## 1a). Appendix: the diffusion model.

We consider the modelled part of the leaf to be a porous medium, comprising a layer of thickness h, bounded by an upper and lower surface,  $S_u$  and  $S_l$ . The continuous diffusion equation is discretised using the finite volume method (see Eymard et al. 2000). The general idea is to write the flux balances of individual "control volumes" and to assign one discrete unknown,  $C_i$ , to each volume. The fluxes at the boundaries of the volumes are then discretised by a centered finite difference method. The model considers concentric volumes around a patch centre, with radial coordinates, r and  $\theta$  and lateral surfaces  $S_r$  and  $S_{r+dr}$  as shown below.



We assume the patch to be perfectly circular and the porous medium to be homogeneous in the *r* and  $\theta$  directions and use a "*z*-averaged" 2-D model that averages *A* and C<sub>i</sub> across the leaf thickness (the *z* dimension). Under these conditions the average concentration, C<sub>i</sub>, only varies with the radius, so that the treatment is computationally 1 dimensional. Each control volume, which is a torus of volume *V*, is determined by its position at a radius *r* from the patch center and its radial diameter  $\delta r$ . In each volume there are three exchange processes: (1) a flux from the atmosphere, through the surfaces S<sub>u</sub> and S<sub>1</sub> that is determined as  $g_s^c(C_a - C_i)$ , where  $g_s^c$ , the stomatal conductance to CO<sub>2</sub>, is set to 0 for the patched areas; (2) a sink term, the net CO<sub>2</sub> assimilation rate, *A*, which in these constant temperature and light conditions is a function of C<sub>i</sub> only; (3) a lateral diffusion flux from Fick's Law, which depends on the diffusion coefficient for CO<sub>2</sub> within the leaf,  $D_c'$  and is given by  $-D_c'\nabla C_i$ . The diffusion coefficient within the leaf is reduced from that in free air  $D_c$ , (= 15.1 mm<sup>2</sup> s<sup>-1</sup> or 617 µmol m<sup>-1</sup> s<sup>-1</sup> at 25°C, Monteith 1973) by a factor  $\phi$  (the "effective porosity" defined by Parkhurst, 1994). In steady state, the fluxes balance the sinks so that for any particular control volume, using the *z*-averaged values of  $C_i$  in the expression of the diffusion of the fluxes and source term in the balance equation yields :

$$\int_{S_r \cup S_{r+\delta r}} -D'_c \nabla C_i \cdot \mathbf{n} \, \mathrm{d} \, S + \int_{S_u \cup S_l} -\frac{g_s}{2} (C_a - C_i) \, \mathrm{d} \, S = -VA(C_i) \quad (1)$$

where **n** is the outward unit normal vector to  $S_r \cup S_{r+dr}$ . Note that in the model A must be expressed per unit volume, not per area.

Making explicit the areas of  $S_r$ ,  $S_{r+\delta r}$ ,  $S_u$  and  $S_l$  gives:

$$\int_{S_r \cup S_{r+\delta r}} D_c' \nabla C_i \cdot \mathbf{n} \, \mathrm{d} \, S = 2h\pi D_c' \left[ r \frac{\partial C_i}{\partial r} (\underline{r}) - (r + \delta r) \frac{\partial C_i}{\partial r} (\underline{r+\delta r}) \right]$$
(2)

and :

$$\int_{S_{u}\cup S_{i}} -\frac{g_{s}^{c}}{2} (C_{a} - C_{i}) dS = -g_{s}^{c} \pi (2r \delta r + \delta r^{2}) (C_{a} - C_{i})$$
(3)

where the underscore indicates a spatial coordinate.

The volume V of each torus is  $h\pi((r+\delta r)^2-r^2)$ , and this and Equations (2) and (3) can be substituted into (1) to give:

$$2D_{c}\left[r\frac{\partial C_{i}}{\partial r}(\underline{r}) - (r+\delta r)\frac{\partial C_{i}}{\partial r}(\underline{r+\delta r})\right] - \frac{g_{s}^{c}}{h}(2r\delta r+\delta r^{2})(C_{a}-C_{i}) = -(2r\delta r+\delta r^{2})A(C_{i})$$
(4)

Let N be the number of control volumes needed to represent the modelled part of the leaf. The discrete unknowns are the values of the CO<sub>2</sub> molar fraction in each of these volumes k, k = 1,...,N., denoted  $C_i^{(k)}_{k=1,...,N}$ . If r is the radius of the interface between control volumes k and k+1, the partial derivative  $\partial C_i / \partial r(\underline{r})$  is approximated by  $(C_i^{(k+1)} - C_i^{(k)})/\delta r$ . Equation (4) is discretised for each volume k, k=1,...,N. We assume that the outer boundary of the modelled part of the leaf is far enough away from the patch so that the lateral diffusion flux can be considered to be zero, so that  $\partial C_i / \partial r(\underline{r+\delta r})$  for the last control volume is zero. We then obtain a non linear system of equations, the unknowns of which are  $C_i^{(k)}_{k=1,...,N}$ . It can be shown that this system has at least one solution (see Gallouët & Herbin 2005), which can be obtained as a limit of a sequence constructed by a fixed point monotonic method, (see Herbin, 2004). To fit the model to experimental data,  $\delta r$  was set to be equal to the pixel length, which is 0.15 mm. The program then iterates to find  $\phi$ , the

reduction factor for  $D_c$ , that produces the minimum root mean square relative error between  $C_i$  values estimated from the model and  $C_i$  calculated along an arbitrary horizontal transect across the  $F_q'/F_m'$  image, passing through its centre.

The inputs to the model were typical leaf thickness from leaf sections,  $g_s^c$  and  $C_a$  from the gas exchange measurements during patching, and values for the coefficients *a*, *b* and *c* from the hyperbolic function relating *A* to  $C_i$  ( $A = [(aC_i)/(b+C_i)]$ -*c*), and the slope and intercept coefficients of the linear regression of  $1/C_i$  on  $F_m'/F_q'$ , both determined measured prior to patching. The model was only used where  $C_i \leq 400 \ \mu\text{mol mol}^{-1}$ , because at higher values, the  $F_q'/F_m'$  versus  $C_i$  relationship becomes poorly determined due to saturation (Fig 1).