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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Comparison of eddy covariance and modified Bowen ratio methods for measuring gas fluxes and implications for measuring fluxes of persistent organic pollutants" *by* D. J. Bolinius et al.

Anonymous Referee #2

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The manuscript raises an interesting and useful assessment of the Modified Bowen Ratio used to derive air-surface fluxes of trace gases. The authors make the case for supporting the use of the MBR for trace semi-volatile chemicals like POPs. They base their case on comparison and performance of the MBR against Eddy Covariance (EC) derived fluxes for CO2 and H2O-vapour for a forested FLUXNET site. The premise behind the study is that current limitations of sampling required to achieve detectable levels of persistent organic pollutants (POPs) for highly-time resolved measurements (∼10 Hz) effectively rules out Eddy Covariance and possibly restricts Relaxed Eddy

Accumulation techniques as well. The paper is well written and well-argued and, importantly, highlights the conditions when MBR is most likely to apply for estimating fluxes of semi-volatile chemicals like POPs. The authors also make a convincing case for using a time-integrated eddy diffusion coefficient suitable for POPs work where sampling times will be long (multiple hours). I think the manuscript is suitable for publication in ACP, but the following areas should be addressed by the authors first.

(1) I am surprised the authors do not refer to the commonly used Relaxed Eddy Accumulation method in their introduction (or later on in the paper for that matter). REA is often the technique of choice for trace species for which measurements do not conform to the very high time-resolution required by EC. For any atmospheric gas where highly time resolved measurements are not possible then REA is often the method of choice. Perhaps the time constraint required even for REA may not make this flux estimation method entirely suitable for POPs but the authors need to highlight and discuss this and justify why the MBR is the method of choice for POPs.

(2) There aren't many studies that have empirically derived fluxes using micromet techniques for semi-volatile chemicals like POPs. However, one study that does stand out is that of Kurt-Karakus et al ES&T 2006, 40, 15, 4578 who used the MBR method to derive fluxes of DDT components from agricultural soils. A point of note with this study was that the DDT air samples were taken quite close to the ground surface (between 0.05 m and 2 m above the surface) and a pronounced gradient in concentrations was most apparent in the lower 0.05 to 0.5 m. The premise here was that the agricultural soil was a strong source to the overlying atmosphere. However, the data and example illustrated in this study is based on FLUXNET data on a tower above a tree canopy. Gradients in H2O and CO2 were apparent and allow comparison between EC and MBR derived fluxes. Importantly, MBR, based on the concept of turbulent diffusion, requires the measurement of a clear gradient. For the canopy scenario given here, would this be apparent (i.e. measurable) for POPs, given the heights where CO2/H2O data were collected ($\sim$30 and $\sim$40 m) would likely result in concentration differences that

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could be non-existent for POP chemicals? While this study is not necessarily advocating the use of the FLUXNET/boreal towers for applying MBR to estimate POP fluxes, there is an implicit assumption that this will be the basis of follow up studies- is this the case?

The authors need to qualify their discussion relating to '..if the concentration gradients are high enough..' (final paragraph) by providing some choice examples of where these high gradients are likely to exist for POPs and other semi-volatile contaminants (e.g. above agricultural soil for pesticides, landfill or contaminated land for industrial POPs/PAHs, sewage-sludge lagoon etc, etc).

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 32759, 2015.