Interactive Discussion (Reviews) – Bg-2015-467

Seasonal variations in metallic mercury (Hg^0) vapor exchange over biannual wheat - corn rotation cropland in the North China Plain

J. Sommar, W. Zhu, L. Shang, C.-J. Lin and X. B. Feng

Response to interactive comments of Referee #1

Comment:

… The topic covers an important issue which is relevant and of interest for an international audience. The topic fits well into the scope of Biogeoscience. The scientific approach of this study is adequate to achieve the objective. The methodology is basically sound and described in detail. Few additions are required. The manuscript is generally well-written. However, several issues need to be addressed and improved. The further hints may helpful for the revisions: Methodology: Concerning flux measurements: several other alternative flux measurements and the respective papers should be integrate into the methodology chapter of the ms. such as Rinklebe, J. et al. 2009. Optimization of the simple field method to determine mercury volatilization from soils – Examples of 13 sites in floodplain ecosystems at the Elbe River (Germany). Ecological Engineering. 35. 319-328. And Böhme., F. et al. 2005. A simple field method to determine mercury volatilisation from soils. Environmental Science and Pollution Research. 12 (3), 133-135. Dynamics of Hg flux patterns & Environmental conditions: The authors should embed into the discussion of the dynamics of Hg flux patterns during various seasons and the linked environmental conditions the respective papers dealing with this issue. Rinklebe, J. et al. 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. Environmental Pollution. 158. 308-318. During, A. et al. 2009. Mercury Volatilization from Three Floodplain Soils at the Central Elbe River (Germany). Soil and Sediment Contamination: An International Journal. 18. 4. 429-444. The Impact of variable temperature and moisture conditions. . .etc. Summarizing, it is a valuable paper which should be of interest for the respective scientific community. I recommend moderate revisions.

Reply:

We appreciate that Referee #1 acknowledges our methodology to be fundamentally sound. However, in our opinion, by being somewhat vague and contradictory (*Few additions are required* vs. *several issues need to be addressed and improved…*), the referee renders a concise revision of the manuscript more difficult. For the only tangible comment concerning a discussion of alternative flux measurement methods insisted by the reviewer and hinted by the given references to potentially involve flow-through chamber with non-steady state operating conditions (e.g., a static type not commonly used among Hg researchers), we feel that such a discussion dilutes the scientific points and appears out of the scope of our paper. This paper deals with agro-ecosystem Hg^0 fluxes over cereal croplands, which can not be resolved by merely soil-wetted chamber measurement but also require input of above-canopy flux. Indeed, air-soil measurements make up a minor part of this study. The rationale of using a novel type of dynamic flux chambers (DFCs) in concert with MM-measurements has been introduced and substantiated in our previous papers (Lin et al. EST, 2012 and Zhu et al. ACP, 2015a, b) referred to in the manuscript. As a compromise to the comments of referee #1, we

refer to Rinklebe et al. 2010 concerning their findings of controlling factors of Hg^0 efflux from soil (Line 66). Further references to Rinklebe et al. etc. in connection with observation of temporal (diel, seasonal) flux patterns appears redundant since these papers deal with contaminated floodplains, instead of agricultural soils that this study focuses on.

Response to interactive comments of Referee #2

In this study, Sommar et al., by employing a relaxed eddy accumulation (REA) method, conducted comprehensive investigations over a full year period on air-surface exchange of gaseous elemental mercury (Hg0) over a wheat-corn rotation cropland in the North China Plain. The main findings of the study the authors reported here suggest that this wheat-corn rotation cropland acts predominantly as a source of Hg0 emission from soil into the atmosphere, as evidenced by the dominance of Hg0 soil efflux during the wheat growing season (approximately 2/3 of a year period) and a weak sink role exhibited by corn field. In addition, the authors also examined the response of air-surface Hg^0 flux to incidental events associated with agricultural management operations, such as irrigation and in-field burning of crop biomass, and found that both field flooding irrigation (particularly the initial flooding of dry soil) and crop burning could enhance Hg^0 emission into the atmosphere. The study design and techniques employed here are sound, and the results are dependable and of broad implications on studying local and regional air-surface Hg cycling. Overall, the manuscript is well written and of good quality. Nonetheless, some clarifications may be needed during discussion section about the enhanced Hg0 emission from soil during irrigation:

1. *Did the authors measure Hg concentrations in the water used for irrigation?*
2. *Or, did the authors estimate the potential contribution of Hg in the irrigation water to the Hg released into the atmosphere during these events?*
3. *Are there any possibilities that the Hg from the irrigation water contributed to the enhanced Hg^0 emission to certain degrees?*

Reply:

We thank Referee #2 for notifying about a potential source of evading Hg^0 not mentioned and overlooked in the discussion. **1.** Unfortunately, we did not measure either THg or dissolved Hg^0 in the irrigation water being pumped from aquifers. **2.** A literature search proves very limited data on Hg^0 in groundwater worldwide. There are only a few reported data on bulk Hg concentrations in ground water of the NCP region and none of these cover measurement of dissolved Hg^0. For example, Wu and Cao (Mercury and Cadmium Contamination of Irrigation Water, Sediment, Soil and Shallow Groundwater in a Wastewater-Irrigated Field in Tianjin, China, *Bulletin of Environmental Contamination and Toxicology*, 84, 336-341, 2010) reported a mean THg concentration of ~16 ng/L in shallow groundwater of an agricultural area with ppm-level of Hg in surface soils (due to sewage water contamination). We estimated the potential role of irrigation water by conservatively assuming a similar THg level in ground water of YCES (only ~45 ppb THg in surface soil). When investigated, the

fraction of Hg^0 present in Hg content of groundwater is low with a high extent being bound to particulates rather than existing as free dissolved Hg^0 that can be volatilized during the flood irrigation (Richard, J. H., Bischoff, C., Ahrens, C. G. M., and Biester, H.: Mercury (II) reduction and co-precipitation of metallic mercury on hydrous ferric oxide in contaminated groundwater, *Science of the Total Environment*, 539, 36-44, 2016; Wang, Y., Li, Y., Liu, G., Wang, D., Jiang, G., and Cai, Y.: Elemental Mercury in Natural Waters: Occurrence and Determination of particulate Hg(0), *Environmental Science & Technology*, 49, 9742-9749, 2015). Setting the fraction Hg^0(aq) conservatively to 10% in the irrigation water (column depth of ~100 mm) would yield a flux potential of ~0.16 µg m^{-2} which is far smaller than the observed Hg^0 flux pulse of ~1 µg m^{-2}. Our hypothesis is that the majority of observed Hg^0 evaded from the field stem from the soil matrix rather than from the irrigation water. Support for this statement can be derived from previous studies with low-Hg water irrigation of air-dry soil (Lindberg *et al.* 1999; Song & van Heyst 2005) documenting a significant Hg^0 evasion pulse as response. The lack of direct Hg^0(aq) measurement at YCES precludes the possibility of deterministic conclusion regarding the role of irrigation water as a source of atmospheric Hg^0. Since the assessment given above does not trigger any substantial alarm, it appears presumptuous to discuss this matter in the paper without any observational evidence.