SUPPLEMENTARY MATERIAL FOR

Phosphorus desorption and dynamics in calcareous Mediterranean agricultural soils assessed by DET (Diffusive Equilibrium in Thin-films) and DGT (Diffusive Gradients in Thin-films) passive sampling combined with analytical modelling

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1. List of symbols

MAIN LATIN SYMBOLS

A: exposed surface area of DET (window opening)

A_{piston}: surface area of the piston or the diffusive gel disc

A(s): integration constant in the Laplace space that defines the solution in terms of the boundary conditions

B(s): integration constant in the Laplace space that defines the solution in terms of the boundary conditions

c_{DGT}: concentration assumed at the interface filter-soil computed from the accumulation assuming first Fick's law with steady state

$c_{\text{M}}(x,t)$: analyte concentration profile

$c_{\text{MS}}(x,t)$: concentration profile of occupied soil sites

c_{M}^{*} : analyte concentration in the soil solution which is also the analyte concentration in equilibrium at time zero (i.e. bulk porewater concentration)

c_{MS} : concentration of occupied soil sites (i.e. M adsorbed on soil)

D_{M}^{g} : analyte diffusion coefficient in the material diffusion layer (diffusive gel + filter)

D_{M}^{s} : analyte diffusion coefficient in the soil phase

$\bar{D}_{\text{M}}^{\text{s}}$: "effective" (or average) analyte diffusion coefficient in the soil phase

ℓ: total thickness of the DET material diffusion layer (gel layer or layers plus filter)

n_{M}: number of accumulated moles of analyte M in the eluted region

q_{g}: gathering $\sqrt{s / D_{\text{M}}^{\text{g}}}$ when finding the analytical solution

q_{s}: gathering $\sqrt{s / D_{\text{M}}^{\text{s}}}$ when finding the analytical solution

k: gathering of parameters given by eqn. (S-23) when finding analytical solution

K'_{ads}: Henry's adsorption constant in the soil sites

s: Laplace transform parameter

t: time

t_{c}: characteristic time (used in DIFS model, (Harper et al., 2000))

v: analyte concentration variable to solve the continuity equation

$\bar{v}$: solution of the ordinary differential equation for the analyte concentration in the Laplace space

x: space coordinate

z: non-integration distance (i.e. size of the non-eluted region)

MAIN GREEK SYMBOLS

β(s): integration constant in the Laplace space that defines the solution in terms of the boundary condition

φ_{g}: porosity of diffusive gel (and filter)

φ_{s}: porosity of soil phase

$\bar{\varphi}_{\mathrm{s}}$: "effective" porosity in the case of Henry adsorption with fast kinetics

MAIN ACRONYMS

DET	Diffusive Equilibrium in Thin-films
DGT	Diffusive Gradients in Thin-films
mdl	Material diffusion layer (i.e. diffusive layer gel or gels plus filter)

2. Derivation of the analytical solution for DET taking into account just diffusion of M in the material diffusion layer and in the soil solution

2.1 DET schematic geometry

If we assume only one relevant spatial dimension, we can lump the diffusive gel layer and the filter in the material diffusion layer ("mdl"), whose total thickness will be denoted ℓ. The letter "g" in superscripts and subscripts will refer to the mdl, e.g. $D_{\mathrm{M}}^{\mathrm{g}}$ represents the diffusion coefficient of the analyte M in any position of the mdl (be it in the filter or in the diffusive gel). The letter "s" stands for soil (or sediment).

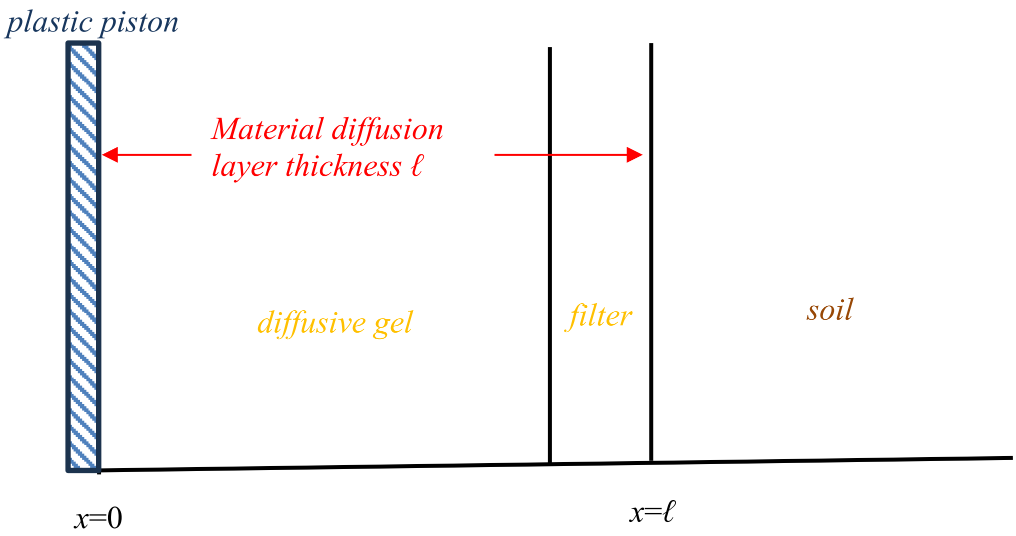

Fig S1: Schematic outline of a DET device. The blue dashed region represents the plastic piston. We assume common values for porosities and diffusion coefficients in the the diffusive gel and in the filter (i.e. all along the mdl).

The origin of the axis is taken at the interface between the diffusive gel and the DET piston.

2.2 Setting the model equations

For just diffusion, the continuity equations to be solved are:

$$\frac{\partial c_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{g}} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} \qquad 0 < x < \ell \tag{S-1}$$

in the mdl and

$$\frac{\partial c_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{s}} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} \qquad \ell < x < \infty \tag{S-2}$$

in the soil.

Initial conditions are

$$c_{\mathrm{M}}\left(x, t=0\right) = 0 \qquad 0 < x < \ell \tag{S-3}$$

$$c_{\mathrm{M}}\left(x, t=0\right) = c_{\mathrm{M}}^{*} \qquad \ell < x < \infty \tag{S-4}$$

and boundary conditions of no-flux at the piston-gel interface:

$$\left.\frac{\partial c_{\mathrm{M}}}{\partial x}\right|_{x=0} = 0 \tag{S-5}$$

Continuity of the concentration at the diffusive gel-soil solution interface

$$c_{\mathrm{M}}\left(x=\ell^{-}, t\right) = c_{\mathrm{M}}\left(x=\ell^{+}, t\right) \tag{S-6}$$

conservation of the flux of M across this interface:

$$\varphi_{\mathrm{g}} D_{\mathrm{M}}^{\mathrm{g}} \left.\frac{\partial c_{\mathrm{M}}}{\partial x}\right|_{x=\ell^{-}} = \varphi_{\mathrm{s}} D_{\mathrm{M}}^{\mathrm{s}} \left.\frac{\partial c_{\mathrm{M}}}{\partial x}\right|_{x=\ell^{+}} \tag{S-7}$$

and semi-infinite diffusion (in the soil solution)

$$c_{\mathrm{M}}\left(x=\infty, t\right) = c_{\mathrm{M}}^{*} \qquad t > 0 \tag{S-8}$$

2.3 Change of variables

We essentially follow the procedure indicated in page 320 of the book by Carslaw and Jaeger (1959) and applied recently to DGT modelling (Galceran et al., 2026)

The coordinate axis is re-defined in such a way that x=0 now corresponds to the interface between the two media (the mdl or "gel" and the soil).

A new concentration variable (see Fig S2 below) is also defined as

$$v = c_{\mathrm{M}}^{*} - c_{\mathrm{M}} \qquad \text{(S-9)}$$

From now on, v_g refers to the function v in the (new) spatial domain $-\ell < x < 0$ while v_s refers to v in the spatial domain $0 < x < \infty$.

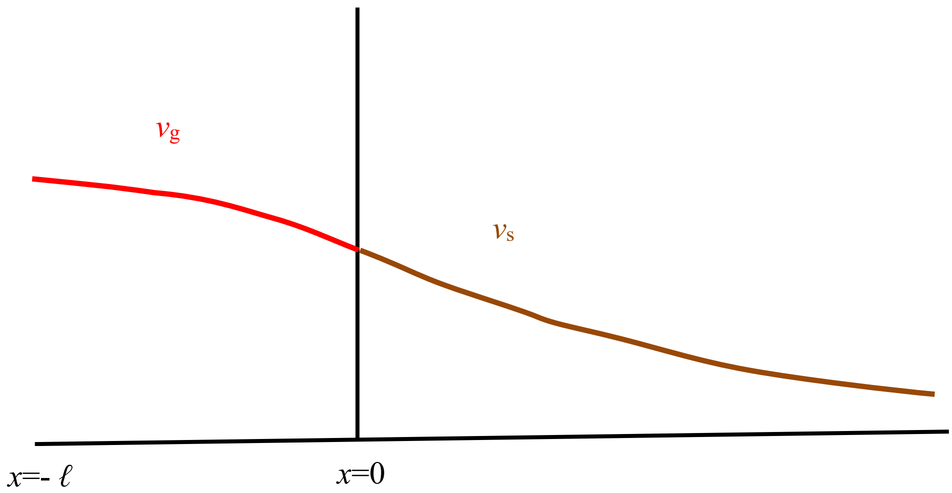

Fig S2: Schematic outline of the profile of the new concentrations v_{g} (in the mdl domain) and v_{s} (in the soil domain). Notice the change in the origin of the spatial coordinate.

2.4 Solution in the Laplace space

With the new variables and new origin, eqn. (S-1) becomes

$$\frac{\partial v_{\mathrm{g}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{g}} \frac{\partial^2 v_{\mathrm{g}}}{\partial x} \qquad -\ell < x < 0 \qquad \text{(S-10)}$$

Applying the Laplace transform to this equation with the initial condition (S-3),

$$s\overline{v}_{\mathrm{g}} - c_{\mathrm{M}}^{*} = D_{\mathrm{M}}^{\mathrm{g}} \frac{d^2\overline{v}_{\mathrm{g}}}{dx^2} \qquad -\ell < x < 0 \tag{S-11}$$

where overbar indicates the function in the Laplace space and s is the Laplace parameter. We define

$$q_{\mathrm{g}} \equiv \sqrt{\frac{s}{D_{\mathrm{M}}^{\mathrm{g}}}} \tag{S-12}$$

Equation (S-11) is now a second order ordinary differential equation whose solution can be written as

$$\overline{v}_{\mathrm{g}} = \frac{c_{\mathrm{M}}^{*}}{s} + A(s)\sinh\left(q_{\mathrm{g}}x\right) + B(s)\cosh\left(q_{\mathrm{g}}x\right) \tag{S-13}$$

where A(s) and B(s) are to be determined from the boundary conditions. The no-flux boundary condition, eqn. (S-5), becomes

$$\left.\frac{d\overline{v}_{\mathrm{g}}}{dx}\right|_{x=-\ell} = 0 \tag{S-14}$$

This leads to

$$A(s) = -B(s)\tanh\left(-q_{\mathrm{g}}\ell\right) \tag{S-15}$$

so that (S-13) becomes

$$\overline{v}_{\mathrm{g}} = \frac{c_{\mathrm{M}}^{*}}{s} + B(s)\left[\cosh\left(q_{\mathrm{g}}x\right) - \tanh\left(-q_{\mathrm{g}}\ell\right)\sinh\left(q_{\mathrm{g}}x\right)\right] \tag{S-16}$$

In the soil domain, with the new variables, the continuity eqn. (S-2), becomes

$$\frac{\partial v_{\mathrm{s}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{s}} \frac{\partial^2 v_{\mathrm{s}}}{\partial x} \qquad x > 0 \tag{S-17}$$

and its Laplace transform, taking into account the initial condition of bulk concentration (S-4), is

$$s\overline{v}_{s} = D_{M}^{s}\frac{d^{2}\overline{v}_{s}}{dx^{2}} \qquad x>0 \tag{S-18}$$

Its solution, when taking into account the boundary condition of semi-infinite diffusion (S-8) is

$$\overline{v}_{g} = \beta\, e^{-q_{s}x} \tag{S-19}$$

where we have also defined

$$q_{s} \equiv \sqrt{\frac{s}{D_{M}^{s}}} \tag{S-20}$$

and $\beta(s)$ is another constant, to be determined together with $B(s)$, from the boundary conditions at x=0.

The conservation of flux, eqn. (S-7), becomes

$$\varphi_{g}D_{M}^{g}\left.\frac{\partial\overline{v}_{g}}{\partial x}\right|_{x=0^{-}} = \varphi_{s}D_{M}^{s}\left.\frac{\partial\overline{v}_{s}}{\partial x}\right|_{x=0^{+}} \tag{S-21}$$

Replacing, in this last equation, the solutions found in (S-16) and (S-19), one constant can be written in terms of the other:

$$\beta(s) = k\tanh\left(-q_{g}\delta^{g}\right)B(s) \tag{S-22}$$

with

$$k = \frac{\varphi_{g}}{\varphi_{s}}\sqrt{\frac{D_{M}^{g}}{D_{M}^{s}}} \tag{S-23}$$

On the other hand, the continuity of concentrations, (S-6), implies

$$\overline{v}_{\mathrm{g}}=\overline{v}_{\mathrm{s}}\ \text{ at }\ x=0 \tag{S-24}$$

Replacing, in this last equation, the solutions found in (S-16) and (S-19),

$$\frac{c_{\mathrm{M}}^{*}}{s}+B(s)=\beta(s) \tag{S-25}$$

Combining (S-22) and (S-25), one finds

$$B(s)=\frac{c_{\mathrm{M}}^{*}}{s\left(k\tanh\left(-q_{\mathrm{g}}\ell\right)-1\right)} \tag{S-26}$$

So, combining (S-13) and (S-16), the solution in the diffusive gel domain is

$$\overline{v}_{\mathrm{g}}=\frac{c_{\mathrm{M}}^{*}}{s}+\frac{c_{\mathrm{M}}^{*}}{s\left(k\tanh\left(-q_{\mathrm{g}}\ell\right)-1\right)}\left[\cosh\left(q_{\mathrm{g}}x\right)-\tanh\left(-q_{\mathrm{g}}\ell\right)\sinh\left(q_{\mathrm{g}}x\right)\right] \tag{S-27}$$

2.5 Computing the accumulated moles in some fraction of the mdl

We aim at finding an expression for the expected accumulated moles of analyte M in one diffusive gel layer (n_{M}), because the experimental measurement is not the concentration profile (of M at various x-positions within the diffusive gel), but a kind of lumped value of the selected eluted region. For simple DET configurations with just one diffusive gel, to find n_{M} means that one has to integrate the concentration $c_{\mathrm{M}}(x,t)$ along the distance from the piston/diffusive gel interface up to the filter, because the filter is not eluted. For "double gel" configurations, to find n_{M} (of the back diffusive gel) means to integrate from the piston/diffusive gel interface up to the frontier between both diffusive gel discs. To allow for this flexibility, we introduce the non-integration distance z from the last desired integration position up to the total mdl thickness (see Fig S3). In this section, the Laplace transform $\overline{n}_{\mathrm{M}}$ will be derived, and in the next one, it will be back-transformed to the time space to find n_{M}.

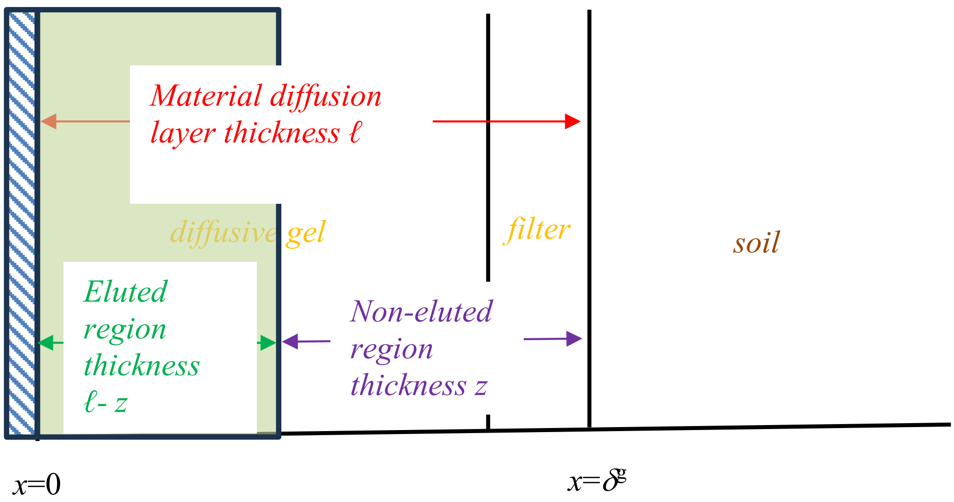

Fig S3: Particular case where the diffusive gel region comprises a stack of two diffusive gel layers and we only want to measure the accumulated moles in the back layer. The expected moles in the eluted region are obtained by integrating the concentration in the green-shaded region.

The number of moles can be obtained from the variable concentration times the effective volume (so that gel porosity has to be included):

$$\frac{\overline{n}_{\mathrm{M}}}{A\varphi_{\mathrm{g}}}=\int_{x=-\ell}^{x=-z}\overline{c}_{\mathrm{M}}dx=\frac{c_{\mathrm{M}}^{*}}{s}(\ell-z)-\int_{x=-\ell}^{x=-z}\overline{v}\;dx=\frac{-c_{\mathrm{M}}^{*}}{q_{\mathrm{g}}s}\left[\frac{\sinh\left(q_{\mathrm{g}}\left(\ell-z\right)\right)}{\left(k\tanh\left(-q_{\mathrm{g}}\ell\right)-1\right)\cosh\left(q_{\mathrm{g}}\ell\right)}\right] \qquad \text{(S-28)}$$

where eqns. (S-9) and (S-27) have been used.

Now, following section 12.5 in page 309 of Carslaw and Jaeger (1959) or the Supporting Information file of (Galceran et al., 2026), the point is to write the denominator as 1 minus an exponential with a negative exponent of s, so that the formula for the summation of an infinite geometrical series with ratio less than 1 can be applied.

The terms in between square brackets in (S-28) can be written as

$$\frac{\sinh\left(q_{\mathrm{g}}\left(\ell-z\right)\right)}{\left(k\tanh\left(-q_{\mathrm{g}}\ell\right)-1\right)\cosh\left(q_{\mathrm{g}}\ell\right)}=\frac{\left(-\mathrm{e}^{-q_{\mathrm{g}}\ell}+\mathrm{e}^{-q_{\mathrm{g}}\left(2\ell-z\right)}\right)}{\left(1+k\right)}\frac{1}{1-\frac{k-1}{k+1}\mathrm{e}^{-2q_{\mathrm{g}}\ell}} \qquad \text{(S-29)}$$

The last factor can be considered as the infinite summation of a geometrical series of ratio $\frac{k-1}{k+1}\mathrm{e}^{-2q_{\mathrm{g}}\ell}$, with first term 1. So,

$$\frac{\overline{n}_{\mathrm{M}}}{A\varphi_{\mathrm{g}}}=\frac{c_{\mathrm{M}}^{*}}{q_{\mathrm{g}}s}\left[\frac{1}{\left(1+k\right)}\sum_{j=0}^{\infty}\left[\frac{k-1}{k+1}\right]^{j}\mathrm{e}^{-q_{\mathrm{g}}\left(z+2\ell j\right)}-\frac{1}{\left(1+k\right)}\sum_{j=0}^{\infty}\left[\frac{k-1}{k+1}\right]^{j}\mathrm{e}^{-q_{\mathrm{g}}\left(2\ell-z+2\ell j\right)}\right] \qquad \text{(S-30)}$$

2.6 Solution in the time domain

Equation (S-30) can be easily back-transformed from the Laplace space to:

$$\frac{n_{\mathrm{M}}}{A\varphi_{\mathrm{g}}}=\frac{c_{\mathrm{M}}^{*}\sqrt{D_{\mathrm{M}}^{\mathrm{g}}}}{\left(1+k\right)}\sum_{j=0}^{\infty}\left(\left[\frac{k-1}{k+1}\right]^{j}\left\{2\sqrt{\frac{t}{\pi}}\left(\mathrm{e}^{-\frac{\left(z+2\ell j\right)^{2}}{4D_{\mathrm{M}}^{\mathrm{g}}t}}+\mathrm{e}^{-\frac{\left(2\ell-z+2\ell j\right)^{2}}{4D_{\mathrm{M}}^{\mathrm{g}}t}}\right)-\right.\right.$$
$$\left.\left.-\frac{z+2\ell j}{\sqrt{D_{\mathrm{M}}^{\mathrm{g}}}}\mathrm{Erfc}\left[\frac{z+2\ell j}{2\sqrt{D_{\mathrm{M}}^{\mathrm{g}}t}}\right]+\frac{2\ell-z+2\ell j}{\sqrt{D_{\mathrm{M}}^{\mathrm{g}}}}\mathrm{Erfc}\left[\frac{2\ell-z+2\ell j}{2\sqrt{D_{\mathrm{M}}^{\mathrm{g}}t}}\right]\right\}\right) \qquad \text{(S-31)}$$

and, using the definition of k given in (S-23), one can replace

$$\frac{k-1}{k+1}=\frac{\varphi_{\mathrm{g}}\sqrt{D_{\mathrm{M}}^{\mathrm{g}}}-\varphi_{\mathrm{s}}\sqrt{D_{\mathrm{M}}^{\mathrm{s}}}}{\varphi_{\mathrm{s}}\sqrt{D_{\mathrm{M}}^{\mathrm{s}}}+\varphi_{\mathrm{g}}\sqrt{D_{\mathrm{M}}^{\mathrm{g}}}} \qquad \text{(S-32)}$$

3. Extension to a soil where the adsorbed M is always in equilibrium with the dissolved M following a Henry isotherm

We describe adsorption as a first-order reaction that converts non-adsorbed M into adsorbed M, which we call MS (as if it were an immobile "complex" formed between M and the free soils sites S).

$$c_{\mathrm{MS}} = K'_{\mathrm{ads}} c_{\mathrm{M}} \tag{S-33}$$

where the proportionality constant K'_{ads} can be seen as Henry's adsorption constant for the soil sites (Lehto et al., 2012).

The continuity for the total M in the soil corresponds to just "free" M being able to diffuse:

$$\frac{\partial c_{\mathrm{M}}}{\partial t} + \frac{\partial c_{\mathrm{MS}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{s}} \frac{\partial^2 c_{\mathrm{M}}}{\partial x^2} \tag{S-34}$$

Using eqn. (S-33), it boils down to

$$\left(1 + K'_{\mathrm{ads}}\right) \frac{\partial c_{\mathrm{M}}}{\partial t} = D_{\mathrm{M}}^{\mathrm{s}} \frac{\partial^2 c_{\mathrm{M}}}{\partial x} \qquad 0 < x < \infty \tag{S-35}$$

(in the new origin of the space axis). Thus, the new case of a fast-kinetics soil MS in excess of soil sites requires to solve the same set of equations as (S-1)-(S-8) except that instead of eqn. (S-2), one needs to solve eqn. S-35) while keeping the boundary conditions. As in reference (Galceran et al., 2026), it is convenient:

a) to define an average M diffusion coefficient in soil

$$\bar{D}_{\mathrm{M}}^{\mathrm{s}} = \frac{D_{\mathrm{M}}^{\mathrm{s}}}{1 + K'_{\mathrm{ads}}} \tag{S-36}$$

(compare eqn. S-35) with (S-2)).

b) to define a new effective porosity $\bar{\varphi}_{\mathrm{s}}$ so that the boundary condition (S-21) is kept:

$$\varphi_{\mathrm{g}} D_{\mathrm{M}}^{\mathrm{g}} \left.\frac{\partial c_{\mathrm{M}}}{\partial x}\right|_{x=0^-} = \bar{\varphi}_{\mathrm{s}} \bar{D}_{\mathrm{M}}^{\mathrm{s}} \left.\frac{\partial c_{\mathrm{M}}}{\partial x}\right|_{x=0^+} \Rightarrow \bar{\varphi}_{\mathrm{s}} = \frac{\varphi_{\mathrm{s}} D_{\mathrm{M}}^{\mathrm{s}}}{\bar{D}_{\mathrm{M}}^{\mathrm{s}}} = \varphi_{\mathrm{s}} \left(1 + K'_{\mathrm{ads}}\right) \tag{S-37}$$

Thus, one can use the solution (S-31) while replacing $D_{\mathrm{M}}^{\mathrm{s}}$ with $\bar{D}_{\mathrm{M}}^{\mathrm{s}}$ (given by (S-36)) and φ_{s} with $\bar{\varphi}_{\mathrm{s}}$ given by (S-37).

4. Correction for the edge effect

In practice, the outer sleeve with window of the DGT holders (used to contain the diffusive gel of DET) has a “bracket” (parallel to the piston surface, see upper blue dashed rectangles in the left-hand side of Fig S4) that induces a “shaded” region (see orange rectangles in the left-hand side). This “bracket” disrupts the ideal 1D dimensionality of the problem, as M can also diffuse (albeit relatively more slowly than in the “straight” region) surrounding the bracket.

One rough equivalence of the original problem can be obtained by reorganizing the “shaded” regions and “place” them in the ideal 1D problem (see right hand side of Fig S4). If we prescribe conservation of the volume:

$$A_{\mathrm{piston}}\,\ell_{\mathrm{real}} = A\,\ell \tag{S-38}$$

where A_{piston} stand for “area of the piston” as a label for the area of one (top or bottom) side of the filter (which is the same for the diffusive gel). ℓ_{real} stands for the geometrical (raw, physical) length obtained by summation of the filter and diffusive gel lengths.

The same re-scaling affects the non-integration distance

$$z = z_{\mathrm{real}}\frac{A_{\mathrm{piston}}}{A} \tag{S-39}$$

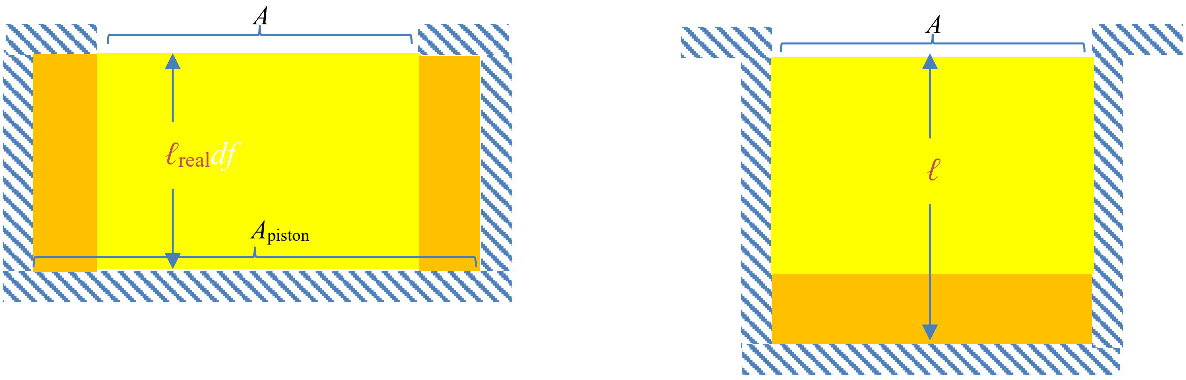

Fig S4: Schematic representation of the approximate equivalence to compensate for the edge effect in the 1D expression. The parts of the drawing are not at scale. The filter is considered as embedded in the diffusive gel. The blue diagonal-dashed region stands for the plastic piston (bottom horizontal) and cap. The yellow region stands for the diffusive gel that needs not to be re-allocated. The orange regions stand for the re-allocated parts of the diffusive gel.

5. Supplementary figure

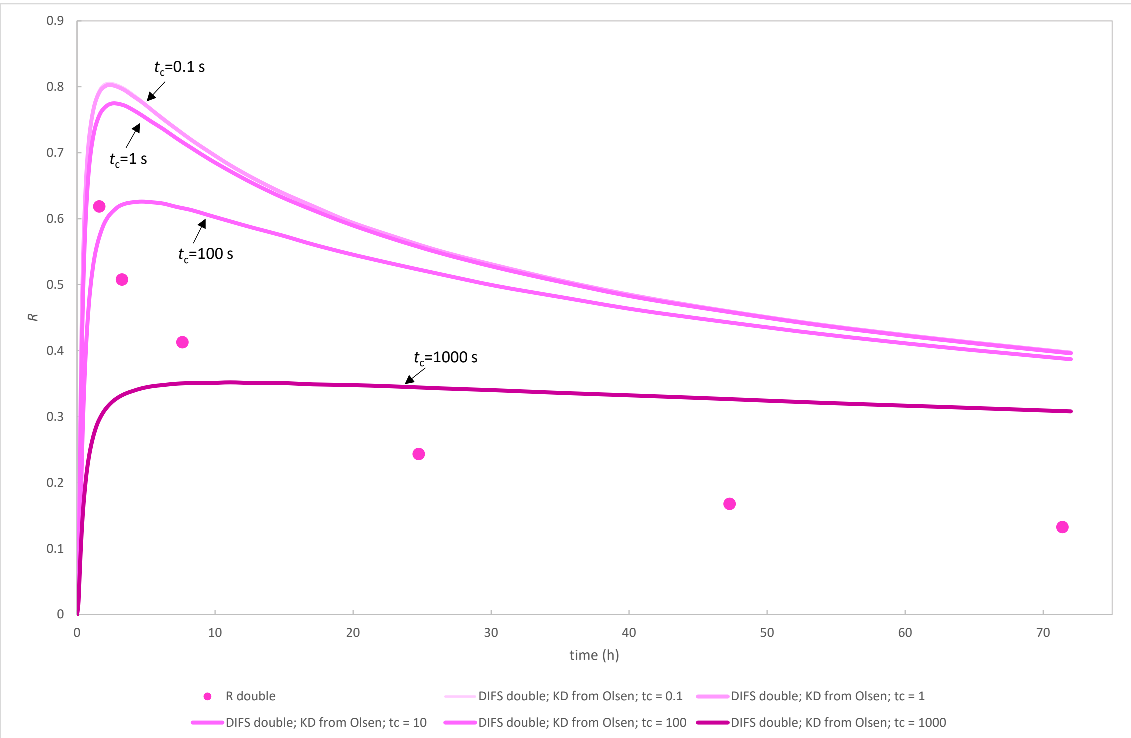

Fig S5: DIFS simulations being unable to fit the experimental DGT data when the soil capacity derives from Olsen determination, in the case of the double resin experiment in Jaca soil.

6. References

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