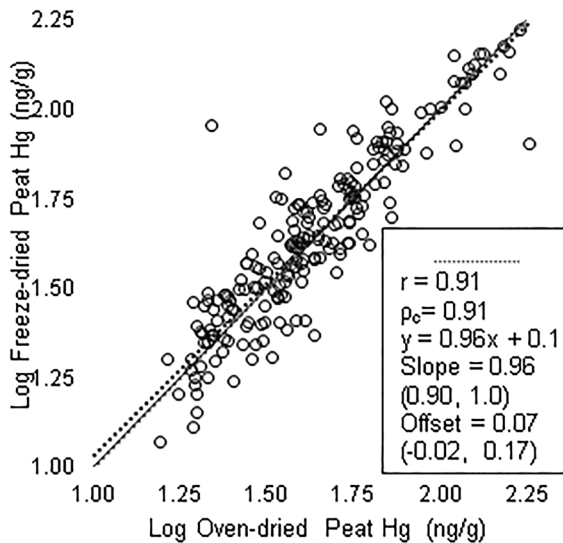


Fig. 2 Regression of oven-dried vs. air-dried peat log Hg concentration. The full line is a reference line with a 1:1 ratio. The dashed line is the regression line. r =Pearson’s correlation coefficient. ρ_c =Lin’s concordance correlation coefficient. y =linear regression line equation. For *Slope* and *offset*, the 95% confidence interval is reported in parentheses (-0.02, 0.17)

Residuals of the regression between predicted and actual freeze-dried Hg concentrations were plotted to further examine our model (Figs. S1–2). Though our residuals are not normally distributed ($p=0.05$; Shapiro–Wilk test (Shapiro & Wilk, 1965)), the residuals are symmetrically distributed around zero. There is thus no subspan in our range of investigated concentrations where our model is particularly weak (Table 1).

Based on a comparison of the water lost during drying, a pairwise Wilcoxon signed-rank test did not result in any significant difference in water lost during drying between freeze-dried and oven-dried samples ($p=0.52$, two-tailed, the average weight of freeze-dried samples being 0.042% larger than oven-drying.). A Pearson correlation between log-transformed water loss on freeze-drying vs. oven-drying indicated a correlation coefficient (r^2) of 0.94 ($p < 0.001$).

4 Discussion

Using oven-drying as an alternative to the more resource-demanding freeze-drying comes with the concern about Hg loss through volatilization in a heated oven (Hojdová et al., 2015;

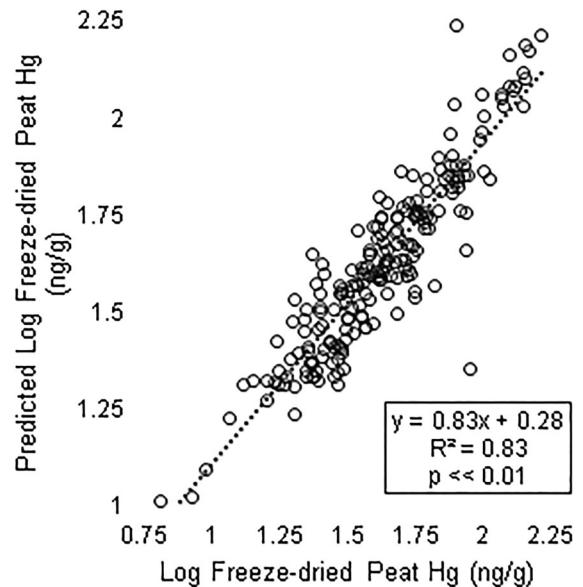


Fig. 3 Logarithm of observed Hg concentration from freeze-dried samples vs. predicted Hg concentrations of freeze-dried samples

Table 1 Summary of results

Statistical measure	Result
Pearson correlation coefficient ρ	0.91
Lin concordance correlation coefficient ρ_c	0.91
Accuracy C_b	1.0
Scale shift ω	0.95
Offset v	0.038
One-tail paired Wilcoxon signed-rank test, p -value	0.017
Median Hg deficit, oven-dried samples (%)	4.2
Hg loss rate ($\text{ng kg}^{-1} \text{h}^{-1}$)	19

Roos-Barraclough et al., 2002). The average 4.2% lower Hg concentrations found in 60 °C oven-dried peat samples relative to freeze-drying indicates that oven-drying does cause some Hg loss. It is likely that the loss of Hg we observed stems from the release of elemental Hg in our samples. Gaseous elemental Hg is volatile that is easily released into the atmosphere when exposed to temperatures approaching 100 °C (Windmüller et al. 1996), but it is evident that volatilization significantly affecting Hg determination in peat samples can occur at even lower temperatures.

Although some other comparisons of freeze-drying and oven-drying have been reported in the literature, few have looked specifically into the drying of organic soils, and specifically peat soils. Hg loss from oven-drying compared to freeze-drying of organic soil samples reported in the literature is scattered around zero (Table 2). Two of the four previous studies experienced similar Hg loss (0–5%) found in our study.

There are also studies of Hg loss when drying other soil types besides peat/organic soil. Some studies did not observe any Hg loss from mineral sediment samples dried in the 50–60 °C range (Crece-lius et al., 1975; Mudroch & MacKnight, 1994). Crece-lius et al. (1975) even dried estuarine sediments from Puget Sound, WA, USA, at 80 °C for 48 h without significant loss of Hg. For materials other than soil, e.g. animal tissue and wood studies, no Hg loss has also been reported after drying at 60 °C, as compared to freeze-drying (Schmidt et al., 2013; Yang et al., 2017). The variation in loss of Hg during oven-drying clearly indicates the importance of chemo-physical properties of the sample matrix in controlling the difference in [Hg] loss between oven- and freeze-dried samples.

Even if oven-drying gave a significant difference in peat [Hg] concentrations, 45% of the oven-dried samples had higher Hg concentration than the freeze-dried samples, which indicates that other factors than the drying temperature influenced our result (Fig. 1). A major source of the variation is most likely the variation between sample duplicates, i.e. the difference between analytical replicate samples. As mentioned in the method section, the paired samples used for comparing freeze- and oven-drying stem from a 2-cm slice of a 16-cm diameter disc split in two. It is possible that centimetre-scale differences in the peat influence the sample duplicates. Other studies have reported significant differences in Hg concentration between vegetation species growing side to side (Rydberg et al., 2010). We therefore stress the importance of careful homogenization before analysing peat samples for Hg.

Table 2 Loss of Hg when oven-drying organic soil samples reported in the literature and this study. Loss of Hg is defined as the Hg deficit after drying relative to freeze-frying if not otherwise specified

Study	Soil	Temp. (°C)	Drying time	Hg loss
Norton et al., 1997*	Peat	50	7 days	3.4% (relative 30 °C drying)
Roos-Barraclough et al., 2002†	Peat	60	5 days	~0%
Hojdova et al. 2015‡	Oe forest soil horizon	105	3 days	Significant Hg gain
Hojdova et al. 2015‡	Oa forest soil horizon	105	3 days	Significant Hg loss
This study	Peat	60	4 days	4.2%

*Norton et al. reported two values for Hg loss on drying from peat depths of 52.5 and 55 cm. The value found in the table below is an average of these two results.

†Although Roos-Barraclough et al. (2002) had several treatments for their peat samples, this value is from their experiment with unfertilised peat.

‡Value reported from uncontaminated soils.

It could also be discussed if 60 °C is the optimal temperature to dry peat in an oven. Drying at room temperature or at a maximum of 40 °C are two methods that have been proposed (de Groot et al., 1982; Ettler et al., 2007; Fernández-Martínez et al., 2005; Higuera et al., 2003). The problem is however that peat samples of our size contain around 100 g of water, with a high abundance of microorganisms in the samples. A week-long period for the peat samples to dry risks substantial microbial activity with concomitant biogeochemical changes, especially since room temperature, or slightly higher, is an optimum temperature window for many microorganisms found in peat soil (Liu et al., 2018; Schuster, 1991). Hg reduction by bacteria reducing Hg(II) to volatile Hg(0) is undesirable when preparing samples (Kritee et al., 2008; Zhou et al., 2020). Contrary to Hg evasion, cases have also been documented where samples dried in the open air have absorbed Hg from the laboratory surroundings (Roos-Barracough et al., 2002; Yang et al., 2017). Overall, the downsides of drying at low temperatures (20–50 °C) have to be balanced against the risk of Hg evasion at higher temperatures such as 60 °C.

Another cause for concern when drying peat samples is the absorption of moisture after drying. The risk of water vapour condensation and subsequent moisture absorption is particularly high when warm samples cool down at room temperature. However, even if following standard procedures, i.e. the oven-dried samples were immediately put in a desiccator for cooling, the risk of moisture absorption needs to be monitored. In the case of water absorption after oven-drying, the oven-dried samples would have been heavier than freeze-dried samples after cooling. The net loss of water, i.e. water lost during drying plus potential moisture absorption, did not differ significantly (oven-dried samples being 0.042% higher than freeze-dried samples) between oven-dried and freeze-dried samples. This number is also small in relation to the difference in Hg concentration of 4.2%. Moisture absorption and subsequent increase in density was thus not an explaining factor for the lower Hg concentration in oven-dried peat samples but might be a source of noise in these data.

To facilitate analysis of large sample volumes on total Hg concentrations in organic soils, we explored the possibility of freeze-drying a subset of the oven-dried samples to predict the Hg concentration in freeze-dried peat. Since the relationship between

oven-dried and freeze-dried samples is under the influence of other effects than the drying method (i.e. subsampling), the model would likely perform better if the effects of drying were isolated. Linear modelling to predict Hg concentrations stemming from freeze-dried samples therefore seems like a reasonable approach to adjust the Hg concentration in oven-dried peat. This methodology will simplify the processes of analysing the total Hg in peatlands. To use peatlands as an archive for past atmospheric Hg concentration or to assess the amount of Hg stored in the soil, sampling is necessary both depthwise and spatially. This renders a large number of samples where an evident bottleneck is the drying procedure. Our study offers a way of navigating around this obstacle, which will lead to more accurate assessments of Hg in peatlands and a step towards mitigating the risks of Hg exposure.

5 Conclusion

Oven-drying of peat samples at 60 °C resulted in a median 4.2% Hg loss (−13%, 15% quartiles). Whether this is acceptable or not depends on the purpose of the study. Equipment resource limitations could be a bottleneck to large-scale surveys of Hg content, especially in organic soils. Using oven-drying instead of freeze-drying could increase the number of samples analysed, which ultimately has to be weighed against the uncertainty that the risk of Hg loss brings. Using freeze-drying on a subset of samples could allow for the correction of any potential bias between the two methods.

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Data Availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics Approval The authors have no relevant financial or non-financial interests to declare.

Competing Interests The authors declare no competing interests.

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