Supporting information for: Gas-phase and Transpiration-driven Mechanisms for Volatilization through Wetland Macrophytes

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Five pages with one figure and an extended description of certain methods.

1 Materials and Methods

Flux Chambers. Static flux chambers (*1*) were constructed with transparent 0.013 cm-thick Teflon film (American Durafilm) mounted on a 2m tall PVC frame with a square 324 cm^2 footprint. Pressure inside the chamber was equilibrated with atmospheric pressure with a $\sim$1m long, 0.32 cm diameter vent tube. Three 12V fans were mounted on the frame to ensure a well-mixed headspace, and a bulkhead fitting installed on the film for collecting air samples. iButton hygrometers (Maxim) measured temperature and relative humidity inside the chamber, while Photosynthetically Active Radiation (PAR) was measured outside the chambers using a hand-held meter (Spectrum Technologies). Attenuation of PAR by the Teflon film was negligible. Humidity and temperature were controlled by recirculating chilled water through a coil of copper tubing inside the chambers.

Analytical Measurements. SF_6 concentrations were measured using a Gas Chromatograph (GC) with an electron capture detector (ECD) (Shimadzu GC-2014). The stainless steel analytical column was 2m long and packed with 60/80 mesh molecular sieve 5A (Supelco). An SF_6 standard (Scott-Marrin) was measured every 10-15 minutes to quantify analytical precision, determined to be $\pm 2\%$ for the 1 ml sample loop used for sample analysis. A 5-point calibration curve was made using sample loops of different volumes. The ECD response to SF_6 was linear over the concentration range encountered in these experiments.

Air samples were injected from syringes over a magnesium perchlorate dessicant into the sample loop, and then pushed into the detector by nitrogen (N_2) carrier gas. Dissolved SF_6 concentrations were determined by collecting 5-15 ml of porewater in a 30 ml glass syringe and then filling the balance of the volume with a headspace of ultra high purity N_2. The syringe was then shaken for at least 5 minutes on a wrist-action shaker to equilibrate the SF_6 between the headspace and water. The headspace was then injected into the sample loop using the same procedure as air samples, and concentrations in the original water sample were calculated using the volume of water, headspace, and temperature-dependent water-air partition coefficient.

2 Results and Discussion

Model Validation. The numerical model produced k_v estimates [T^{-1}] which were compared to per-area CH_4 fluxes, F, [$ML^{-2}T^{-1}$] in (*2*) using the equation:

$$F = k_v \theta h C \tag{1}$$

where h is the depth of the roots [L], k_v is the simulated volatilization rate constant, θ is the soil porosity, and C is the dissolved CH_4 concentration [ML^{-3}]. It was necessary to estimate these values, so representative values of C = 400μM, θ=0.5, and h=40 cm were used to obtain first-order estimates.

The model estimates for benzene volatilization were compared to results from (*3*). The transpiration-driven component of the model was parameterized with ET data from their experimental conditions. Daily ET of 80 L was recorded, corresponding to an ET rate of 14.5 mm d^{-1} based on the dimensions of the model wetland (5.0 m long x 1.1 m wide). This ET rate is equivalent to a transpiration rate of ~8 mm d^{-1}, using estimates that transpiration accounts for 53% - 62% of total ET during peak growth of *Phragmites* (*4*).

The k_v produced by the model was converted to an areal flux using equation (1) with h = 0.4 m and C = 21 mg L^{-1} or C = 2.75 mg L^{-1}, which were the influent and effluent concentrations to the pilot treatment wetland. The concentration within the wetland will thus be bracketed by these values, so these values can be used with k_v to provide upper and lower estimates of volatilization fluxes. θ was assumed to be 0.25, a typical value for gravel, which was the substrate in their model wetland.

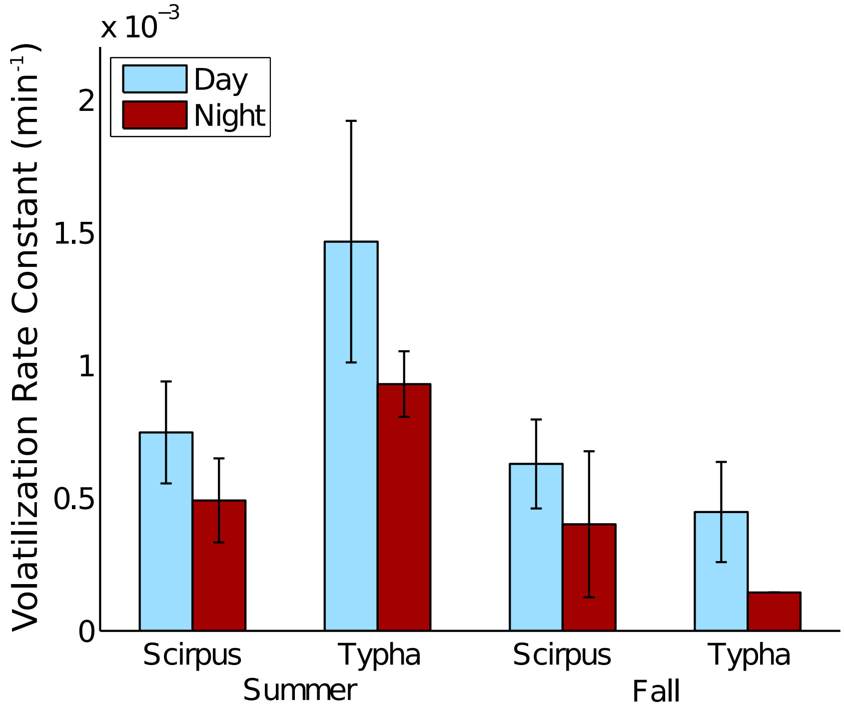

Figure S1: Interspecies and temporal variability in mean SF_6 fluxes in daytime (PAR > 0) and at night (PAR = 0) through *Typha* and *Scirpus*. Error bars show the standard deviation of the flux measurements. Only one nighttime datum was usable for fall *Typha* data.

References

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