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Assessing the air-surface exchange and fate of mercury in a subtropical forest using a novel passive exchange-meter device

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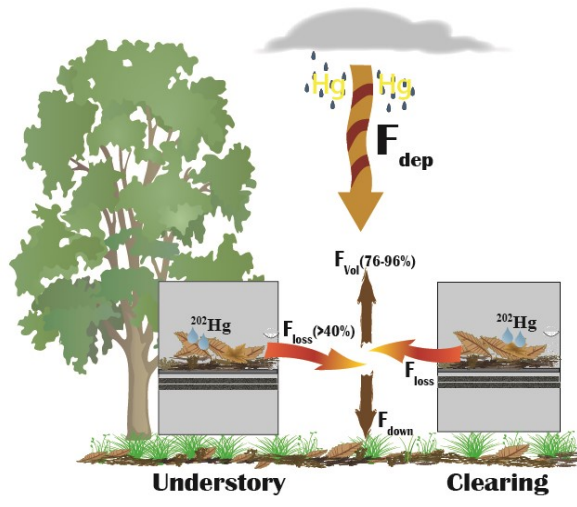
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1 **Abstract:** A novel passive exchange meter (EM) device was developed to assess air-surface exchange and leaching of Hg in a forest floor. Flux measurements
2 were carried out in a subtropical forest ecosystem during a full year. Over 40% of the Hg fixed in fresh forest litter was remobilized in less than 60 days in
3 warm and humid conditions as a response to rapid turnover of labile organic matter (OM). A two-blocks experiment including understory and clearing showed
4 that losses of Hg co-varied with seasonal conditions, and was significantly affected by forest coverage. The process controlling the bulk loss of total Hg from
5 the litter was volatilization, which typically represented 76% to 96% of the loss processes (F_{loss}). F_{loss} ranged 520-1370 ng m⁻² d⁻¹ and 165-942 ng m⁻² d⁻¹, in
6 the understory and clearing, respectively. On a yearly basis, deposition of airborne Hg exceeded the total losses by a factor 2.5 in the clearing and 1.5 in the
7 understory. Vegetation litter in this subtropical forest therefore represented a net sink of atmospheric Hg. This study provided a novel approach to Hg air-soil
8 exchange measurements and further insights on the link between Hg remobilization and OM turnover along with its environmental drivers.

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15 **Introduction**

16 Hg is an ubiquitous neurotoxic pollutant. Anthropogenic emissions of Hg to the atmosphere are primarily in the form of elemental mercury (Hg(0)) and divalent
17 mercury (Hg(II)), while redox chemistry controls the transition between these two species. Hg(0) is relatively volatile, whereas Hg(II) is less volatile, more
18 soluble and rapidly scavenged by wet depositions and direct adsorption to soils and vegetation¹⁻⁴. Evidences suggest that scavenging by forests is an important
19 sink of atmospheric Hg while organic soils and vegetation represent important long-term reservoirs⁵⁻⁸. Once in the soil Hg can undergo a methylation reaction
20 to form a highly neurotoxic and bioaccumulative species.

21 Earlier assessments estimated that the global annual Hg deposition through litterfall is $1180 \pm 710 \text{ Mg yr}^{-1}$, while the OM bounded Hg in background soils
22 and vegetation is in the order of 240,000 Mg, globally^{7,9}. This figure exceeds of two orders of magnitude the steady state atmospheric budget of total Hg
23 (~5,000 Mg) suggesting that re-mobilization from aging organic matter can easily affect atmospheric loads and, consequently, global distribution. Hg emitted
24 from soil organic matter (OM) and biomasses is calculated to represent 31% of the sum of total anthropogenic secondary emissions and natural sources⁴.

25 Hg(II) and Hg(0) can be adsorbed to OM through ionic exchange and simple condensation processes on organic surfaces, respectively¹⁰⁻¹². These bounds are
26 reversible and Hg can be re-emitted if environmental conditions of OM characteristics change over time^{10,13}. The predominant pool of Hg associated to OM
27 is thought to be taken-up by the foliage and covalently fixed. To this regard, reduced sulphur groups in the OM efficiently bind Hg (II), preventing reduction
28 processes^{9,14,15}. Recent studies showed that most Hg in plant leaves is sequestered as divalent mercury-sulphur nanoparticles¹¹. This promotes long term
29 storage in vegetation and soil. The re-emission of Hg to the atmosphere is therefore expectedly subordinated to the degradation of these binding structures. In
30 nature this can occur accidentally through fires, or naturally and more diffusely through biochemical degradations.

31 Despite the potentially high relevance of the re-mobilization from vegetated soils for the global Hg mass balance, the coupling between volatilization and the
32 turnover of labile organic matter is poorly understood. Empirical assessments are available only from few controlled laboratory experiments¹⁶⁻¹⁸ which showed
33 a correlation between Hg volatilization and OM degradation. In field assessments, correlative studies have shown a potential link between these two processes^{18,}
34 ¹⁹, but a causal relationship could not be confirmed. Covariance of OM turnover with temperature and humidity can in fact blur causal relationships.

35 Laboratory experiments demonstrated slow mobilization of only a relatively minor fraction (between 5 and 23%) of the mass of Hg initially bound to OM, in
36 response to a two-fold loss in the OM mass during a 18 months-long observations¹⁸. The use of traditional deposimeters to assess air-OM exchange does
37 however not allow disentangling the influence of co-occurring processes affecting Hg and OM mass budgets. Continuous depositions of "fresh" airborne Hg
38 during OM ageing may in fact mask volatilization fluxes²⁰.

39 In order to study Hg mobilization from OM in forest floors at the net of atmospheric depositions in in-situ OM ageing experiments, we developed a novel
40 passive exchange meter (EM) that, utilizing a mass balance approach, simultaneously and dynamically resolves OM and Hg budgets in vegetation litter over
41 arbitrarily chosen integrated time periods. To assess causality in the relationship between litter dry mass and Hg re-mobilization and assess the entity of Hg
42 fluxes under fast OM turnover, an experiment was conducted in a subtropical humid forest of southern China, subjected to monsoon climate. The subtropical
43 monsoon climatic conditions maximize the seasonal variance of OM degradation assessed here through losses of litter dry weight and losses in organic carbon
44 content from forest litter.

45 To control for possible spurious correlations between Hg re-mobilization and OM degradation (possibly mediated by precipitation, air humidity or temperature
46 as lurking variables), the experiment was conducted in two blocks using 5 replicated EMs deployed in a forest plot under a dense canopy (estimated leaf area
47 index was 5), and 5 replicated EM in an adjacent (less than 30 m distant) understory gap (clearing diameter was about 10 m). Previous studies showed that
48 canopy gaps significantly inhibit degradation of litter, while experiencing nearly identical conditions of air temperature, humidity and precipitations²¹.

49 **Material and methods**

50 **Site description**

51 The study site is located in the Dinghu National Nature Reserve (DNNR) area in mid-western Guangdong province, China (Figure 1). DNNR is part of the
52 "Man and the Biosphere" (MAB) Programme of United Nations Educational, Scientific and Cultural Organization (UNESCO) network of protected areas. It
53 has typical subtropical monsoon climate with hot and wet seasons (from Apr. to Sep.) and dry and cold seasons (from Oct. to Mar.) The annual average
54 temperature is 20.9 °C with the hottest month in July (average 26.0 °C) and the coldest in January (average 12.6 °C). The annual average rainfall is 1929 mm,²²
55 with 75% of precipitations occurring from March to August²³. The land use is characterized by evergreen coniferous and broad-leaved mixed forests. Dominant
56 tree species are broad-leaves (mainly *Schima superba* and *Castanopsis chinensis*) and pine needles (mainly *Pinus massoniana*). Surface litter covers 80%-90%
57 of the ground with a thickness of 1-3 cm²⁴.

58 **Exchange Meters**

59 The EM (Figure 2 and Figure S1) consists of a stainless-steel tripod with a cylindrical cross-section holding an open borosilicate glass cylinder (diameter 16
60 cm, height 25 cm). The glass cylinder seals up two pieces of silver mesh discs (pore size of 0.8 µm, thickness 51 µm, SPI-Pore™) placed at its base. Above
61 the silver mesh, a nickel net (<2 mm mesh) is placed, holding a sample of litter collected in-situ and spiked with a known amount of ²⁰²Hg(II). ²⁰²Hg(II) is used
62 as a field reference to determine the volatilization and leaching fluxes (as described in a following section). This isotope is an ideal surrogate for tracking
63 fate processes in OM as the bulk of mercury bound to forest litter is in the form of Hg(II). This is supported by previous findings showing that mercury in
64 foliage is prevalently oxidized and exists in complex forms such as organic Hg-S species^{6,11,25-27}. A small portion of Hg(II) in litterfall may convert into Hg(0)
65 from time to time through Hg(II) reduction, but in this form will rapidly be released back to the atmosphere^{28,29}.

66 **EM handling and sampling**

67 For each sampling period forest litter (including broad-leaves (mainly *Schima superba* and *Castanopsis chinensis*) and pine needles (mainly *Pinus*
68 *massoniana*)) was collected from the forest site. In order to determine the water content an aliquote of the litter was vacuum dried for 24 h. Large dead leaves

69 and detritus present in the remaining litter was mechanically broke-down to achieve a texture with the largest pieces in the order of 1 cm². This was done to
70 allow adequate homogeneization and distribution of samples in replicates EMs. The remaining litter was then spiked with 2.00 µg of inorganic divalent ²⁰²Hg
71 by adding 100 mL of 20ng/ml ²⁰²Hg(NO₃)₂ solution to 200 g (dw) of litter. The solution of ²⁰²Hg²⁺ was prepared by dissolving 1 mg of ²⁰²HgO in 1 ml of
72 HNO₃ solution and diluted to 20 ng ml⁻¹ by adding Milli-Q water. The spiked litter was transferred into an ambered borosilicate glass jar, vigorously shaken by
73 hand for several minutes and stored in the dark jar for at least 24 h before deployment in the field. This procedure was carried out to allow homogenization
74 and partial re-distribution and of ²⁰²Hg in the litter sample. The spiked litter was then distributed in situ into 10 aliquots of 20 g each and deployed in different
75 EMs (five in understory and five in the adjacent clearing) (Figure S1). The EMs were deployed so that the spiked litter sample was only a few cm above the
76 soil level to approximate natural exposure conditions. After field deployment, the spiked litter was sampled twice: 6 h after deployment and after two months
77 to calculate changes in the masses of Hg (THg), ²⁰²Hg, dry organic matter, organic carbon (OC), N and water content before (*t*₀) and after (*t*_f) the exposure
78 period. Sampling at *t*₀ was conducted by collecting 5 g of litter from each EM. These were carefully sealed, individually, into plastic bags and brought back to
79 the laboratory. At *t*_f the remaining litter was collected and handled in a similar way. At *t*_f silver meshes, conceived to sample the leaching flux of ²⁰²Hg(II) were
80 also retrieved and stored in sealed bags. Before analysis, litter and silver meshes were stored at 4 °C. This procedure was repeated 6 times covering time
81 intervals of two months throughout a full year.

82 Hg analysis

83 Litter samples were freeze dried and grinded to a fine powder in a pre-cleaned food blender (200 meshes). The blender was extensively cleaned with Milli-Q water and ethanol
84 between different sample batches to prevent cross contamination^{20,30}. THg in litter samples were determined by Zeeman Lumex mercury analyzer (model RA915+, Lumex
85 Co. Inc., Russia) attached with Pyro-91 thermal decomposition accessory from Lumex Ltd. The solid samples were directly decomposed in atomizer chamber
86 at 800 °C with the aided catalytic action. THg was then measured by RA-915t analyzer³¹. Standard reference samples were measured every 10 field samples
87 yielding recoveries in the range of 95%–105%. GBW10020 (GSB-11) was used as the litter Hg standard. Approximately 0.15 g of the samples were digested in 50
88 mL of freshly mixed HNO₃/H₂SO₄ (4:1 v/v) for 6 h at 95 °C in a water bath^{32,33}. The digested solution was then diluted by adding Mili-Q water to a volume of 25 mL. For Hg
89 isotope analysis, the analyte preconcentrated by BrCl oxidation, SnCl₂ reduction, purge and trap step onto a gold trap was thermo-desorbed quadrupole inductively coupled
90 plasma mass spectrometry (ICP-MS; Agilent 7700X). The detection limit was 100 pg/L for Hg^{34,37}.

91 For the analysis of ²⁰²Hg in the silver meshes, filters were transferred in quartz glass tubes into a furnace. The quartz tube was subsequently connected to a
92 generator of Hg-free air (Nitrogen gas, ≤ 0.1 ng m⁻³). Temperature was increased to ~450 °C. The silver amalgam was then decomposed into Hg(0) vapor,
93 which was brought by the air stream into a bubbler containing an acidic KMnO₄ solution that quantitatively oxidized the generated Hg(0). An aliquot of the
94 KMnO₄ solution was used for analysis. Prior to analysis, excess KMnO₄ was reduced with NH₂OH·HCl (aq) and subsequently Hg(II) (aq) was back-reduced
95 to Hg(0) by addition of SnCl₂ (aq). Hg(0) was subsequently purged from the solution and pre-concentrated onto a gold trap to be finally quantified by ICP-
96 MS.

97 QA/QC

98 All borosilicate glass cylinders were pre-cleaned following the US EPA Method 1631 (<https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P10081W8.txt>).
99 Briefly, the outside and inside surfaces of the Ems glass cylinders were first washed with laboratory analytic grade acetone in a fume hood, then washed with
100 alkaline detergent, and finally rinsed five times with de-ionised water. The cylinders were immersed in 3.5 % HNO₃ for 6 hours at 65-75 °C through submerging
101 the cylinders in a polyethylene bucket containing a HNO₃ solution. We ensured all the cylinder surfaces were in contact with the HNO₃ solution. After this,
102 the cylinders were rinsed five more times with de-ionised water and let drying in a fume hood. They were finally placed in a muffle furnace and baked at
103 500°C for 5 hours. Prior deployment they were individually sealed in teflon bags. In general, glass surfaces exhibit a low adsorption of mercury³⁸. Nickel metal
104 was chosen on the same principles based on the low degree of Hg amalgamation. On the other hand, silver metal shows a nearly quantitative collection
105 efficiency for Hg(0) and inorganic Hg(II) species³⁹. The feasibility of using silver mesh filters as passive samplers of leaching Hg was tested prior the
106 experiment. The retention of silver mesh filter to Hg is very high (95.50% and 96.84%) and was tested by feeding a Hg standard solution at different
107 concentrations (200 pg/ml and 500 pg/ml) through the silver mesh at a flow rate of 100 ml/h. In order to control for breakthrough, during field deployments
108 two silver meshes were piled in each EM and analyzed separately. Negligible breakthrough was observed.

109 Before any field deployment, the silver meshes were blanked from Hg by positioning them in a Hg free inert gas stream and heating at 450 °C. This allowed
110 reaching a stable blank value of 232.7 ± 102.6 pg (n=10). In this way the silver mesh could be reused in subsequent deployments. After repeated uses, visual
111 inspection of the silver mesh occasionally revealed a patchwise change in the surface lustre. This might have resulted from mechanical deterioration and/or
112 chemical oxidation. Various treatments to restore the surface were tested. Gentle treatments with diluted acid or small amount of commercial silver polish
113 were generally found to produce a satisfactory results.

114 In ICP-MS measurements, isotopes of ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰²Hg of the spiked sample were collected in time-resolved, single point per-peak mode with dwell
115 times of 20 ms. Carried gas flow was optimized every day to obtain maximum and stable signal. Detailed operating conditions for ICP-MS are listed in Table
116 S2. A 5 ml standard solution (100 pg/ml) were measured prior to every 4-5 samples as a QA/QC measurements. Limits of detection for ICP-MS measurements
117 of ²⁰²Hg isotope was 50 pg. The forest litter spiking procedure was a critical step. For the homogeneous distribution of the spiked mercury in the organic
118 matter, we used a diluted spiking solution via diluting 10 times the concentrated ²⁰²Hg solution. In this study, 17% of the mass balance assessment of Hg in
119 the EM provided "non-sense" negative values of Fvols. This was possibly due to poor homogeneisation of spiked litter. These outliers were excluded from
120 statistical analysis.

121 Flux calculations

122 F_{net} (ng m⁻² d⁻¹) is the net result of all the deposition and loss processes involving THg, and is calculated as:

123
$$F_{net} = \frac{[THg_{native}^{litter}]_{t_f} - [THg_{native}^{litter}]_{t_0}}{At} = F_{dep} - F_{loss} \quad (1)$$

124 Where $[THg_{native}^{litter}]_{t_0}$ and $[THg_{native}^{litter}]_{t_f}$ are initial and final amounts of total native Hg in the litter, respectively, A is the opening area of the EM (= 0.02 m²) and $t = t_f - t_0$ (d) is the deployment time (here 60 d). F_{dep} represents the native Hg added through the various deposition processes to the EM during the sampling period while F_{loss} is the results of all the loss processes

127 F_{loss} can be further described as:

128
$$F_{loss} = F_{down} + F_{vol} \quad (2)$$

129 where, F_{down} is the downward export flux (i.e. the leaching from the EM) and F_{vol} is the volatilization flux from the organic matter. The downward transport (F_{down}^s , ng m⁻² d⁻¹) of spiked ²⁰²Hg from the litter to the silver mesh disks can be measured as follows:

131
$$F_{down}^s = \frac{[^{202}Hg_{silver}^{litter}]_{t_f}}{At} \quad (3)$$

132 where $^{202}Hg_{silver}^{litter}$ represent the amount of ²⁰²Hg found in the silver mesh disks at the end of the exposure. Hereone the supersription "s" will indicate fluxes for ²⁰²Hg. ²⁰²Hg is rare in the environment, therefore the deposition flux for this isotope is approximated to be $F_{dep}^s = 0$, and equation 1 for the labeled ²⁰²Hg can be rewritten as:

135
$$F_{net}^s = -F_{loss}^s = -(F_{down}^s + F_{vol}^s) \quad (4)$$

136 Let's define now the function $f_{loss(t)}$ describing the instantaneous value of F_{loss} . If the concentrations of spiked ²⁰²Hg in the litter is in the order of or lower than that of the native THg, and assuming the spiked ²⁰²Hg behave as its native homologue, the relationship between the instantaneous loss fluxes of native and spiked ²⁰²Hg can be written as:

139
$$f_{loss(t)} = f_{loss(t)}^s \quad (5)$$

140 where $r_{(t)} = [THg_{native}^{litter}]_t / [^{202}Hg_{litter}^{litter}]_t$ is the ratio between the amount of native and spiked ²⁰²Hg in the EM litter, and $f_{loss(t)}^s$ is the istantaneous value of F_{loss}^s . Since $r_{(t)}$ is not constant (despite losses of native Hg are assumed to be the same as those of ²⁰²Hg, native Hg continuously receive inputs from the atmosphere), the shape of the functions $r_{(t)}$ and $f_{loss(t)}^s$ are not known. It is therefore not possible to exactly derive the value of F_{loss} for native Hg over the integrative sampling period. However, it can be argued that $r_{(t)}$ is a growing function of time, where the minimum ($r_{(t_0)}$) and maximum ($r_{(t_f)}$) values are experimentally known. Therefore, assuming in first approximation, that $r_{(t)}$ is linearly growing during the two month sampling period, the following relationship can be introduced as a first approximation:

146
$$\int_{t_0}^{t_f} r_{(t)} dt \approx \frac{(r_{(t_f)} + r_{(t_0)})}{2} t = \theta \quad (6)$$

147 and

148
$$F_{loss} = \theta F_{loss}^s \quad (7)$$

149 Similarly, the downward export flux and volatilization flux of native Hg from the organic matter can be expressed as:

150
$$F_{down} = \theta F_{down}^s \quad (8)$$

151
$$F_{vol} = \theta F_{vol}^s \quad (9)$$

152 Finally, from equation 1, 4 and 7, F_{dep} for native Hg can be calculated as follows,

153
$$F_{dep} = F_{net} - \theta F_{net}^s \quad (10)$$

154 **Quality of Hg flux measurements**

155 Screening EM flux results for measurement quality included checking for consistency of the following assumptions: i) the concentration of $^{202}\text{Hg}^{\text{litter}}$ is in
156 the order or lower than that of native Hg; ii) $r(t)$ is a growing function of time and therefore the condition assumed in equation 6 is verified; and iii) $^{202}\text{Hg}^{\text{litter}}$
157 is a useful tracer of the behavior of THg. Assumption i) is verified since r values representing the ratio of concentrations between THg and $^{202}\text{Hg}^{\text{litter}}$ ranged
158 18-20 at $t(0)$ and 20-60 at $t(f)$. This result also confirms the validity of assumption ii) given that $r_{(t_f)}$ was always $>$ than $r_{(t_0)}$ (it has to be acknowledged
159 however that the magnitude of the difference $\Delta r = r_{(t_f)} - r_{(t_0)}$, have implication for tracking the accuracy of flux measurements as described above). If the
160 growth trend of the function $r(t)$ is highly non linear the identity assumed in equation 6 can introduce an error. Assuming an unlikely worst case scenario with
161 all deposition of Hg occurring only during the first day of exposure and considering the maximum observed values of Δr , it is possible to demonstrate that the
162 resulting theoretical error in flux accuracy will not exceed 50% of the estimated mean value. Finally, assumption iii) has been adopted in other notable studies^{40,}
163 ⁴¹.

164 It can be critically argued that the spiked ^{202}Hg could be more loosely bound to OM compared to the native Hg. A quick initial release of ^{202}Hg was indeed
165 observed during the equilibration phase preceding the experiment, suggesting rapid volatilization of the superficially adsorbed pool. During the experiment,
166 however, Δr values were directly correlated with the change in THg concentration in the litter at $t(0)$ and $t(f)$, showing that the increase in the r values are fully
167 explained by fresh deposition of native Hg on the litter and not by higher mobilization of ^{202}Hg . An additional confirmation of is that during the sampling
168 period of Aug-Oct and Feb-Apr, when very low net deposition of fresh THg occurred, no significant change in r values was observed.

169 **Statistics**

170 Normality in the distribution of replicated Hg flux measurement and litter dry mass loss was assessed using the Lillefors test with $N=10$. To compare Hg fluxes between canopy
171 and gap conditions, we de-trended the dataset by dividing the individual Flux measurement for their overall (understory and clearing) mean value within each
172 period. We obtained two groups of data (understory and clearing) and we perform a F precision test to assess similarity in their variance. We applied the Student's t-test to
173 compare the mean of the groups in the case F-test was positive and the Cochran's variant of the t-test when variance was significantly different. Regression models were based
174 on the ordinary least squares method. Correlation was quantified using Pearson's correlation coefficient. Significance of regression coefficients was tested by analysis of
175 variance (ANOVA).

176 **Organic matter analysis**

177 Information on the method to analyze organic matter characteristics including dry weight, total OC and total N is presented in the supplementary information (Text S1).

178 **Results and Discussion**

179 **Seasonality of litter turnover**

180 Dry mass OC mass losses from vegetation litter measured using the EM confirmed that understory conditions significantly ($P<0.05$) promoted turnover of OM
181 with dry mass losses up to 55% during the warmest and most humid periods (Figure 3). Dry mass loss data from the EM were validated by consistent
182 measurements simultaneously performed using traditional litter bags in the understory. The data on litter degradation (i.e. mass loss) reveal the highly seasonal dynamic
183 of OC respiration in this subtropical forest. The loss rate of litter mass had a maximum during the hot and wet seasons, in particular in June-August, then it consistently declined
184 to a minimum in the dry and cold seasons, in particular January-March, to increase again with temperature and precipitation toward the last sampling campaign. During the
185 dry and cold seasons, the litter deployed in the understory and the clearing experienced similar dry mass losses in the range of 15-25%, however the variability
186 over time of dry and OC mass loss under the canopy was 140% of that observed in the clearing. Litter degradation rate positively correlated ($P<0.01$) with
187 rainfall, air temperature and humidity (Table S1) both in clearing and understory.

188 Litter mass loss derives from the activity of detritivorous macro-invertebrates and microbe, and the loss rate depends on climate (in particular temperature and litter water
189 content) and on the nature of the litter⁴²⁻⁴⁵. A significant decline of the C:N ratio was observed during the hot and wet seasons, consistent with the period in which the
190 highest water content in litter was measured (Table S3). The hypothesis addressed in this study is that OC mineralization and the decline of C:N drives and correlates to Hg
191 losses from the forest litter. Water content of litter deployed in the hot and wet seasons was generally higher than in dry and cold seasons, probably due to heavy
192 rainfall in the hot and wet seasons. Organic matter turnover was higher in the hot and wet seasons than in the dry and cold seasons ($p<0.05$), and under the canopy
193 compared clearing ($p<0.05$).

194 Experimental observations were designed to represent two blocks (understory and clearing) where environmental conditions (namely: rainfall, air temperature
195 and humidity) were the same but distinct dynamics of OM degradation occurred. The correlation among environmental conditions data and litter dry mass, OC
196 and N loss (Table S1) showed that OM turnover was under similar drivers both in understory and clearing conditions. The clearing conditions, however
197 inhibited the rate of degradation, possibly due to altered water balance in the EM (e.g. more rapid evaporation in response to direct exposure to incident
198 shortwave radiation in the clearing, compared to the understory conditions), as exhaustively discussed elsewhere^{42-45, 50}. Our results on litter mass dynamics are
199 therefore fully consistent with previous observations in similar environments²¹.

200 **Seasonality of ^{202}Hg fluxes**

201 The F_{vol}^s and F_{down}^s fluxes in each sampling period and canopy conditions were higher in the hot and wet season than in the dry and cold season (Figure S2),
202 suggesting that high precipitation, high temperature and enhanced dynamics of organic matter turnover favored ^{202}Hg mobilization. To our knowledge this is
203 the first study to show a relationship between Hg mobilization from litter and OM turnover in field conditions^{54, 55}.

204 Organic matter in forest litter is largely constituted by complex polysaccharides including cellulose, more labile hemicellulose and pectine⁵⁶. Lignin is also an
205 important component of litter, however, unlike cellulose and hemicellulose only a limited classes of fungi and bacteria can completely mineralize it^{57, 58}. The
206 observed dependence of ^{202}Hg mobilization on litter decomposition (and the conditions that promoted it) suggests that Hg might be prevalently bound to the
207 labile constituents. Litter mass loss derive from complete mineralization of the labile constituents and the production of water-soluble components which are

208 then released by leaching to the underlying soil. The leaching of water-soluble constituents may contribute to the higher values of F_{down}^S . Similar to soil, litter
209 (as an organic matrix) can effectively trap Hg depositions. Litter mineralization is however fast in subtropical wet forests and tightly controlled by temperature
210 and humidity. Previous experiments in the laboratory showed that 5%-23% Hg could be released into the atmosphere during one-year litter decomposition
211 process due to the rapid mineralization of litter carbon¹⁸. In our study, higher air temperature and litter moisture during the hot and wet season, promoted faster
212 decomposition of litter and Hg release. During the dry and cold season, instead, lower air temperature and lower litter moisture inhibited litter decomposition
213 and Hg releases. Loss fluxes under the canopy were relatively high compared to the clearing. To this regard, it is important to recall that water budget in litter
214 is strongly influenced by land cover. Canopies, prevent rapid evaporation of water in the litter, maintaining better conditions for microorganisms growth.
215 Decomposition of litter has been observed to be generally faster in understories than in clearing⁵⁹⁻⁶¹.

216 **The fluxes of native Hg in litter**

217 Hg fate in litter underwent a strong climate control during the different seasons (Figure 4). The net air-litter exchange F_{net} had a positive value during October-February
218 and April-August, and the deposition flux F_{dep} displayed a higher value in the same sampling period compared to other periods, indicating prevailing deposition
219 of atmospheric Hg, and forest litter serving as a net sink (Figure 4). In contrast, during the other sampling periods, the loss of Hg from litter was prevalent,
220 primarily due to re-volatilization of Hg. Generally, over the whole sampling period, both F_{vol} and F_{down} of native Hg were higher under the canopy than in the clearing.
221 The process controlling the bulk loss of total Hg from the litter was volatilization typically representing 76% to 96% of the total loss. After de-trending to
222 exclude the effect of seasonality, F_{loss} measured under canopy throughout the year were generally higher than in the clearing (Mann-Withney test, $P < 0.05$;
223 Figure 4). Data from the wetter and warmer part of the year were determinant for this result.

224 The total Hg loss from litter (F_{loss} , encompassing both volatilization and the leaching flux captured by the silver mesh) under the canopy was statistically
225 correlated to litter dry mass loss, OC loss, N loss, rainfall, air temperature and humidity (Figure 5, Table S1). These relationships dramatically fell when
226 considering the clearing dataset. The mean value of F_{loss} over the year ranged 520-1370 $\text{ng m}^{-2} \text{d}^{-1}$ and 165-942 $\text{ng m}^{-2} \text{d}^{-1}$ in the understory and clearing,
227 respectively. These fluxes resulted in a total loss ranging between 8% and 45% in two months-time of the total Hg present in the litter at the beginning of each
228 exposure period. The EM method allowed resolving net air/litter exchange into the volatilization and deposition component. On a yearly base, deposition of
229 airborne Hg during litter exposure exceeded the total losses by a factor of 2.5 in the clearing and 1.5 in the understory. Vegetation litter represented therefore
230 a net sink of atmospheric Hg. This is in agreement with previous results showing the mass of Hg in litter of temperate forests increasing over time during litter
231 decomposition^{18, 46, 47, 62}. In our study, however we observed that the general trend was inverted during certain period of the year, with volatilization higher
232 than deposition. The mechanism of Hg accumulation during litter decomposition is still uncertain. One hypothesis is that despite ongoing decomposition,
233 binding sites for Hg on litter OM never become saturated. In this case, accumulation mechanisms will be similar to the adsorption of Hg by the cuticle of the
234 leaf surface⁶³. Another hypothesis is that the organic functional groups formed in the litter decomposition process can also serve as new binding sites^{48, 64, 65}.

235 The first block of the experiment (understory) showed consistent results with previous laboratory-based studies in which Hg mobilization correlated with OM
236 turnover¹⁶⁻¹⁸ as well as other measured environmental variables (namely: rainfall, air temperature and humidity). The results of the second block (clearing)
237 however, helped to disentangle the role of litter degradation as a driver of Hg loss from other correlated factors (namely: Temperature and humidity). Despite
238 the clearing and the understory set experienced the same average conditions of temperature, waterfall and air humidity, no significant correlation was observed
239 in the clearing with temperature and humidity. Only a positive correlation with N loss ($P < 0.05$) was observed, corroborating the hypothesis that higher Hg
240 mobilization fluxes under and outside canopies were primarily driven by litter OM turnover.

241 Lack of significant correlation between F_{loss} and litter dry mass loss observed in the clearing could have been determined by either lack of statistical resolution
242 due to the limited variance of OM degradation rate (in comparison to the forest block), or by the influence of an emerging confounding factor associated to the
243 clearing conditions, possibly controlling Hg dynamics (e.g. direct exposure to solar radiation during some hours of the day); alone or in combination. The
244 comparison of the residuals from the correlation between F_{loss} values and the first order least square model linking F_{loss} and dry mass loss in the understory
245 and clearing conditions helps to evaluate these cases. Consistent scedasticity (Figure S3) was observed for the residuals from the understory and clearing
246 datasets, suggesting common drivers in the relationships linking Hg and dry mass losses. Such a consistent behaviour supports the hypothesis that: F_{loss} is
247 under the same biogeochemical drivers in the understory and the clearing, while the lack of correlation with the OM loss flux in the clearing was likely due to
248 the insufficient variability of OM degradation rates measured in the clearing during the year.

249 Total Hg loss rates observed in the present study were much higher (about one order of magnitude) than those previously observed in the laboratory-based
250 studies¹⁶⁻¹⁸ or in previous field studies¹⁹ reporting limited mobility of OM-bounded Hg. Our study is the first to be performed in a subtropical warm and humid
251 environment. OM degradation rates measured here were one order of magnitude higher than those reported in those previous studies¹⁸. Additionally, litter
252 decomposition rate is strongly influenced by the type of litter. In general, litter decomposition rate is higher for subtropical forest dominated by evergreen or
253 deciduous broadleaf species than for coniferous forests with pine needles^{46, 66-68}. Inclusively, lower capacity of accumulating Hg in the former than the latter
254 were also observed^{47, 69}. Remarkably, the only available theoretical assessment of the influence of OM turnover on the global mass balance of Hg was performed
255 taking into consideration parameters derived for temperate and boreal environments⁹. Subtropical and tropical forests represent more than 50% of the total
256 forest land cover. Assessments of global mass balance of Hg could therefore have significantly underestimated the influence of rapid turnover of Hg fixed in
257 the litter and superficial soil of subtropical and tropical humid climates. The enhanced mobility of Hg shown here deserve therefore further scientific attention,
258 especially when assessing general fate and distribution of Hg under a globally warming climate.

259 **Significance of EM based measurements and comparisons with previous studies**

260 The conventional widely used technique for measuring the air-surface exchange flux of Hg(0) is the DFC method⁷⁰⁻⁷². Hg(0) emission fluxes from deciduous
261 forest soils previously collected using this method are summarized in Table S4. The mean volatilization flux ($668 \text{ ng m}^{-2} \text{d}^{-1}$) calculated in the present study
262 was somehow higher but in the sme order of magnitude than previously reported observations by DFC (Table S4) ($12-498 \text{ ng m}^{-2} \text{d}^{-1}$) with a mean of 221 ng

263 $\text{m}^{-2} \text{d}^{-1}$. Similarly, the volatilization fluxes estimated in the present study were comparable to, although slightly higher than those measured by DFC in a study
264 in Mt. Jinyun of China which in a similar forest ecosystem ($342\text{-}498 \text{ ng m}^{-2} \text{ d}^{-1}$)⁷⁸. These differences are not surprising as the DFC measurements target the
265 volatilization flux at the net of gaseous depositions, while the flux calculated through the EM represents the total volatilization. This fully explains the off-set
266 existing between the datasets. It must also be recalled that, similarly to the EM method, DFC flux measurements are also affected by uncertainties⁷³⁻⁷⁷.

267 Previous DFC-based measurements have shown both prevailing volatilization or depositions varying from case to case^{73, 79, 80}. In contrast, measurements using
268 the EM quantifies the total deposition flux including contributions from gaseous oxidized mercury and particulate bound mercury (PBM) dry and wet deposition
269 (mostly from throughfall) besides the total gaseous depositions of Hg(0). Net deposition fluxes estimated from EM approach (annual mean of $276 \mu\text{g m}^{-2} \text{ yr}^{-1}$
270 ¹) suggested that DNNR forest was a net sink of Hg. This conclusion is also supported by earlier findings which showed that throughfall Hg fluxes ($40\text{-}113 \mu\text{g}$
271 $\text{m}^{-2} \text{ yr}^{-1}$) were significantly higher than the Hg(0) emission fluxes in China^{79, 81-83}.

272 Uncertainties in conventional flux measurements, and emission estimates s, (including primary and secondary sources) hinder confidence on current global
273 and regional Hg budgets^{4, 80, 84}. The proposed EM methods can constrain some of this uncertainties, delivering long term temporally integrated flux
274 measurements. Globally, the variability of air-surface exchange flux measurements is larger for forest systems (-727 to $+707 \text{ Mg yr}^{-1}$) than other terrestrial
275 ecosystems⁸⁵. Applying, in first approximation, the result generated in the present study to the total forested area of China
276 (<http://www.resdc.cn/data.aspx?DATAID=99>), the net Hg deposition flux is calculate to be roughly 73 Mg yr^{-1} for the broadleaf forests and 240 Mg yr^{-1} for
277 the coniferous forests. It should be emphasized that the air-surface exchange process strongly depends on land cover and climate^{48, 49, 86, 87}. For example, THg
278 mass positively correlated with latitude with average mass increase of 10.6 g ha^{-1} per degree latitude^{48, 49}. High contents of Hg in litterfall and throughfall
279 were observed in coniferous forests^{47, 66, 88, 89}, confirming boreal forests as important capacitors for Hg. It is thus recommended to expand the application of
280 EM to address ecosystem exchange of Hg in different forest biomes.

281 **Supporting information:**

282 Additional information on the pearson correlation coefficients and *P* values of the correlation analysis, detailed operating conditions for
283 ICP-MS, the trends of mean air temperature, rainfall, water content and C/N in every sampling period, Hg(0) emission fluxes from
284 deciduous forest soils collected by DFC method, the field deployment and mass balance of Hg in the exchange meters (EMs), The fluxes
285 of ²⁰²Hg in the litter after 2 months of deployment and the consistent scedasticity for the residuals from the understory and clearing datasets.

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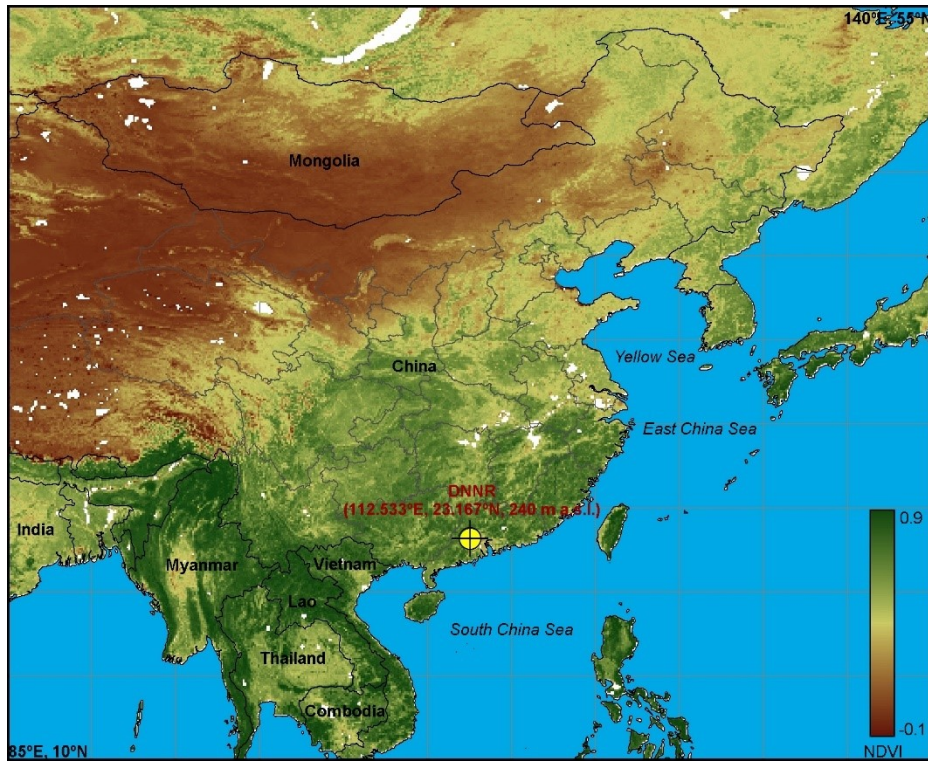
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507 **Figure 1:** The location of sampling site DNNR (Yellow circle) and gridded ($0.1^{\circ} \times 0.1^{\circ}$) mean of monthly NDVI (satellite-based normalized
508 difference vegetation index, representing the vegetation activity) in East Asia during the study period.⁸



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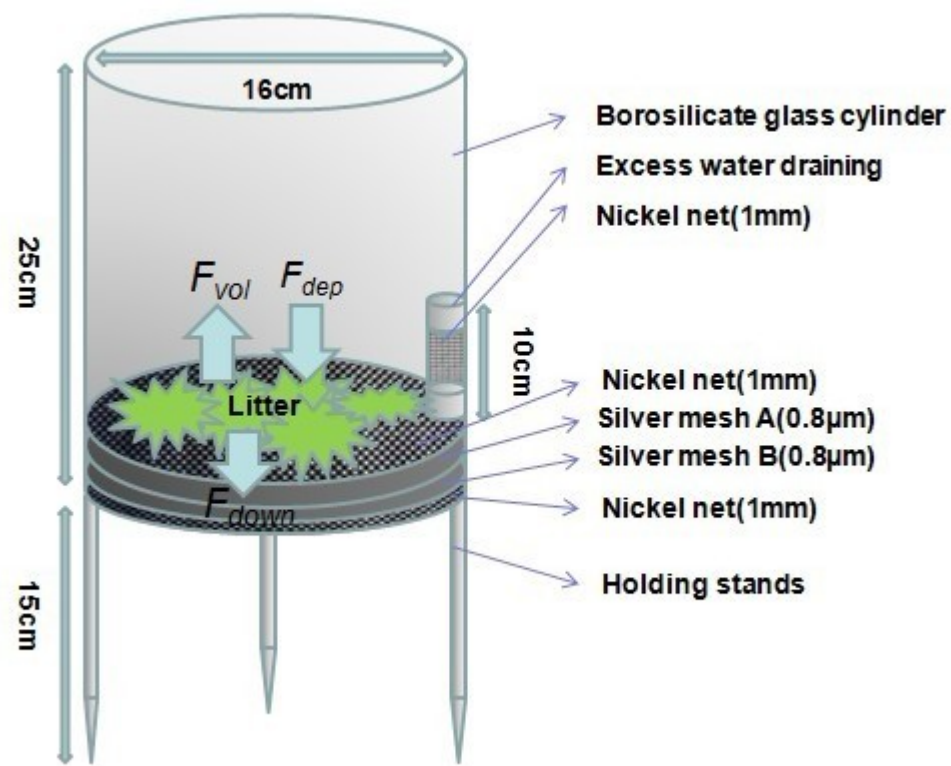
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Figure 2: The diagram of the exchange meters (EMs). F_{dep} was the Hg flux deposited to the EM during the sampling period, F_{down} is the Hg flux downward export (e.g. leaching (including run-off) from EM and F_{vol} is the Hg flux emitted up to the air from EM.



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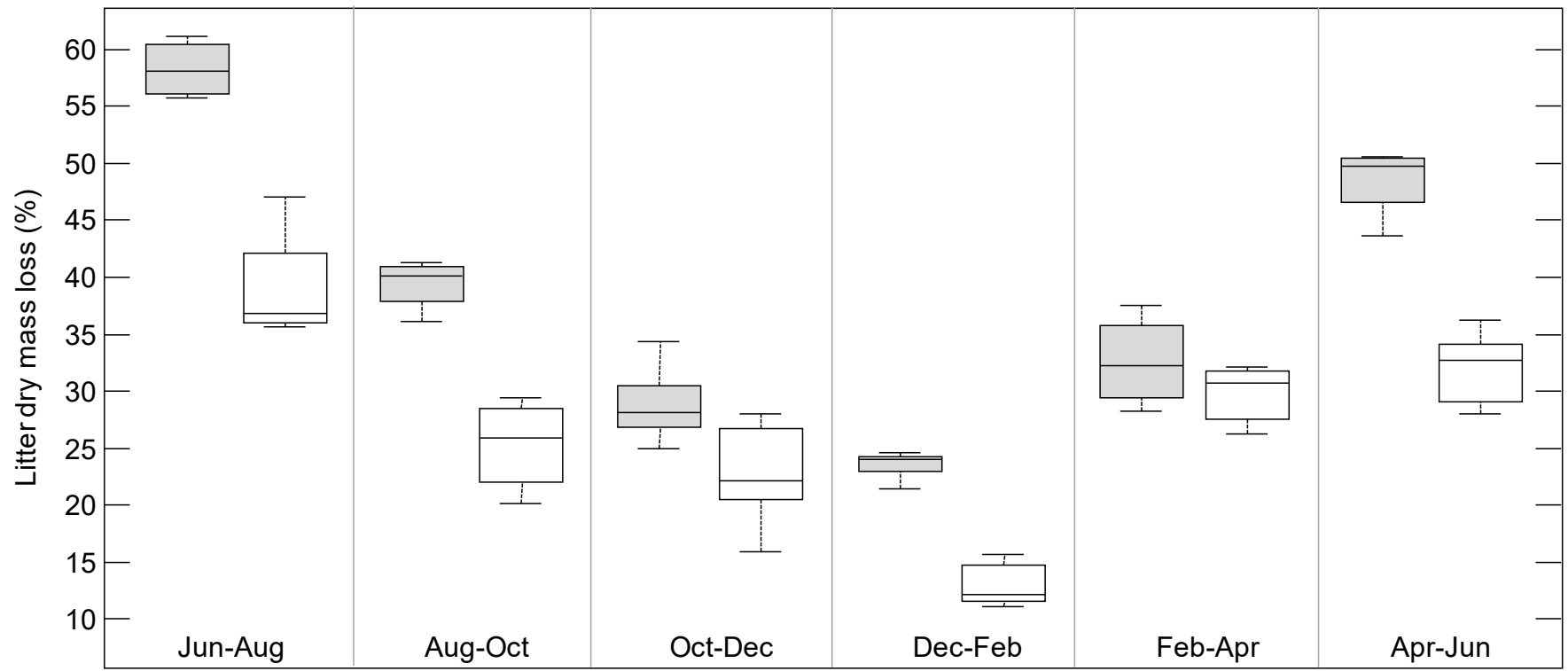
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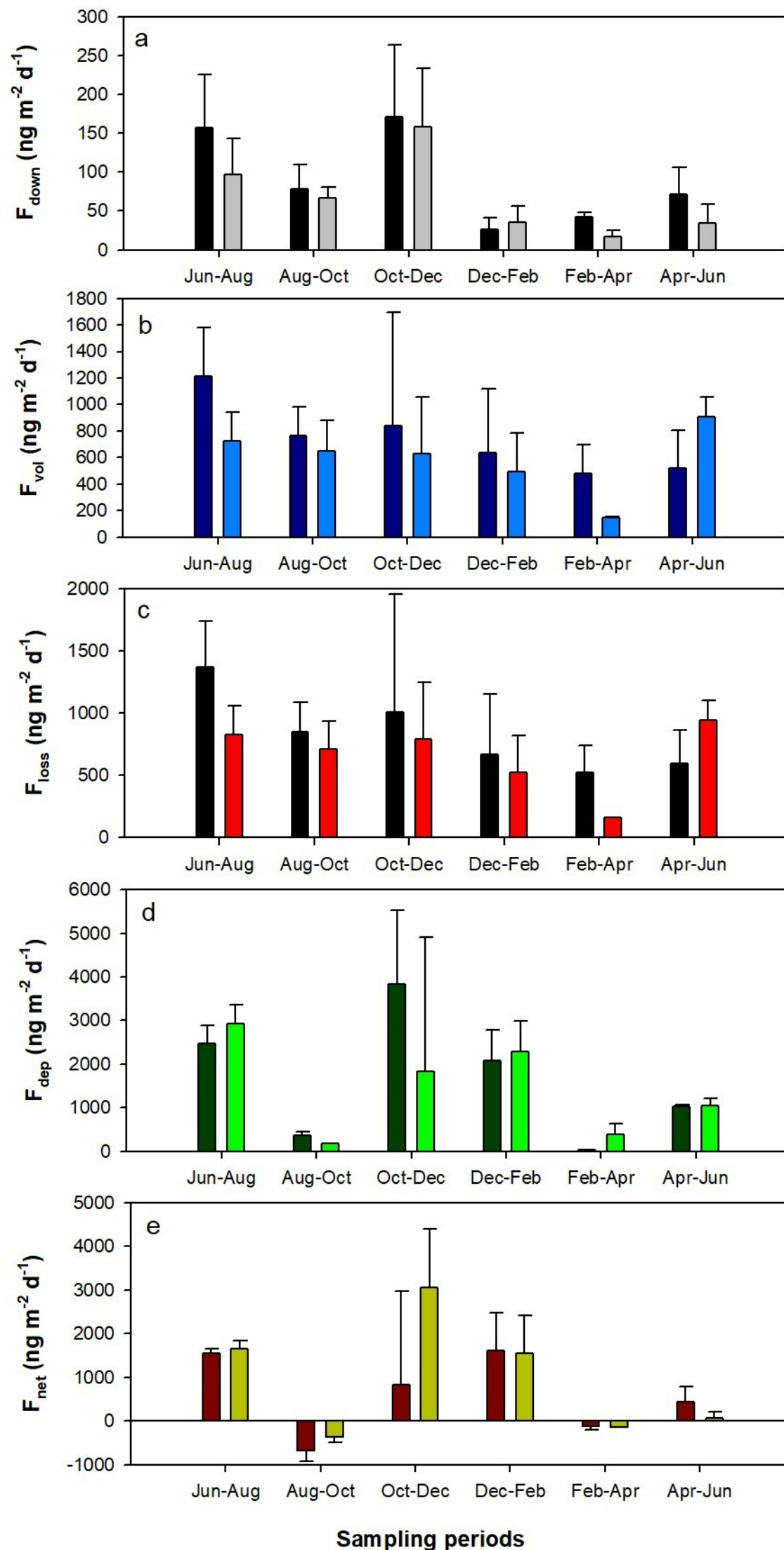
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548 **Figure 3.** Bow plots of the litter dry mass loss expressed as percentage of the initial dry mass for the understory (grey boxes) and the
549 clearing. Boxes show sample mean, 25th and 75th percentiles. Whiskers extent to the lowest (or highest) value within 1.5 of the lower (or
550 higher, respectively) interquartile range.



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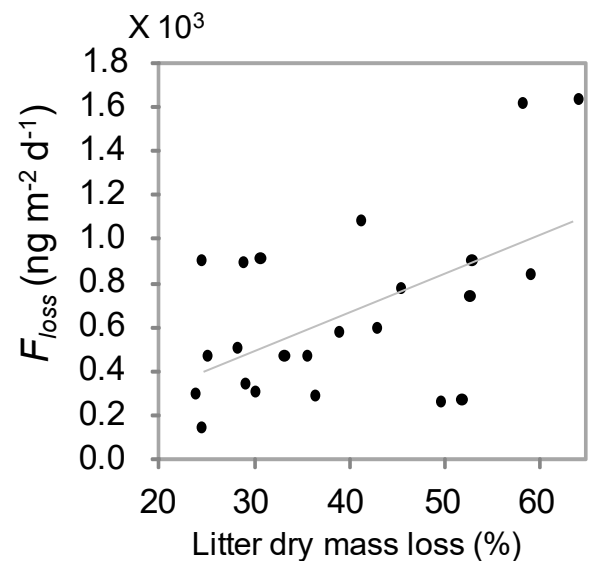
571 **Figure 4.** Hg loss, deposition and net fluxes of native Hg as well as their volatilization and leaching components in the litter after 2 months
 572 of deployment. (a) Left (black) bars represent the leaching fluxes of native Hg (F_{down}) in the understory and right (gray) bars represent the
 573 leaching fluxes of native Hg (F_{down}) in the clearing. (b) Left (dark blue) bars represent the volatilization fluxes of native Hg (F_{vol}) in the
 574 understory and right (blue) bars represent the volatilization fluxes of native Hg (F_{vol}) in the clearing. (c) Left (black) bars represent the loss
 575 fluxes of native Hg (F_{loss}) in the understory and right (red) bars represent the loss fluxes of native Hg (F_{loss}) in the clearing. (d) Left (dark
 576 green) bars represent the deposition fluxes of native Hg (F_{dep}) in the understory and right (bright green) bars represent the deposition fluxes
 577 of native Hg (F_{dep}) in the clearing. (e) Left (dark red) bars represent the net fluxes of native Hg (F_{net}) in the understory and right (light
 578 green) bars represent the net fluxes of native Hg (F_{net}) in the clearing.



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581 **Figure 5.** Scatter plot and first order least square model for F_{loss} vs litter dry mass loss.



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