

Interactive comment on “Soil emissions, soil air dynamics and model simulation of gaseous mercury in subtropical forest” by J. Zhou et al.

Anonymous Referee #1

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The authors motivate their field study in a forest catchment in China by improving soil-atmosphere flux understanding in general. However, I missed any discussion on how representative their study area (climate, Hg input due to elevated Hg emission in South-East Asia, soil characteristics) is for global forest ecosystems. A better characterization of their study site and general comparison with global ecosystems is necessary to be able to judge how representative the study site is. The authors should also address potential limitations of their approach.

The TGM flux measurements have been poorly validated and more QA/QC should be provided in order to allow the readers to judge if the flux measurements were robust. In particular the high flow rate of 15 Lpm in the flux chamber might have caused measurement artefacts that need to be assessed. Such measurement artefacts have been

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previously suggested in literature. There are a number of indications that the TGM flux could have been overestimated by pulling out soil pore DGM through a vacuum caused in the flux chamber, such as e.g. lower TGM fluxes at the wetland site or after rain events when the soil pores were partly saturated with water thereby increasing the resistance or a higher diffusion coefficient at daytime than at nighttime.

The authors present a multi-regression model with 14 coefficients. This model was fitted for each study plot and 14 study-site specific coefficient were determined. These coefficients vary between the study sites by factors of up to 2 orders of magnitude. If each study site has its specific factors, the model presented by the authors does not really represent an advanced understanding of the processes and can also not serve as a tool to generalize flux estimated and improve global uncertainties with soil TGM fluxes.

The writing of the manuscript needs an extensive round of edits, I highlighted a number of grammatical or logic errors below but there are more. Also, the referencing needs to be improved.

Specific comments:

L45-47: Please explain how you derived the uncertainty values from the Outridge et al. study, I could not find the numbers in the original study.

L54-58: This sentence is very long and somehow confusing, Hg(II) from wet deposition e.g. is missing in the extensive list of deposition pathways. I suggest to order the pathways by Hg(0) deposition and Hg(II) deposition.

L70: Please specify what you mean by “physical and chemical dynamics”

L73: Agnan et al. and Zhu et al. Are reviews of studies and did not present original data, in such a statement you should provide credits to the original papers or declare that the original studies are reviewed in Agnan et al. and Zhu et al..

L73: delete “attempted”, the studies actually measured the TGM concentrations in soil

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pores.

L76-78: This statement is not correct, check out Obrist et al. 2017, Nature, They measured soil pore TGM concentrations and TGM fluxes continuously for two years.

L79: Please describe what you mean by “diffusive immobilization”, I’m not aware of this process.

L95: explain TFP

L100: Please provide more details on the soil characteristics.

L102: check grammar

L105-127: Add QA/QC for your flux measurement method: what are method detection limits and measurement uncertainties? What were chamber blanks?

L106-107: This statement is not justified, there are numerous studies on Hg⁰ flux measurements from soils, some of which cover even larger measurement periods.

L123: Please explain why you chose to have a flux of 10 Lpm through the DFC. Previous studies have shown that measured TGM fluxes can be variable depending on DFC fluxes applied. E.g. the review by Agnan et al. found significantly larger fluxes in DFC measurements that applied flow rates of >2 Lpm compared to measurements with flow rates <2 Lpm. Applying a large flow rate could lead to a vacuum in the flow chamber that actively sucks out air from the soil pore space. Please provide an explanation and validation showing that the flux measurements are robust. See also: Wallschlagl, D.; Turner, R.R.; London, J.; Ebinghaus, R.; Kock, H. H.; Sommar, J.; Xiao, Z. Factors affecting the measurement of mercury emissions from soils with flux chambers. *J. Geophys. Res.* 1999, 104 (D17), 21859–21871. L126: Check grammar

L127: specify how many diurnal measurements were conducted.

L129: The model description needs some more details.

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L162: where are the two resistances in equation 2, this looks like a simple Fick’s diffusion equation.

L174: replace “collected” by “measured”

L192: This is a very general statement and needs support from data, how e.g. did the soil properties or parent material vary over the catchment scale, please add this information.

L204: check grammar

L205: Please explain the underlying biogeochemical mechanisms. One would assume that water stagnation leads to reducing conditions that would in fact be in favor for Hg reduction processes rather than inhibiting. The low soil pore gas volume under saturated conditions could also lead to less air drawn out from the soils by measurements at the wetland site (see comment above). Can you rule this out?

L227-234: Providing a single averaged flux of 3.2 ng/m² is not a very convincing way of advocating large in-ecosystem variability. It would be more convincing if you discussed the within ecosystem variability first and then identify some patterns how the individual measurements can be integrated to the whole ecosystem scale.

L246-248: This is a valid statement that yearly flux estimates must be based on measurements made over the entire time period, but it’s also quite trivial. Can you show studies (reference them) that calculated a yearly flux just from a Summer campaign? I would however suggest to move such a statement to the discussion part.

L249: Again, this rainfall event could decrease the soil pore space and lead to less air being pulled out of the soil by the vacuum in the flux chamber. Can you rule this out?

L255: Provide some references where a correlation between soil Hg and re-emission fluxes was observed on an individual ecosystem scale.

L259: check grammar

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L259-262: Change wording of sentence

L263: The p value is not a good metric for the correlation analysis, provide other metrics (R² and the slope)

L291: Please rephrase, replace “observed” by “was measured”

L303: Please explain what you mean by air-to-air emission?

L308: replace “dominate” by “dominant”

L317: Please justify why you can extrapolate from your catchment to forest soils in southwestern China in general.

L417: This is a strange reference for Hg sorption to thiol groups, please give credits to the original reference: Sklyberg, U.; Bloom, P. R.; Qian, J.; Lin, C. M.; Bleam, W. F., Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environ. Sci. Technol.* 2006, 40, (13), 4174-4180.

L433-435: Please revise this statement, a systematic offset cannot be indicative for spatial variability

L437: Please support this very general statement by your data.

L447: Provide detection limit of your measurements

L473: reword sentence

L482-485: Why should the diffusion coefficient vary between day and nighttime or between the different sites. The fact that the daytime diffusion coefficient for the open field site is 23 times larger than the nighttime diffusion coefficient raises some serious concern. Since the authors studied the field site extensively and measured various auxiliary parameters, they should be able to explain the reason for this difference. Can this higher diffusion coefficient at daytime be an indication of flux over-estimation due

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to pulling out soil air by the generation of a vacuum in the flux chamber?

L498: I acknowledge the extensive dataset presented by the authors but I would not call the measurement campaign (130 measurement days in total) a long-term study, given other ecosystem studies that are conducted over years to decades.

L510: Check unit, TGM concentrations are in the order of 1.5 ng m⁻³.

L513-514: In my view this statement oversells the performance of the model presented in this study. The model was fitted for each study plot and 14 study-site specific coefficients were determined. These coefficients vary between the study sites by factors of up to 2 orders of magnitude.

Figure 4: This Figure is hard to read, the position of the flux values is hard to judge by eye, please provide the reader some guidance, at least add a line at the 0 flux level. Also describing to which ecosystem plots A-E belong would help the readability of the figure.

Supporting Information:

L138: Change the Figure caption of Figure S1 and provide a meaningful description.

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