Limits of applicability of using the modified Bowen ratio to estimate gas fluxes of persistent organic pollutants.

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Though often banned in production and usage, POPs (persistent organic pollutants) continue to linger in the environment due to their long persistence and properties. Direct measurements of the fluxes of POPs between the earth's surface and the atmosphere are difficult, resulting in a lack of data to ground truth chemical fate models. For greenhouse gasses such as CO₂ and methane, flux estimations are based on eddy flux covariance measurements that rely on high frequency detectors that accurately differentiate between small changes in concentration on time scales less than a second. Measuring concentrations at such high frequencies is often not possible when studying atmospheric micro-pollutants such as POPs which are present at trace levels. For these substances, high sampling volumes are required to accurately measure the small differences in atmospheric concentrations, and sampling times of the order of several hours are usually required. One technique that has been used to estimate fluxes of POPs is the modified Bowen ratio. This approach is based on measurements of concentrations of the pollutant at two heights in combination with a value for the eddy diffusivity coefficient for chemicals, Kc (m² s⁻¹). In the modified Bowen ratio method, it is assumed that the diffusive transport of chemicals and heat in the atmosphere is governed by the same turbulent mechanisms and thus Kc is equal to the eddy diffusivity of heat (Kh), that can be derived from the sensible heat flux and air density, which can both be measured directly at a high frequency. In this study we compared fluxes estimated with the modified Bowen ratio when used in combination with long sampling times to eddy covariance measurements, by using FLUXNET-data for CO₂ and H₂O. The results indicate that predictions from the modified Bowen ratio stay within 1 order of magnitude from measurements made by the eddy flux covariance method, when working with unidirectional fluxes that are not dominated by episodic events. The outcome of this study will aid in the design and execution of future studies that aim to quantify the fluxes of POPs in the atmosphere using the modified Bowen ratio.

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