Response to Reviewer 2's comments

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.*

   Our main motivation for studying the modified Bowen ratio method was the increasing number of studies that use the MBR to measure fluxes of POPs such as PAHs, DDT and PCBs (e.g. Choi et al. for PAHs, Kurt-Karakus et al. for DDT and Rowe et al. for PCBs). In particular, the paper by Choi et al, served as the main inspiration for this study, and motivated us to test the accuracy of the MBR relative to the EC technique.

   We did not refer to the REA in our paper because we are not aware of any recent studies in the literature where the REA has been used for POPs or compounds with similar analytical chemistry and sampling challenges.

   From a theoretical standpoint, we see no reason why the REA could not be used for POPs and similar compounds. This is also demonstrated in the papers by Majewski et al. (Majewski et al., 1993) and in a later paper by Pattey et al. (Pattey et al., 1995) where the authors measured volatilization fluxes of triallate and trifluarin from recently treated soils. The fact that accurate flux measurements using the REA approach are technically more challenging (e.g. the use of solenoid valves and possible biases in isolating up and down drafts) however, might have been a motivation for other authors to choose the MBR to measure fluxes of POPs. In contrast to the REA method, the MBR method only requires small modifications to the traditional setup using high volume active air samplers that are common when sampling POPs.

   In our revisions we will add a reference to the REA technique as a possible alternative to the MBR, but we will note that to our knowledge it has not been widely applied to POPs or POP-like pollutants. We will also add a reference to Kurt-Karakus et al. as another example of the application of the MBR to POP-like chemicals.

   We will add the following paragraph to the revised text, on page 3, before the last paragraph:

   "Relaxed eddy accumulation (REA) is another method that is used to measure fluxes of chemicals for which the EC approach is not feasible. Unlike the MBR method, the REA only samples air at one height but uses fast switching valves in combination with high frequency measurements of the wind speed and direction to split the incoming airflow according to the prevailing vertical wind direction (Businger and Oncley, 1990). The air can then be collected in bags or other reservoirs (Pattey et al., 1993) for further analyses or be passed through denuders or sorbents such as polyurethane foam (PUF) (Majewski et al., 1993) as is done with conventional high volume sampling to accumulate the levels needed for analysis. To our knowledge, the REA method has not seen any recent uses to measure the fluxes of POPs or POP-like pollutants, unlike the MBR method which has seen an increasing number of applications in recent years. The likely reason is that it is technically more demanding to set-up the REA, and it requires specialized equipment."

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 (~30 and ~40 m) would likely result in concentration differences that 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 motivation for us to use a dataset from FLUXNET was its previous usage in the study of Choi et al. where the authors studied the fluxes of PAHs above a forest canopy. In that study, the authors reported a clear gradient in the concentrations of several PAHs in air at 30m and 40m height. The observed gradient was attributed to the presence of leaves in the canopy which were fully developed and provided a significant sink for the PAHs.

The forest filter effect describes the phenomenon in which the deposition of semi-volatile compounds to forested soils is larger than to non-forested soils due to the uptake in leaves and subsequent transport to the soil by shedding of leaves and waxes. The forest filter effect is thought to be most pronounced for chemicals with a log Koa between 7 and 11 and a log Kaw larger than -6. The compounds for which a significant downward flux to the canopy was observed in the study by Choi et al. included phenanthrene, anthracene and pyrene which have log Koa values of 7.5, 7.6 and 8.8 and log Kaw values of -2.8, -2.6 and -3.3 respectively which fit well within the range for the forest filter effect to be substantial. It can be expected that for other compounds with similar properties, a similar gradient could be measured above a developed forest canopy.

Currently we have no plans to do any flux measurements of POPs using FLUXNET/Boreal towers ourselves. However, we see a wide range of possible applications of the MBR method to measure fluxes of POPs and POP-like chemicals. We will include the following paragraph in the discussion section of the revised text to clarify and point out the broad range of potential applications:

“There is a wide scope for applying the MBR method to measure fluxes of POPs and POP-like chemicals in the atmosphere. A key data gap for many POPs is a lack of measurements of the fluxes of POPs from dispersed sources to the atmosphere (McKone and MacLeod, 2003), and the studies by Rowe et al. for PCBs from the Hudson river (Rowe and Perlinger, 2012), by Perlinger et al. for HCHs and hexachlorobenzene over Lake Superior (Perlinger et al., 2005) and by Kurt-Karakus et al.with treated soils (Kurt-Karakus et al., 2006) demonstrate that the MBR method could help fill that gap. Our results reported in this paper imply that measurements of fluxes of POPs could be accomplished using the MBR method with passive air samplers instead of the active samplers that have so far been used in these studies, as long as the direction of flux does not change during the sampling period and the concentrations gradients are large enough to be measured.”

3) *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).*

The reviewer makes a good point here. Our statements about “high enough” concentration gradients in the original draft of the paper were imprecise.

We have addressed this issue with the addition of a new paragraph as proposed above in comment 2 by giving more examples of where the MBR method might be useful and by stating explicitly that concentration gradients must be large enough to be measured.

Reference list:

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