Supplement of Geosci. Model Dev., 8, 3055–3070, 2015
http://www.geosci-model-dev.net/8/3055/2015/
doi:10.5194/gmd-8-3055-2015-supplement

Geoscientific Model Development
Open Access

Supplement of

A soil diffusion–reaction model for surface COS flux: COSSM v1

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To demonstrate quantitatively that aqueous diffusive flux is small compared to gaseous diffusive flux, we assume a soil column of vertically uniform profiles of porosity, temperature and moisture,

$$\theta_{\mathrm{sat}} = 0.50\ \mathrm{m^3\ m^{-3}}$$
$$T = 25^{\circ}\mathrm{C}$$
$$\theta_{\mathrm{w}} = 0.25\ \mathrm{m^3\ m^{-3}}$$

The factor b in Eq. (13) in the main text is set to 5.3 here, without losing generality. The soil gaseous diffusivity for COS calculated based on Eq. (13) in the main text is, $D_{\mathrm{g}} = 5.64 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}$. The molecular aqueous diffusivity for COS calculated from Ulshöfer et al. (1996) is $D_{\mathrm{m,aq}} = 1.94 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$. Then by counting the tortuosity effect using Eq. (3) in Moldrup et al. (2003), we obtain the actual soil aqueous diffusivity for COS, $D_{\mathrm{aq}} = 7.13 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$.

We consider the steady-state COS flux of the soil (i.e. $\partial C/\partial t$=0) with a sink proportional to the concentration and no production term. We obtain the equation,

$$D\frac{\mathrm{d}^2 C}{\mathrm{d}z^2} = -S = kC \qquad (1)$$

with the boundary condition $C(z=0) = C_{\mathrm{atm}}$. We obtain the general solution,

$$C(z) = C_{\mathrm{atm}} \exp(-\sqrt{k/D} \cdot z) \qquad (2)$$

The surface flux is thus

$$F = -D\frac{\mathrm{d}C}{\mathrm{d}z}\Big|_{z=0} = \sqrt{kD}C_{\mathrm{atm}} \qquad (3)$$

which is proportional to $\sqrt{D}$. We can then calculate the ratio of aqueous diffusive flux (F_{aq}) to gaseous diffusive flux (F_{g}),

$$\frac{F_{\mathrm{aq}}}{F_{\mathrm{g}}} = \sqrt{\frac{D_{\mathrm{aq}}}{D_{\mathrm{g}}}} = 0.0112 \qquad (4)$$

Under most conditions, the aqueous diffusive flux is a small fraction of the total flux (Fig. S1). Hence, any errors from neglecting aqueous diffusion are usually small (< 10% at water filled pore space below 83%), except at high soil moisture when the overall flux also tends to be small (see Fig. 9).

References

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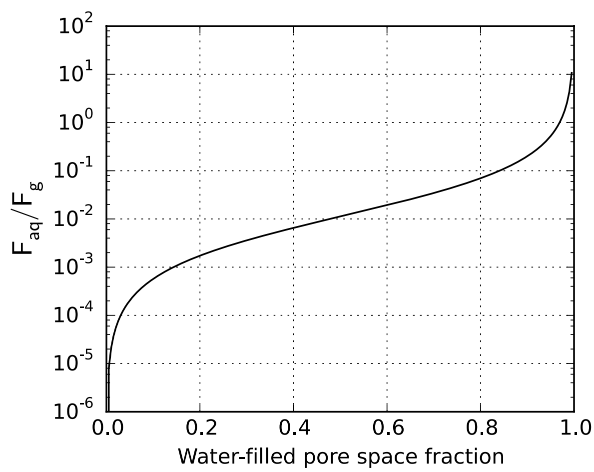

Figure S1. The ratio of aqueous flux to gaseous flux for an ideal case with soil porosity 0.50 $\mathrm{m^3\ m^{-3}}$. COS uptake velocity is assumed constant.