

Response to Reviewer 1's comments

- 1) *The text of this manuscript has very little, if any, relation to its title which says that it's a guideline for using MBR to estimate POP fluxes. In fact, POPs is only mentioned once on each of the last two pages of text. ... As for the appropriateness of publishing this manuscript in Atmos. Chem. Phys., if the authors change the title to reflect what is actually in the text, then yes, it is appropriate.*

We agree with the reviewer that the proposed title was not a good reflection of the actual contents of the paper. In response we have changed our title to: "Comparison of eddy covariance and modified Bowen ratio methods for measuring gas fluxes and implications for measuring fluxes of persistent organic pollutants", which we think is a better summary of the findings brought forward in this study.

- 2) *... All these K estimations were made for fluxes measured over a mixed deciduous forest between about 30 and 45 m. This would be fine if POP fluxes were to be estimated there, but I suspect that deciduous forests are not POP "hot spots." Nowhere in the text is there any mention of where POP volatilization fluxes are likely to be measured.*

This comment is very similar to that received from Reviewer 2: "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?" And we feel that the same reply is applicable here as well.

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 K_{oa} between 7 and 11 and a log K_{aw} 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 K_{oa} values of 7.5, 7.6 and 8.8 and log K_{aw} 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) *... There is no discussion as to the surface and source conditions that need to be met for any of the flux estimation methods to work properly and yield reasonable results and how having “non-ideal” conditions will affect the flux estimations.*

We agree with the reviewer that we did not provide a detailed specification of conditions needed to perform to perform flux measurements using the MBR method. We believe that our new title: “Comparison of eddy covariance and modified Bowen ratio methods for measuring gas fluxes and implications for measuring fluxes of persistent organic pollutants” reflects the contents of our study better and that it makes it clear that we’re not offering step by step guidelines for the use of the MBR method.

There is a wide range of literature available which focuses mostly on the conditions needed to make reliable measurement with the eddy covariance approach, which we think is outside the scope of our study. Our study shows however, that changes in the direction of fluxes during the sampling period can affect the flux estimations with the MBR method. This is an example of a non-ideal condition that affects the MBR method but not the EC measurements which fits well within the scope of our study, where we compare the two methods.

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 K_{oa} between 7 and 11 and a log K_{aw} 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 K_{oa} values of 7.5, 7.6 and 8.8 and log K_{aw} 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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List of changes made in response to the reviewers' comments

- 1) We have changed the title from “Guidelines for applying the modified Bowen ratio method to estimate gas fluxes of persistent organic pollutants” to “Comparison of eddy covariance and modified Bowen ratio methods for measuring gas fluxes and implications for measuring fluxes of persistent organic pollutants.” To better reflect the contents of the study.
- 2) We have included a new paragraph on page 3, on the relaxed eddy accumulation method and a motivation on why we have chosen to work with the MBR method instead.
- 3) We have included a new paragraph on page 14, where we discuss the scope for application of the MBR method.

Comparison of Eddy Covariance and Modified Bowen Ratio Methods for Measuring Gas Fluxes and Implications for Measuring Fluxes of Persistent Organic Pollutants

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Abstract

Semi-volatile persistent organic pollutants (POPs) cycle between the atmosphere and terrestrial surfaces, however measuring fluxes of POPs between the atmosphere and other media is challenging. Sampling times of hours to days are required to accurately measure trace concentrations of POPs in the atmosphere, which rules out the use of eddy covariance techniques that are used to measure gas fluxes of major air pollutants. An alternative, the modified Bowen ratio (MBR) method, has been used instead. In this study we used data from FLUXNET for CO₂ and water vapor (H₂O) to compare fluxes measured by eddy covariance to fluxes measured with the MBR method using vertical concentration gradients in air derived from averaged data that simulates the long sampling times typically required to measure POPs. When concentration gradients are strong and fluxes are unidirectional, the MBR method and the eddy covariance method agree within a factor of 3 for CO₂, and within a factor of 10 for H₂O. To remain within the range of applicability of the MBR method field studies should be carried out under conditions such that the direction of net flux does not change during the sampling period. If that condition is met then the performance of the MBR method is not strongly affected by the length of sample duration nor the use of a fixed value for the transfer coefficient.

1 **1 Introduction**

2 Despite the more than decade-old global ban on the production and use of persistent organic
3 pollutants (POPs) such as polychlorinated biphenyls (PCBs), hexachlorobenzene and several
4 organochlorine pesticides, these chemicals are still present in the environment and continue to
5 raise concerns due to their persistence, bioaccumulation, toxicity and potential for long-range
6 atmospheric transport (The Secretariat of the Stockholm Convention, 2010). As the
7 production and use of POPs continues to decline, large cities, old stocks and re-volatilization
8 from soil are expected to become more important sources to the atmosphere (Nizzetto et al.,
9 2010). Studying the sources and fate of organic pollutants in the environment is an important
10 prerequisite to exposure and risk assessment, and environmental fate models that calculate
11 fluxes of pollutants between air, water, soil, vegetation and other media have proven to be a
12 valuable tool in this respect (McKone and MacLeod, 2003). Measurements of fluxes of POPs
13 emanating from source areas and between the atmosphere and other environmental media are
14 needed to parameterize and evaluate the chemical fate models that are used as scientific
15 support for international conventions on POPs (Gusev et al., 2012).

16
17 The preferred approach to measure the flux of major air pollutants between the earth's surface
18 and the atmosphere is the eddy covariance (EC) technique (Baldocchi et al., 1988). It is based
19 on measuring the covariance of the concentration of a pollutant and the vertical wind velocity,
20 using data from very fast measurements (e.g. 5-10 Hz). This approach works well for
21 compounds such as CO₂, methane, ozone and more recently also for mercury (Pierce et al.,
22 2015), since concentrations can be measured at a high temporal resolution. However, it cannot
23 be applied directly when studying trace-level organic micropollutants that require sampling
24 times of at minimum several hours when using active high-volume sampling, or even several
25 weeks when using passive samplers (Hung et al., 2013) to result in reliable, quantifiable data.

26
27 One way to estimate chemical fluxes from measurements based on sampling times of hours to
28 days is to use the modified Bowen ratio (MBR) method (Businger, 1986). The MBR method
29 is based on the assumption that turbulent atmospheric transport occurs indiscriminately for
30 chemicals, heat and other scalar quantities that can be described entirely by their magnitude
31 without reference to direction. It can be used to measure the flux of a chemical pollutant (x)

from measurements of its concentration at two heights and the measured transfer coefficient of another scalar such as heat (y) over the same height interval (Meyers et al., 1996, eq. 1):

$$F_x = -K_y * \frac{\Delta C_x}{\Delta Z} \quad \text{eq. 1}$$

Where F_x ($\text{ng m}^{-2} \text{h}^{-1}$) is the flux of the chemical x of interest, K_y ($\text{m}^2 \text{h}^{-1}$) is the measured eddy diffusion coefficient for a scalar y over the height interval ΔZ (m) and ΔC_x (ng m^{-3}) is the measured concentration gradient of x over the height interval. The negative sign on the right hand side of the equation enforces the convention that downward fluxes have a negative sign, and upward fluxes a positive sign.

Among other applications, the MBR method has been used to measure volatilization fluxes of pesticides applied to agricultural fields (Majewski, 1999), to estimate PCB fluxes from Lake Superior to the overlying air phase (Rowe and Perlinger, 2012) and fluxes of polycyclic aromatic hydrocarbons (PAHs) above a forest canopy in Canada (S.-D. Choi et al., 2008). In the study of Choi et al., air was sampled for 24 h every 3 days at different heights for a period of one month while leaves in the forest canopy were developing. The samples were analyzed for PAHs and the data was combined with the eddy diffusivity of heat (K_{heat}) determined from eddy covariance measurements from the FLUXNET network to estimate vertical PAH fluxes using the MBR method.

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.

Our goal in this study was to test the limits of applicability of the MBR method and to evaluate its accuracy relative to the ‘standard’ EC technique. We used data from the FLUXNET network to calculate fluxes of CO₂ and water vapor (H₂O) with the MBR method under different sampling duration scenarios and different assumptions about data availability for the eddy diffusion coefficient K_y . Thus, we took advantage of the high-frequency measurement data for CO₂ and H₂O, and used them as proxies for organic micropollutants in order to analyze the performance of the MBR method compared to the EC method. By averaging the FLUXNET data over periods that ranged from 1 hour to 1 week, we simulated sampling times that are typically required to measure POPs and other organic micropollutants in air. Our approach is similar to the one used by Majewski (see (Majewski, 1999a), who simulated 24 h sampling periods from higher frequency data to characterize the potential for long sampling times to introduce error to the aerodynamic profiling method.

2 Methods

2.1 Datasets

All data used in this study can be accessed freely on the web via the FLUXNET homepage (<http://fluxnet.ornl.gov/>). A figure showing the flux tower and associated instruments can be found in the Supplementary material Fig. S.M. 1. The dataset used in this study contains eddy flux parameters and micrometeorological measurements for the year 2009 taken at the Borden mixed deciduous forest site in Ontario, Canada (FLUXNET site code: CA-Cbo). A list of all parameters is given in the Table S.M. 1. We selected measurements taken at heights of 33.3 m and 40.7 m. Air sampling in the study by Choi et al. (S.-D. Choi et al., 2008) was conducted at the same site in 2003 at heights of 29.1 m and 44.4 m.

Prior to any calculations, we filtered the data to remove about 25% of the observations that were flagged as unreliable for CO₂ or H₂O. Details on the criteria for the flags can be found on the FLUXNET homepage. Common reasons for flagging are instrument malfunctions, calibration problems and outliers. All flagged data was filtered out simultaneously, such that our analysis only includes data points collected at times when data were not flagged for either CO₂ or H₂O.

On inspection of the distribution of the CO₂ and H₂O concentration gradients, it was apparent that a few outliers that had not been flagged could significantly alter the average gradient when pooling the data to simulate long sampling times. These outliers in some cases led to net flux estimations based on the MBR method that were in the opposite direction compared to the EC method. To exclude such outliers and reduce the influence of extreme values of measured parameters, the highest and lowest 2.5% of values of the CO₂ gradient and the H₂O gradient were removed from the dataset prior to further calculations.

2.2 Modified Bowen Ratio

We used K_{heat} derived from EC flux measurements and measurements of the scalar temperature at two heights, as described in the paper by Choi et al. (S.-D. Choi et al., 2008) to specify the eddy diffusivity in the MBR method (K_y in eq. 1). Specifically, K_{heat} was inferred from the dataset by first calculating the vertical turbulent flux of the sonic anemometer temperature $\overline{W'T'}$ (K m s⁻¹, eq. 2) from the turbulent sensible heat flux (Q in W m⁻² or J s⁻¹ m⁻²), using the air density (σ_{air} in kg m⁻³) and the gravimetric heat capacity (c_p) of air measured at 33 m height (1005.7 J kg⁻¹ K⁻¹). Spurious K_{heat} values less than or equal to zero were removed from the dataset as these would indicate a heat flux against the measured temperature gradient.

$$\overline{W'T'} = \frac{Q}{c_p \sigma_{\text{air}}} \quad \text{eq. 2}$$

K_{heat} (m² s⁻¹) was then calculated based on temperatures measured at 40.7 m and 33.3 m according to eq. 3:

$$K_{\text{heat}} = -\overline{W'T'} \frac{(40.7 \text{ m} - 33.3 \text{ m})}{(T_{40.7} - T_{33.3})} \quad \text{eq. 3}$$

Finally, vertical turbulent fluxes of CO₂ and H₂O were calculated using the MBR method and measured concentrations at 33 m and 41.5 m averaged over different time intervals selected to represent sampling times typical for organic micropollutants, as described below. Fluxes

calculated with the MBR method were compared with those measured by the EC method available from the FLUXNET dataset.

2.3 Data-analysis

To simulate sampling times typical for organic micropollutants, concentrations of CO₂ and H₂O reported as 30 minute averages in the database were pooled and averaged over periods of 1 h, 2 h, 4 h, 8 h, 24 h, 3 days (72 h), and 1 week (168 h). Fluxes during four two-month periods selected to represent each of the four seasons were then calculated from median values of these pooled data points during the entire period. Thus for example, fluxes calculated from 1 h simulated sampling times are based on the median of average vertical concentration gradients in 1 h pools measured at the same time each day over the entire 2 month period (See Fig. S.M. 2 for a visual representation). Medians were used instead of geometric means because of the presence of negative flux values. January and February represented winter, April and May spring, July and August summer and October and November fall.

We tested two approaches to specify K_{heat} in the MBR method calculations. In the first approach hourly average K_{heat} values were calculated from 30 min averages of temperature measurements reported in the database. In the second approach a geometric mean of K_{heat} was calculated for all time points across the entire period corresponding to the simulated sampling time. The first approach takes advantage of the availability of high temporal resolution information about K_{heat} at the FLUXNET site, but the second approach is likely to be common when applying the MBR since high frequency meteorological data is not always available.

The direction of flux for CO₂ can change on a diurnal basis (See Fig. 1 and Fig. S.M. 3). During the day the flux of CO₂ is often negative (i.e., downward) due to photosynthesis while during the night, plant respiration produces CO₂ and fluxes are positive (i.e. to the atmosphere). In addition, atmospheric conditions during the night are typically much more stable than during the day, resulting in a lack of large turbulent eddies and a higher contribution of additional transport mechanisms, such as horizontal advection, to the total flux. The result is that fluxes measured using EC during the night are often underestimated (Aubinet, 2008).

To understand the impact of changing directions of flux and to investigate potential underestimation of flux at night, fluxes during the day and during the night calculated with the MBR method were evaluated against EC measurements separately. Nighttime data was set to cover from 9 p.m. to 5 a.m. local time across all seasons, and daytime data was set from 9 a.m. to 5 p.m. local time. The nighttime / daytime divisions were selected based on the shortest interval between sunrise and sunset at the site. The 8 hour periods representing day and night allowed us to construct 24 hour, 3 day and 1 week sampling periods by averaging a whole number of 8 hour periods taken at the same time of day over multiple days. In addition to the nighttime/daytime split data, we also examined the performance of the MBR method relative to the EC method when using continuous data that ignored day/night differences.

3 Results

3.1 K_{heat} and concentration gradients

Our calculated K_{heat} values (Fig. 1) are in good agreement with values for the same site during the same time of year in 2003 (S.-D. Choi et al., 2008, shown in Fig. S.M. 4). Values are close to 0 during the night and in the range of $0.0026 \text{ m}^2 \text{ s}^{-1}$ to $35.8 \text{ m}^2 \text{ s}^{-1}$ during the day over the summer period, with 95 % of the values between 0.029 and $22.11 \text{ m}^2 \text{ s}^{-1}$.

The fluxes calculated with the MBR method are proportional to the product of K_{heat} and the concentration gradient of either CO_2 or H_2O (eq. 1). The raw data at 30 min time resolution that was pooled and used to calculate the fluxes with the MBR method is visualized in Fig. 1.

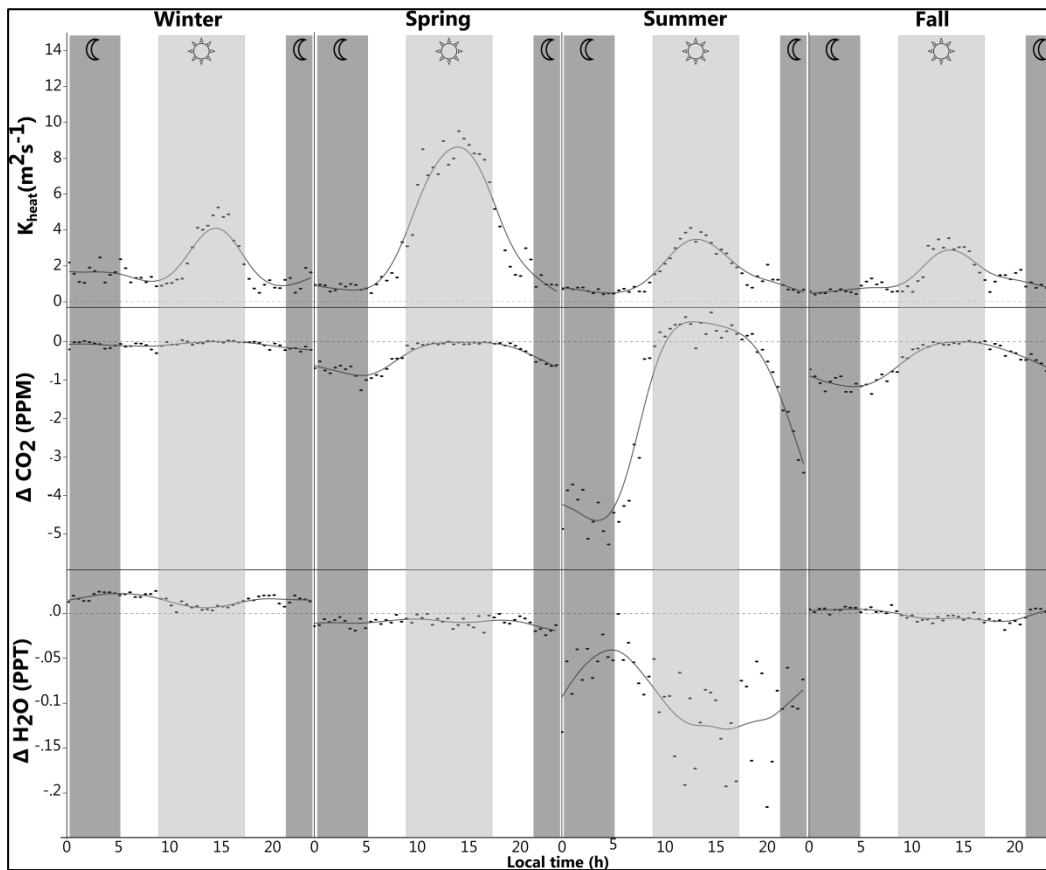


Figure 1: Half-hourly averages of K_{heat} and the concentration gradients of CO_2 and H_2O across the different seasons (concentration at 40.7 m – concentration at 33.3 m). The dotted line indicates 0 in all plots, the grey areas indicate the 8 hour periods representing day and night.

3.2 Performance of the MBR method on continuous time series

When used with continuous time series, fluxes measured with the MBR method are often not of the right magnitude and/or direction for CO_2 relative to the ‘reference’ EC data (see a representative example in Figure 2). Inspection of the results indicated that the MBR method would fail when the direction of the flux of CO_2 changed during the simulated sampling period. Based on this result, we focused our analysis on comparing the performance of the MBR method to the EC method only during the day or only during the night when fluxes are generally unidirectional.

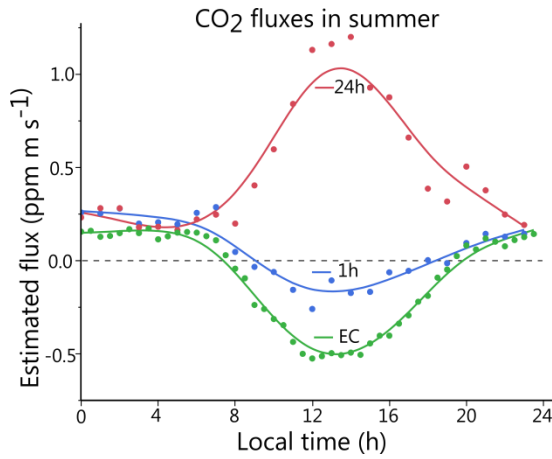


Figure 2: A comparison of measured fluxes using the modified Bowen ratio (MBR) method (1h and 24h pooled data using hourly K_{heat} values) with the eddy covariance (EC) measurements. The simulated 24-h sampling time includes a change in the direction of the CO_2 flux, which results in a measured flux with the MBR method that has the wrong direction and magnitude.

3.3 Performance of the MBR method with hourly-resolved and fixed values of K_{heat}

The use of either hourly-resolved data for K_{heat} or a fixed value did not significantly affect the the MBR method. A student t-test comparing the similarity of the 2 datasets resulted in a P value below 0.0001.

Results using a fixed value for K_{heat} are shown in Table 1; those using hourly-resolved data for K_{heat} are given in the supplementary material (See Table S.M. 2)

3.4 Performance of the MBR method on day/night split data

Fluxes of CO_2 during the nighttime only, measured using the MBR method in combination with simulated sampling times ranging from 1 hour to 1 week are on average a factor of 1.7 and up to a factor of 2.1 larger than those derived with the EC method (see Table 1). Fluxes of CO_2 during the daytime only, measured using the MBR method have, in some cases, the opposite sign of the fluxes reported using the EC technique. Specifically, the MBR method produces daytime fluxes with the opposite sign compared to the EC method during daytime in the spring and for the 1-week duration simulated sampling scenario in the winter (values marked with (!) in Table 1). In those cases where the direction of flux calculated with the MBR does not agree with the EC method, the disagreement is attributable to the median value of ΔCO_2 (between 41.5 m and 33m) selected to represent the sampling period having a sign that implies a flux in the opposite direction of the flux measured with the EC method.

In cases where the direction of daytime flux measured using the MBR method agreed with the EC method, the ratio of the two fluxes ranged from 0.32 to 1.4, implying that the two methods differed by factors that range from 1.4 to 3.0 and that the MBR method may either underestimate or overestimate fluxes relative to the EC method.

Table 1: Cumulative fluxes for 8 h periods representing day and night across the 2 month periods representing spring, summer, fall and winter. Fluxes measured by the MBR method that are in the opposite direction than those measured by the EC method are marked with „!“. Positive fluxes are defined as fluxes moving upwards from the canopy. The ratio of MBR results over EC results is based on the geometric mean of the MBR results divided by the EC result. The MBR fluxes for the 1-week sampling period were left out in the calculation of the geometric mean during the day in winter for CO₂ and during the night in fall for H₂O. This table shows fluxes calculated with a fixed value for K_{heat} .

For H₂O, the fluxes measured with the MBR method are in the same direction as those measured by the EC method during spring, summer, and during the day in the fall. When the two methods agree about the direction of flux, the ratio of fluxes measured by the MBR method to the EC method is between 0.9 and 0.052, implying differences between the methods by factors of 1.1 to 20, and that fluxes of H₂O are underestimated if the MBR method is applied as compared to the EC method. Fluxes measured during the winter season with the MBR method are negative (i.e., from the atmosphere to the surface), while the EC method indicates fluxes are positive (i.e., from the surface to the atmosphere). Fluxes measured by both methods during the night in the fall are small, with a upward flux measured using the EC method and downward fluxes measured by the MBR method in all cases except the longest 1-week simulated sampling period.

In general, the fluxes measured using the two different methods are in better agreement for CO₂ than for H₂O (Table 1). It is interesting to note that the MBR method generally overestimates the flux of CO₂ relative to the EC method, while it in most cases underestimates fluxes of H₂O.

4 Discussion

The MBR method fails for CO₂ when using continuous time series in cases where the simulated sampling period encompasses the shift between night and day and there is also a shift from upward fluxes (dominated by respiration) at night to downward fluxes (dominated by photosynthesis) during daytime. As shown in eq. 3, the flux estimated using the MBR method only depends on K_{heat} and the vertical concentration gradient for the compound of

1 interest. The error arises because the average values of K_{heat} are dominated by high values that
2 occur during the day, while average values of ΔCO_2 are dominated by extreme values that
3 occur at night (see especially the summer season for CO_2 in Fig. 1 and data for CO_2 in the
4 summer visualized in Fig. S.M. 5).

5
6 The CO_2 fluxes determined using the MBR method during the daytime for the spring season
7 and when simulating a sampling time of 1 week during daytime for the winter were in the
8 opposite direction relative to the fluxes determined using the EC method. During spring this
9 could be caused by a reversal of the direction of flux due to the development of leaves and the
10 start of photosynthesis taking place halfway across the season, which would produce a shift
11 from a continuous net flux of CO_2 out of the canopy to a diel cycle of CO_2 uptake and release.
12 Furthermore, it is possible that the simulated 1 week sampling duration during daytime in the
13 winter might have encompassed periods when the net direction of flux of CO_2 changed due to
14 the movement of air masses with variable CO_2 concentrations across the region. Thus, all of
15 the cases of disagreement between the MBR method and the EC method about the direction
16 of flux of CO_2 that are shown in Table 2 might be attributable to applying the MBR method
17 using simulated sampling times that encompass a change of direction of the net flux.

18
19 In general, the duration of simulated sampling does not have a strong influence on the fluxes
20 measured with the MBR method. Exceptions are the longest simulated sampling times in
21 during the daytime in winter for CO_2 and during nighttime in the fall for H_2O . We simulated
22 sampling times of 24 hours, 3 days and 1 week by combining data that were measured over
23 non-consecutive 8 h periods during 2 month time windows selected to represent the four
24 seasons. For the 3 day and 1 week simulated sampling times there are just 3 to 4 data-points
25 per season, depending on the data availability, which may introduce higher uncertainty in the
26 median value used in our MBR method calculations compared to the shorter simulated
27 sampling times.

28
29 For H_2O , which nearly always has a net flux upwards from the canopy during both the day
30 and the night, pooling of the data over longer time intervals and application of the MBR
31 method also led to estimations of the direction of flux that were opposite the EC method in

the winter and fall seasons. In winter, fluxes of H₂O measured by the EC method were small and upwards, while those calculated with the MBR method were small and downwards (Table 2). A recent study focusing on drainage basins in Canada, reported low but positive fluxes of water vapour during the winter season (Wang et al., 2014), which is consistent with measurements using the EC method. In this case we traced the origin of the different directions of flux calculated with the MBR method relative to the EC method to differences in H₂O concentration gradients across different height intervals. Reported fluxes of H₂O using the EC method were measured at 33.3 m while for the MBR method we have used a gradient of concentrations measured at 41.5 and 33 m. During the winter for H₂O there was a clear discrepancy between gradients measured at these heights and between 33 m and 25.7 m, with the latter being more consistent with the EC measurements (Fig. S.M. 6). The cold and low humidity during the winter in Canada might play a role here as discrepancies between the concentration gradients of H₂O at different heights were only observed in the winter and to a lesser extent in the fall.

It is clear from our analysis that a requirement for the MBR method to give accurate results for prolonged sampling times is to only sample during a time period when the chemicals of interest are expected to have a unidirectional flux. The occurrence of a day / night regime has implications for designing sampling campaigns for organic pollutants that require sampling times longer than the 8-hour intervals with stable conditions chosen as daytime or nighttime above, and which may exhibit changes in the direction of flux between daytime and nighttime periods. This can be the case for many POPs, and the direction of fluxes can be estimated using appropriately parameterized dynamic chemical multimedia fate models (see, for example, Gasic et al., 2010). When longer sampling times are needed, samples could be pooled by sampling at the same time of day during consecutive 24-hour periods as was simulated here by combining data from selected 8 hour periods.

When sampling over time periods of several hours to several days, as simulated in this study, it is very likely that steady-state conditions during the sampling period are not achieved. Our results indicate however that when fluxes were unidirectional, measurements using the MBR method were usually within 1 order of magnitude of those from the EC method, and that in most cases the difference was less than a factor of 4. The summer period, in which K_{heat} is low

1 and the gradients of CO₂ and H₂O are large due to stable atmospheric conditions, showed the
2 best agreement between the MBR and EC methods. In the study of Choi et al. (S.-D. Choi et
3 al., 2008), they estimated their uncertainty in fluxes of PAHs derived from the MBR method
4 was an order of magnitude, which is within the range of agreement we obtained between the
5 MBR method and the EC method.

6
7 Fluxes measured with the MBR method corresponded better with the EC data for CO₂ than
8 for H₂O, the reason of which is unknown. However our investigation of the discrepancy in
9 direction of flux between the two methods for H₂O in the winter suggests that the
10 concentration gradient of H₂O is more variable over height than that of CO₂. Therefore the
11 gradient that we selected between 41.5 m and 33m may be more representative of the flux
12 measured at 33.3 m with the EC method for CO₂ than for H₂O.

13
14 In general, the variation between fluxes determined using the MBR method for different
15 sampling frequencies was small, suggesting that longer sampling times did not introduce a
16 higher bias relative to EC measurements. Using a single value for K_{heat} , in this case the
17 geometric mean across the sampling period, was found to be a good substitute for hourly K_{heat}
18 values, indicating that it is possible to use the MBR method when there is no high frequency
19 data available for the transfer coefficient.

20
21 Some studies have shown that additional transport mechanisms aside from eddy diffusion,
22 such as advection, can become more important during night, thereby violating the conditions
23 needed for EC measurements to take place, and resulting in underestimations of the night time
24 fluxes (Aubinet, 2008). In this study, there is no clear difference in the performance of the
25 two methods relative to one another during either day or night. We note however that the
26 MBR method relies on K_{heat} determined under the assumption that only turbulent atmospheric
27 processes occur, so the effect of additional transport mechanisms might not be evident in our
28 analysis.

29 Based on the findings in this study it is clear that field studies that use the MBR method to
30 measure gas fluxes of POPs and other organic micropollutants should be designed such that
31 the direction of the flux does not change during the sampling period. If this condition is

fulfilled and the concentration gradients are large enough to be measured accurately, then we find no strong evidence that the duration of sample collection affects the performance of the MBR method. Furthermore, using a fixed value for the transfer coefficient instead of hourly data is a good alternative that should not introduce a significant bias when there is no high frequency data available.

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.

The MBR method could also be used to measure fluxes of POPs in depositional areas such as forests as shown by the study of Choi et al. (S.-D. Choi et al., 2008) or in source areas such as large cities where recent studies of vertical concentration gradients of POPs did not lead to quantitative flux estimates (Li et al., 2009; Moreau-Guigon et al., 2007). 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.

Author contributions

M. M. had the idea for this study, D. B. and M. M. designed the study and D. B. gathered the data, performed the analysis and prepared the manuscript with contributions from A. J. and M. M..

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5 chemicals in forest systems”.

6

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1 **Tables:**

2 Table 1

CO2 (PPM m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		-0.332	0.295	-3.360	1.071	0.074	0.227	0.189	0.112
modified Bowen ratio constant K_{heat}	1/h	0.275 (!)	0.408	-1.202	1.529	0.073	0.390	0.163	0.224
	1/2h	0.313 (!)	0.434	-1.124	1.703	0.113	0.421	0.187	0.196
	1/4h	0.319 (!)	0.413	-1.107	1.544	0.067	0.396	0.163	0.199
	1/8h	0.250 (!)	0.441	-1.000	1.697	0.093	0.392	0.159	0.159
	1/day	0.353 (!)	0.466	-1.064	2.602	0.145	0.527	0.176	0.185
	1/3days	0.335 (!)	0.658	-0.991	2.258	0.138	0.618	0.096	0.185
	1/week	0.409 (!)	0.459	-1.114	2.576	0.136	0.621	-0.019 (!)	0.032
MBR/EC method		-0.960 (!)	1.566	0.323	1.811	1.425	2.071	0.893	1.317

3

H2O (PPT m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		0.420	0.016	1.118	0.038	0.180	0.005	0.049	0.001
modified Bowen ratio constant K_{heat}	1/h	0.048	0.006	0.243	0.027	0.011	-0.001 (!)	-0.007 (!)	-0.009 (!)
	1/2h	0.052	0.006	0.236	0.030	0.009	-0.001 (!)	-0.007 (!)	-0.008 (!)
	1/4h	0.040	0.007	0.265	0.032	0.008	-0.001 (!)	-0.006 (!)	-0.007 (!)
	1/8h	0.033	0.009	0.239	0.030	0.008	-0.001 (!)	-0.008 (!)	-0.008 (!)
	1/day	0.029	0.009	0.269	0.044	0.007	-0.001 (!)	-0.004 (!)	-0.011 (!)
	1/3days	0.046	0.012	0.332	0.050	0.010	-0.003 (!)	-0.015 (!)	-0.015 (!)
	1/week	0.061	0.007	0.323	0.038	0.014	0.001	-0.009 (!)	-0.014 (!)
MBR/EC method		0.102	0.464	0.241	0.915	0.052	-0.169 (!)	-0.149 (!)	-9.305 (!)

1 Table S.M.1

Parameter	Units
W'TSonic'(rot)	K m s-1
W'CO ₂ *(rot)	PPM m s-1
W'H ₂ O*(rot)	PPT m s-1
CO ₂ _25.7m	PPM
CO ₂ _33.0m	PPM
CO ₂ _41.5m	PPM
H ₂ O_25.7m	mmol mol-1 (PPT)
H ₂ O_33.0m	mmol mol-1 (PPT)
H ₂ O_41.5m	mmol mol-1 (PPT)
AirDensity_33m	Kg m-3
AirTemp_33.3m	Deg C
AirTemp_40.7m	Deg C
SensHtFlux	W m-2

2
3

1 Table S.M. 2

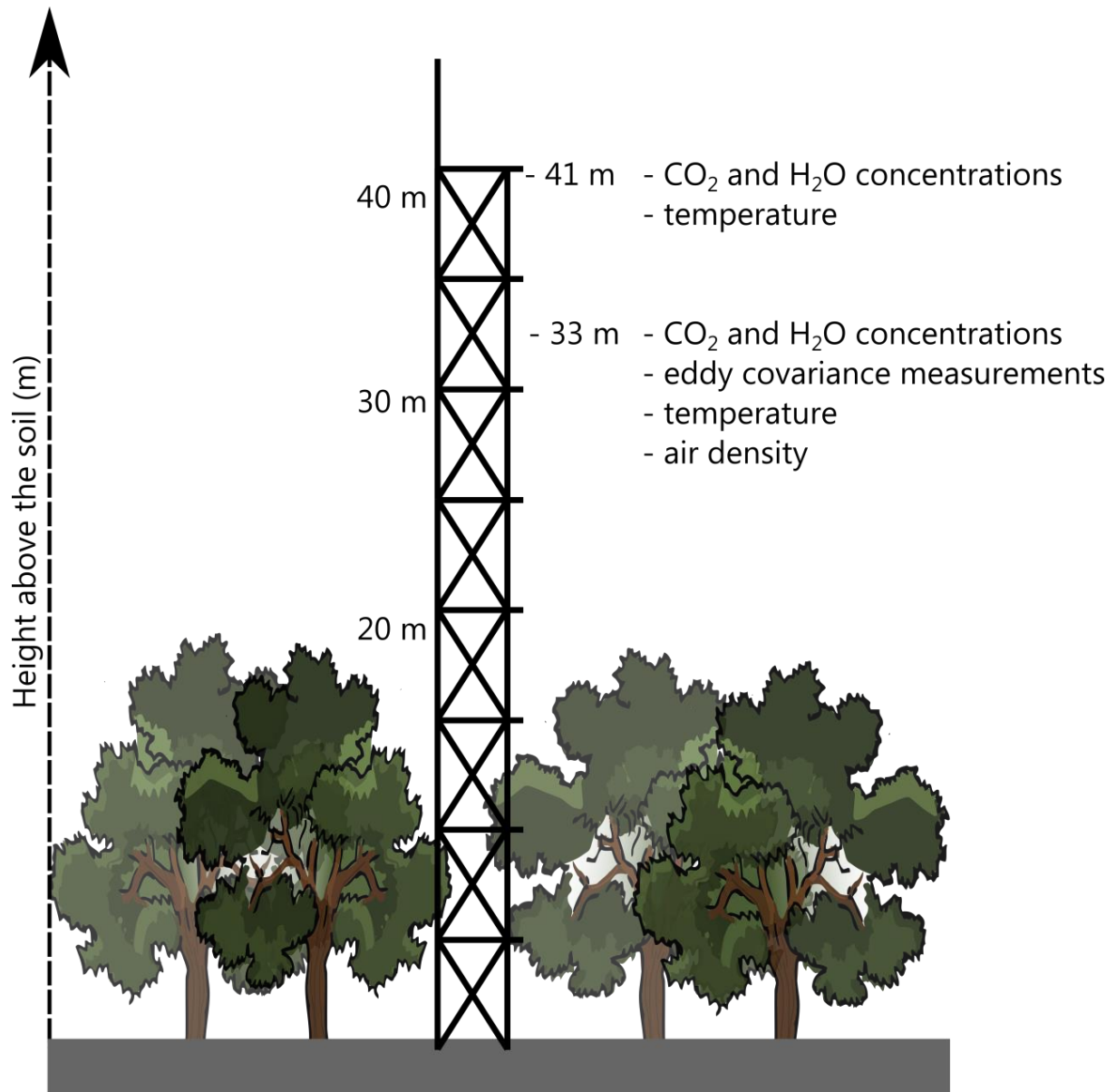
CO2 (PPM m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		-0.332	0.295	-3.360	1.071	0.074	0.227	0.189	0.112
modified Bowen ratio hourly K_{heat}	1/h	0.245 (!)	0.470	-1.223	1.599	0.027	0.388	0.148	0.218
	1/2h	0.29 (!)	0.480	-1.133	1.789	0.061	0.417	0.162	0.189
	1/4h	0.306 (!)	0.473	-1.079	1.694	0.050	0.395	0.141	0.194
	1/8h	0.265 (!)	0.522	-1.069	1.889	0.098	0.416	0.173	0.157
	1/day	0.374 (!)	0.552	-1.137	2.897	0.152	0.559	0.191	0.182
	1/3days	0.355 (!)	0.778	-1.060	2.514	0.145	0.656	0.105	0.182
	1/week	0.432 (!)	0.543	-1.191	2.868	0.143	0.659	-0.020 (!)	0.031
MBR/EC method		-0.959 (!)	1.820	0.335	1.978	1.116	2.137	0.796	1.289

2

H2O (PPT m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		0.420	0.016	1.118	0.038	0.180	0.005	0.049	0.001
modified Bowen ratio hourly K_{heat}	1/h	0.052	0.007	0.266	0.036	0.013	-0.001 (!)	-0.005 (!)	-0.009 (!)
	1/2h	0.057	0.007	0.256	0.038	0.009	-0.001 (!)	-0.004 (!)	-0.009 (!)
	1/4h	0.042	0.009	0.278	0.040	0.007	-0.000 (!)	-0.005 (!)	-0.007 (!)
	1/8h	0.035	0.011	0.259	0.036	0.008	-0.001 (!)	-0.009 (!)	-0.008 (!)
	1/day	0.030	0.011	0.292	0.052	0.008	-0.001 (!)	-0.004 (!)	-0.011 (!)
	1/3days	0.049	0.014	0.361	0.059	0.011	-0.004 (!)	-0.016 (!)	-0.015 (!)
	1/week	0.065	0.009	0.351	0.044	0.016	-0.001 (!)	-0.009 (!)	-0.014 (!)
MBR/EC method		0.109	0.570	0.261	1.117	0.055	-0.156 (!)	-0.132 (!)	-9.554 (!)

3

1 **Supplementary material**



2
3 *Figure S.M. 1: The flux tower and parameters of interest to this study. A more detailed figure can be found on the website of*
4 *Environment Canada (<http://www.ec.gc.ca>).*

1 *Table S.M. 1: Overview of parameters taken from the datasets. The comment “(rot)” is given when coordinates are rotated*
2 *to correct for the sonic anemometer not being perfectly levelled.*

Parameter	Units
W'TSonic'(rot)	K m s-1
W'CO ₂ *(rot)	PPM m s-1
W'H ₂ O*(rot)	PPT m s-1
CO ₂ _25.7m	PPM
CO ₂ _33.0m	PPM
CO ₂ _41.5m	PPM
H ₂ O_25.7m	mmol mol-1 (PPT)
H ₂ O_33.0m	mmol mol-1 (PPT)
H ₂ O_41.5m	mmol mol-1 (PPT)
AirDensity_33m	Kg m-3
AirTemp_33.3m	Deg C
AirTemp_40.7m	Deg C
SensHtFlux	W m-2

3

Half hourly ΔConc

Time points	T1	T2	T3	T4	...	...	T47	T48
Flux measurements	M1	M1	M1	M1	...	...	M1	M1
	M2	M2	M2	M2	...	...	M2	M2
	...	...	...	...	...	...	...	...
	Mn	Mn	Mn	Mn	...	...	Mn	Mn



Hourly ΔConc

Time points	T1	T2	...	T24
Flux measurements	M1	M1	...	M1
	M2	M2	...	M2
	...	...	...	...
	Mn	Mn	...	Mn



Median hourly ΔConc

Time points	T1	T2	...	T24
Median flux	M	M	...	M

Figure S.M. 2: Example of how the data was pooled, with ΔConc as the concentration gradient over the 2 heights. For example, fluxes calculated from 1 h simulated sampling times are based on the median of average vertical concentration gradients in 1 h pools measured at the same time each day over the entire 2 month period.

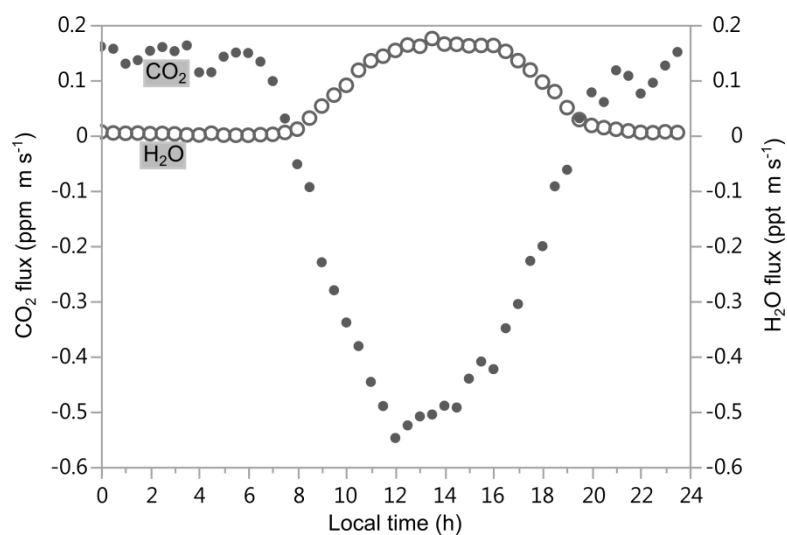


Figure S.M. 3: Comparison of daily averaged fluxes for CO₂ and H₂O in summer. Note the difference in scale between the two compounds.

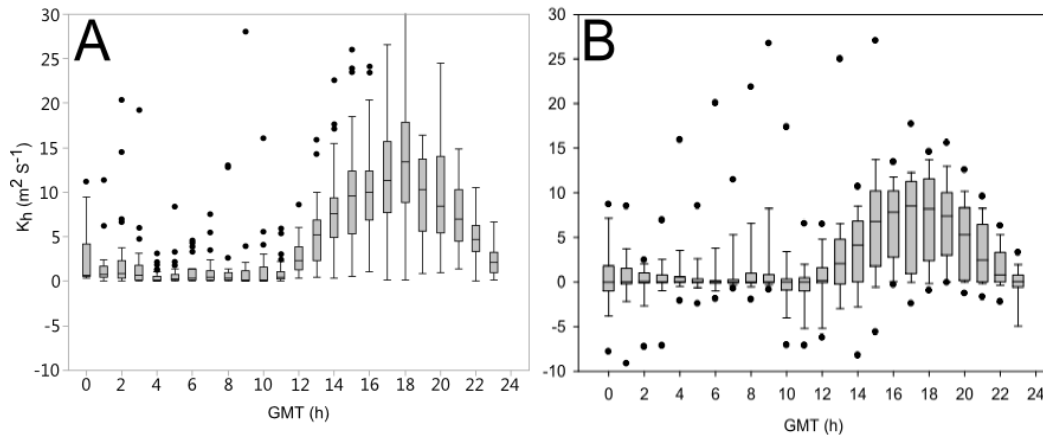
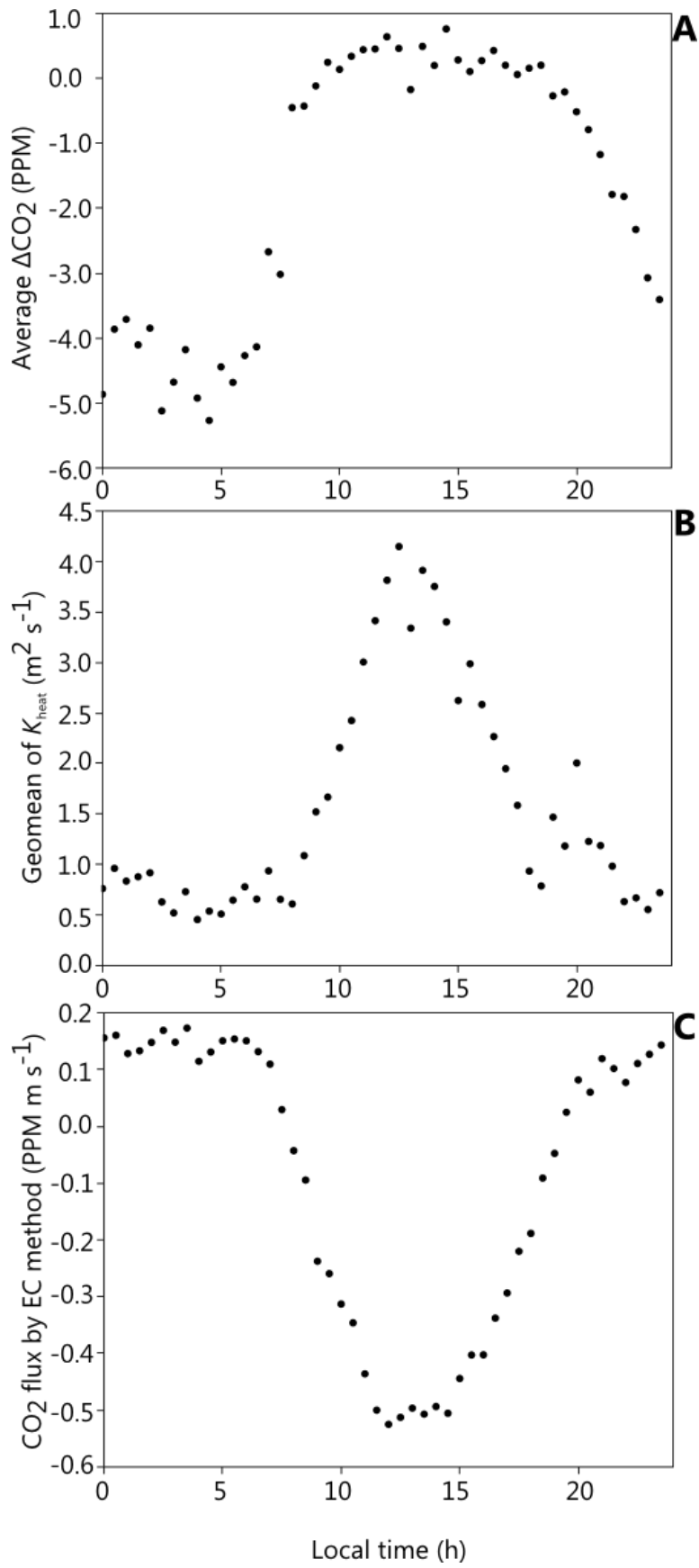


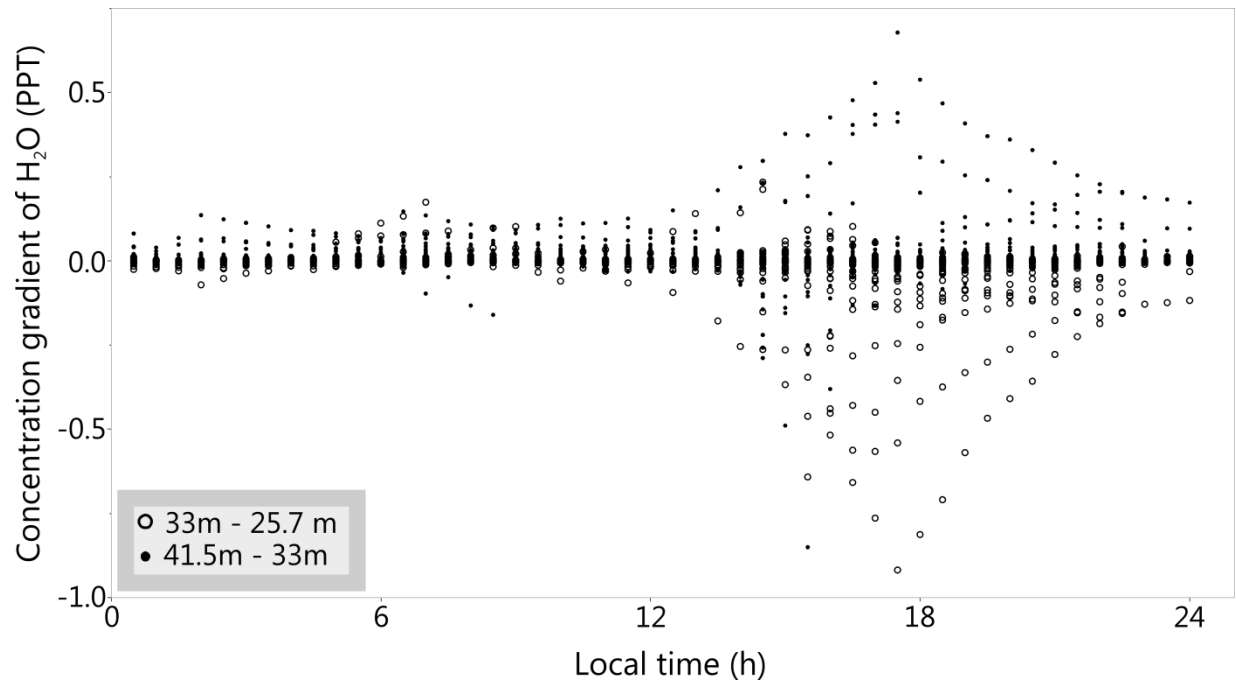
Figure S.M. 4: Comparison of K_{heat} for the Borden forest during days 126 to 153 in 2009 (A) and 2003 (B) respectively. Data from 2003 was taken from Choi et al. (S. -D. Choi et al., 2008). Values in the left plot represent the geometric mean for every half hour across the entire period.



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2 Figure S.M. 5: Plots of the CO_2 gradient (A), the the eddy diffusivity of heat (K_{heat} , B) and the EC measurements for CO_2
 3 during the summer period (July and August).

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Figure S.M. 6: Plot showing the discrepancy between the concentration gradient of H₂O measured over 2 different height intervals in the winter.

Table S.M. 2: Cumulative fluxes for 8 h periods representing day and night across the 2 month periods representing spring, summer, fall and winter. Fluxes measured by the MBR method that are in the opposite direction than those measured by the EC method are marked with „!“. Positive fluxes are defined as fluxes moving upwards from the canopy. The ratio of MBR results over EC results is based on the geometric mean of the MBR results divided by the EC result. The MBR fluxes for the 1-week sampling period were left out in the calculation of the geometric mean during the day in winter for CO₂ and during the night in fall for H₂O. This table shows fluxes calculated with an hourly-resolved value for K_{heat} .

CO2 (PPM m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		-0.332	0.295	-3.360	1.071	0.074	0.227	0.189	0.112
modified Bowen ratio hourly K_{heat}	1/h	0.245 (!)	0.470	-1.223	1.599	0.027	0.388	0.148	0.218
	1/2h	0.29 (!)	0.480	-1.133	1.789	0.061	0.417	0.162	0.189
	1/4h	0.306 (!)	0.473	-1.079	1.694	0.050	0.395	0.141	0.194
	1/8h	0.265 (!)	0.522	-1.069	1.889	0.098	0.416	0.173	0.157
	1/day	0.374 (!)	0.552	-1.137	2.897	0.152	0.559	0.191	0.182
	1/3days	0.355 (!)	0.778	-1.060	2.514	0.145	0.656	0.105	0.182
	1/week	0.432 (!)	0.543	-1.191	2.868	0.143	0.659	-0.020 (!)	0.031
MBR/EC method		-0.959 (!)	1.820	0.335	1.978	1.116	2.137	0.796	1.289

H2O (PPT m)		spring		summer		fall		winter	
		Day	Night	Day	Night	Day	Night	Day	Night
eddy covariance		0.420	0.016	1.118	0.038	0.180	0.005	0.049	0.001
modified Bowen ratio hourly K_{heat}	1/h	0.052	0.007	0.266	0.036	0.013	-0.001 (!)	-0.005 (!)	-0.009 (!)
	1/2h	0.057	0.007	0.256	0.038	0.009	-0.001 (!)	-0.004 (!)	-0.009 (!)
	1/4h	0.042	0.009	0.278	0.040	0.007	-0.000 (!)	-0.005 (!)	-0.007 (!)
	1/8h	0.035	0.011	0.259	0.036	0.008	-0.001 (!)	-0.009 (!)	-0.008 (!)
	1/day	0.030	0.011	0.292	0.052	0.008	-0.001 (!)	-0.004 (!)	-0.011 (!)
	1/3days	0.049	0.014	0.361	0.059	0.011	-0.004 (!)	-0.016 (!)	-0.015 (!)
	1/week	0.065	0.009	0.351	0.044	0.016	-0.001 (!)	-0.009 (!)	-0.014 (!)
MBR/EC method		0.109	0.570	0.261	1.117	0.055	-0.156 (!)	-0.132 (!)	-9.554 (!)

