SUPPORTING INFORMATION

Dynamics of metal uptake by charged biointerphases :

bioavailability and bulk depletion.

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I. Details on the analytical developments leading to eqns (10)-(11), eqn (28), and eqns (33), (36) and (38) in the main text.

1. Expression of the metal concentration profiles (eqns (10)-(11)).

The general solution of the Nernst-Planck equations (4)-(5) with differentiated metal diffusion coefficients inside and outside the microorganism soft surface layer is given by

$$c_{\mathrm{M}}\left(a \leq r \leq r_{\mathrm{o}}\right) = \beta_r\left[c_3 F_{r,r_{\mathrm{o}}} + c_4\right] \tag{S1}$$

and

$$c_{\mathrm{M}}\left(r \geq r_{\mathrm{o}}\right) = \beta_r\left[c_1 F_{r,\infty} + c_2\right], \tag{S2}$$

where we have introduced the integral function $F_{r_1,r_2} = \int_{r_1}^{r_2} r^{-2}\beta_r^{-1}\mathrm{d}r$. The quantities $c_{i=1,...,4}$ are

integration constants to be determined from the boundaries (6)-(9). As argued in the text, it is convenient to

first express $c_{i=1,...,4}$ as a function of the metal concentration $c_{\mathrm{M}}^{\mathrm{a}}$ at the bioactive surface with $c_{\mathrm{M}}^{\mathrm{a}}$ given by

$$c_{\mathrm{M}}^{\mathrm{a}} = \beta_{\mathrm{a}}\left[c_3 F_{a,r_{\mathrm{o}}} + c_4\right], \tag{S3}$$

which is obtained from eqn (S1) applied at the position $r = a$. Using eqns (S1) and (S2), the continuity of

$c_{\mathrm{M}}\left(r\right)$ at $r = r_{\mathrm{o}}$ (eqn (8)) is further written

$$c_1 F_{r_{\mathrm{o}},\infty} + c_2 = c_4 . \tag{S4}$$

The condition given by eqn (9) for the continuity of metal flux at $r = r_o$ may be arranged according to

$$\varepsilon \, dc_M(r)/dr\big|_{r=r_o^-} - dc_M(r)/dr\big|_{r=r_o^+} + c_4(1-\varepsilon/\Im)d\beta_r/dr\big|_{r=r_o^+} = 0, \tag{S5}$$

where we used the equality $c_M(r=r_o) = c_4\beta_{r_o}$ and the eqns (22a)-(22b) that reflect the continuity of the potential and electric field displacement at $r = r_o$. The derivatives $dc_M(r)/dr\big|_{r=r_o^-}$ and $dc_M(r)/dr\big|_{r=r_o^+}$ are evaluated from eqns (S1) and (S2), respectively. After some rearrangements, the substitution of the resulting expressions into eqn (S5) leads to

$$-\varepsilon r_o^{-2}c_3 - c_1\left(F_{r_o,\infty}d\beta_r/dr\big|_{r=r_o^+} - r_o^{-2}\right) + d\beta_r/dr\big|_{r=r_o^+}(c_4 - c_2) = 0. \tag{S6}$$

The electrostatic boundaries given by eqn (22) were considered for deriving eqn (S6), together with the following relationships: $d\beta_r/dr = -z_M z^{-1}\beta_r dy(r)/dr$ and $dF_{r,\infty}/dr = dF_{r,r_o}/dr = -1/(r^2\beta_r)$. The constants $c_{i=1,...,4}$ can be determined from eqns (S3), (S4), (S6) and eqn (6) in the main text, with as final result

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} \left(c_M^a\beta_a^{-1}/c_M^* - 1\right)F_{r_o,\infty}^{-1}\left(1 + F_{a,r_o}\lambda^{-1}\right) \\ 1 \\ \left(1 - c_M^a\beta_a^{-1}/c_M^*\right)\lambda^{-1} \\ -F_{a,r_o}\lambda^{-1} + \left(c_M^a\beta_a^{-1}/c_M^*\right)\left(1 + F_{a,r_o}\lambda^{-1}\right) \end{pmatrix} \times c_M^* \tag{S7}$$

, with $\lambda = -\left(\varepsilon F_{r_o,\infty} + F_{a,r_o}\right)$. Finally, substituting the expressions of $c_{i=1,...,4}$ given by eqn (S7) into eqns (S1) and (S2) leads to eqns (10) and (11) for the metal concentration profile $c_M(r)$.

2. Derivation of the differential equation (28) for metal depletion kinetics under steady-state metal transport condition. Demonstration of the inequality $\Omega_1 < 0$.

The amount of metal ions located outside the microorganism ($r \geq r_o$) and within the Kuwabara cell of radius r_c is given by

$$4\pi\int_{r_o}^{r_c} r^2 c_M(r,t)dr = 4\pi c_M^*(t)\left[G_{r_o,r_c} + \left(c_M^a(t)\beta_a^{-1}/c_M^*(t) - 1\right)\left(1 + F_{a,r_o}\lambda^{-1}\right)H_{r_o,r_c}^{r_c}/F_{r_o,r_c}\right], \tag{S8}$$

where $G_{r_1,r_2} = \int_{r_1}^{r_2} r^2\beta_r dr$ and $H_{r_1,r_2}^{r_3} = \int_{r_1}^{r_2} r^2\beta_r F_{r,r_3}dr$. Equation (S8) is obtained from eqn (11) with replacing '∞' by 'r_c' and further specifying that the bulk metal concentration c_M^* and the metal surface concentration c_M^a

now depend on time t. By the same token, the amount of metals within the microorganism of radius r_0 may be expressed in the form

$$4\pi \int_a^{r_0} r^2 c_M(r,t) \mathrm{d}r = 4\pi c_M^*(t) \left[\lambda^{-1} H_{a,r_0}^a + \left(G_{a,r_0} - \lambda^{-1} H_{a,r_0}^a \right) c_M^a(t) \beta_a^{-1} / c_M^*(t) \right]. \tag{S9}$$

The ratio $c_M^a(t) \beta_a^{-1} / c_M^*(t)$ involved in eqns (S8)-(S9) may be evaluated from eqn (17) and further written in the concise form

$$c_M^a(t) \beta_a^{-1} / c_M^*(t) = U(t)/2, \tag{S10}$$

where $U(t)$ is the time-dependent function given by eqns (29)-(30). In addition, the uptake flux $J_u(t)$ defined by eqn (1) may be expressed in terms of $U(t)$ as follows

$$J_u(t)/J_u^* = 1/\left\{ 1 + \left(2K_M \beta_a^{-1} \right) \left[c_M^*(t) U(t) \right]^{-1} \right\}. \tag{S11}$$

Then, starting from eqn (27) in the main text and further using eqns (S8), (S9) and (S11), we obtain the following differential equation that governs the time-dependent $c_M^*(t)$

$$c_M^*(t) U(t) \left[2K_M \beta_a^{-1} + c_M^*(t) U(t) \right]^{-1} = \Omega_1 \mathrm{d}c_M^*(t)/\mathrm{d}t + \Omega_2 \mathrm{d}\left[c_M^*(t) U(t) \right]/\mathrm{d}t, \tag{S12}$$

where Ω_1 and Ω_2 are provided by

$$\Omega_1 = -\left[G_{r_0,r_c} - \left(1 - \varepsilon^{-1} f_{el}/f_{el,in} \right) H_{r_0,r_c}^{r_c} / F_{r_0,r_c} - H_{a,r_0}^a a\varepsilon^{-1} f_{el} \right] / \left(a^2 J_u^* \right), \tag{S13}$$

and $$\Omega_2 = -\left[\Omega_1 + G_{a,r_c} / \left(a^2 J_u^* \right) \right]/2. \tag{S14}$$

Equations (S12), (S13) and (S14) correspond to eqn (28), (31) and (32) given in the main text, respectively. It is straightforward to verify the following relationships: $a^2 J_u^* > 0$, $H_{a,r_0}^a < 0$, $G_{r_0,r_c} > 0$, $H_{r_0,r_c}^{r_c} > 0$, $F_{r_0,r_c} > 0$ and $\varepsilon^{-1} f_{el}/f_{el,in} > 1$. The latter inequality results from $\varepsilon \leq 1$ and $f_{el} \geq f_{el,in}$ (which is justified from eqn (13) in the text), having in mind that the conductive diffusion factors f_{el}, $f_{el,in}$ and $f_{el,out}$ are dimensionless positive quantities. In turn, Ω_1 defined by eqn (S13) necessarily satisfies $\Omega_1 \leq 0$.

3. Derivation of the limiting kinetic regimes expressed by eqns (33), (36) and (38).

Equation (S12) may be rearranged in the following differential form where time and metal concentration variables are separated

$$\omega\left(c_M^* \right) \mathrm{d}c_M^* = \mathrm{d}t, \tag{S15}$$

where ω is a function of c_M^* according to

$$\omega\left(c_{\mathrm{M}}^{*}\right)=\left[2K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}+c_{\mathrm{M}}^{*}U\left(c_{\mathrm{M}}^{*}\right)\right]\left\{\Omega_{1}+\Omega_{2}\left[U\left(c_{\mathrm{M}}^{*}\right)+c_{\mathrm{M}}^{*}\Sigma\left(c_{\mathrm{M}}^{*}\right)\right]\right\}\left[c_{\mathrm{M}}^{*}U\left(c_{\mathrm{M}}^{*}\right)\right]^{-1}. \tag{S16}$$

The functions $U\left(c_{\mathrm{M}}^{*}\right)$ in eqn (S16) is now written in terms of c_{M}^{*}

$$U\left(c_{\mathrm{M}}^{*}\right)=-u\left(c_{\mathrm{M}}^{*}\right)+\left[u\left(c_{\mathrm{M}}^{*}\right)^{2}+4A\left(c_{\mathrm{M}}^{*}\right)\right]^{1/2}, \tag{S17}$$

with $A\left(c_{\mathrm{M}}^{*}\right)=K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}/c_{\mathrm{M}}^{*}$ and $u\left(c_{\mathrm{M}}^{*}\right)=A\left(c_{\mathrm{M}}^{*}\right)\left(1+Bn^{-1}\right)-1$. The function $\Sigma\left(c_{\mathrm{M}}^{*}\right)$ involved in eqn (S16)

is defined by $\Sigma\left(c_{\mathrm{M}}^{*}\right)=\left[dU\left(c_{\mathrm{M}}^{*}(t)\right)/dt\right]/\left[dc_{\mathrm{M}}^{*}(t)/dt\right]$, which after developments leads to

$$\Sigma\left(c_{\mathrm{M}}^{*}\right)=\left\{K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\left(1+\frac{1}{Bn}\right)-\left[u\left(c_{\mathrm{M}}^{*}\right)^{2}+4A\left(c_{\mathrm{M}}^{*}\right)\right]^{-1/2}\left[u\left(c_{\mathrm{M}}^{*}\right)K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\left(1+\frac{1}{Bn}\right)+2K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\right]\right\}/c_{\mathrm{M}}^{*2}, \tag{S18}$$

where Bn is the (time-independent) bioavailability number Bn defined by eqn (19).

- For situations where $A\left(c_{\mathrm{M}}^{*}\right)\left(1+Bn^{-1}\right)<<1$ (or, equivalently, $u\left(c_{\mathrm{M}}^{*}\right)<<0$), the function ω may be

linearized *via* considering the first order term in its corresponding Taylor development with respect to the

variable $Y\equiv A\left(c_{\mathrm{M}}^{*}\right)\left(1+Bn^{-1}\right)=K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\left(1+Bn^{-1}\right)/c_{\mathrm{M}}^{*}(t)<<1$. Rewriting $\omega\left(c_{\mathrm{M}}^{*}\right)$ in the form $\omega(Y)$,

performing the aforementioned Taylor expansion, we show that eqn (S15) to the first order in Y is

$$\left[1/\left(K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\right)+1/c_{\mathrm{M}}^{*}\right]dc_{\mathrm{M}}^{*}=-dt/\tau_{\mathrm{L}}, \tag{S19}$$

with the time constant τ_{L} defined by

$$\tau_{\mathrm{L}}=-K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\left(\Omega_{1}+2\Omega_{2}\right). \tag{S20}$$

The inequality $A\left(c_{\mathrm{M}}^{*}\right)\left(1+Bn^{-1}\right)<<1$, or $A\left(c_{\mathrm{M}}^{*}\right)<<1/\left(1+Bn^{-1}\right)$, that marks the validity of eqns (S19)-

(S20), goes in pair with $A\left(c_{\mathrm{M}}^{*}\right)<<1$ because $Bn^{-1}\geq0$ and thus $1/\left(1+Bn^{-1}\right)\leq1$. Under the limit examined

here, we then have $K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}/c_{\mathrm{M}}^{*}<<1$ so that eqn (S19) further simplifies into

$$dc_{\mathrm{M}}^{*}/\left(K_{\mathrm{M}}\beta_{\mathrm{a}}^{-1}\right)=-dt/\tau_{\mathrm{L}}. \tag{S21}$$

The solution of eqn (S21) is expressed by eqn (33) in the text. Using the relationship

$\Omega_{1}+2\Omega_{2}=-G_{a,r_{\mathrm{c}}}/\left(a^{2}J_{\mathrm{u}}^{*}\right)$ derived from eqn (S14), the expression (S20) for τ_{L} may be rewritten as

$$\tau_{\mathrm{L}}=K_{\mathrm{M}}G_{a,r_{\mathrm{c}}}/\left(a^{2}\beta_{\mathrm{a}}J_{\mathrm{u}}^{*}\right). \tag{S22}$$

Substituting eqn (3) for J_{u}^{*} into eqn (S22) and further introducing the surface resistance $R_{\mathrm{S}}=1/\left(k_{\mathrm{int}}K_{\mathrm{H}}\beta_{\mathrm{a}}\right)$

and the area of the bioactive surface $S_{\mathrm{a}}=4\pi a^{2}$, we obtain eqn (34) given in the main text for τ_{L}.

• In the other limit $A\left(c_M^*\right)\left(1+Bn^{-1}\right)\gg 1$ (*i.e.* $u\left(c_M^*\right)\gg 0$), the function ω may now be linearized *via* considering the first order term in its corresponding Taylor development with respect to the variable $Z \equiv 1/\left[A\left(c_M^*\right)\left(1+Bn^{-1}\right)\right]=c_M^*\left(t\right)/\left[K_M\beta_a^{-1}\left(1+Bn^{-1}\right)\right]\ll 1$. After rewriting $\omega\left(c_M^*\right)$ in the form $\omega(Z)$, we find that eqn (S15) becomes to the leading order in Z

$$\left[\xi + 1/c_M^*\right]dc_M^* = -dt/\tau_E,\tag{S23}$$

where ξ is defined by the expression

$$\xi = \left\{\Omega_1 + 2\Omega_2\left[2-\left(1+Bn^{-1}\right)^{-1}\right]\right\}\left\{K_M\beta_a^{-1}\left(1+Bn^{-1}\right)\left[\Omega_1\left(1+Bn^{-1}\right)+2\Omega_2\right]\right\}^{-1},\tag{S24}$$

and the characteristic timescale τ_E is provided by the relation

$$\tau_E = -K_M\beta_a^{-1}\left[\Omega_1\left(1+Bn^{-1}\right)+2\Omega_2\right].\tag{S25}$$

For $Bn^{-1}\ll 1$, ξ may be developed as follows

$$\xi \sim 1/\left(K_M\beta_a^{-1}\right)+O\left(Bn^{-1}\right).\tag{S26}$$

where the symbol O denotes order of magnitude. The combination of $A\left(c_M^*\right)\left(1+Bn^{-1}\right)\gg 1$ and $Bn^{-1}\ll 1$ leads to $A\left(c_M^*\right)\gg 1$ or equivalently $K_M\beta_a^{-1}/c_M^*\gg 1$. The latter inequality used with eqn (S26) and eqn (S23) finally yields

$$dc_M^*/c_M^* = -dt/\tau_E,\tag{S27}$$

i.e.
$$c_M^*\left(t\right)/c_M^*\left(0\right)=\exp\left(-t/\tau_E\right),\tag{S28}$$

which is eqn (36) in the main text. For cases where $Bn^{-1}\gg 1$, we have

$$\xi \sim O\left(Bn^2\right),\tag{S29}$$

and eqn (S23) again reduces to eqn (S27) whose solution is expressed by the exponential decay of $c_M^*\left(t\right)$ given by eqn (S28). For cases where none of the inequalities $Bn^{-1}\ll 1$ and $Bn^{-1}\gg 1$ applies, integration of eqn (S23) leads to

$$\xi\left(c_M^*\left(t\right)-c_M^*\left(0\right)\right)+\ln\left(\frac{c_M^*\left(t\right)}{c_M^*\left(0\right)}\right)=-t/\tau_E.\tag{S30}$$

The solution $c_M^*\left(t\right)$ of the transcendental equation (S30) may be formulated in terms of the Lambert function W defined by $W\left(x\right)\exp\left[W\left(x\right)\right]=x$ for any argument x. The solution is then written

$$c_M^*\left(t\right)/c_M^*\left(0\right)=\xi^{-1}W\left(\xi c_M^*\left(0\right)\exp\left[-t/\tau_E+\xi c_M^*\left(0\right)\right]\right)/c_M^*\left(0\right),\tag{S31}$$

which is eqn (38) in the main text. Finally, the expression (S25) for τ_{E} may be written in the form

$$\tau_{\text{E}} = -K_{\text{M}}\beta_{\text{a}}^{-1}\left[\Omega_1 + 2\Omega_2\right] - K_{\text{M}}\beta_{\text{a}}^{-1}\Omega_1 Bn^{-1}. \tag{S32}$$

The first term in the right hand side of eqn (S25) identifies to τ_{L} (eqn (S20) while the second term can be rearranged according to $K_{\text{M}}\beta_{\text{a}}^{-1}\Omega_1 Bn^{-1} = 4\pi a^2 J_{\text{u}}^{*}\Omega_1 R_{\text{T}}/S_{\text{a}}$, where we have used eqn (19), eqn (3) and the definition $R_{\text{T}} = 1/\left(D_{\text{M,out}} f_{\text{el}} a^{-1}\right)$ for the conductive-diffusional mass transfer resistance. In turn, eqn (S32) identifies to that given in eqn (37).

II. Details on the numerical solving of eqns (4)-(5) and eqn (20) in the main text.

1. Solution of the non-linear Poisson-Boltzmann equation (20).

The non-linear Poisson Boltzmann equation governing the potential distribution $y(r)$ across the soft biointerphase depicted in Figure 1 may be written in the general form

$$\varepsilon_{\text{o}}\nabla\bullet\left[\varepsilon(r)\vec{\nabla}y(r)\right] = \left[2z^2 F^2 c^{\infty}/(RT)\right]\sinh\left[y(r)\right] - zF\rho_{\text{o}}f_{\rho}(r)/(RT), \tag{S33}$$

where $\varepsilon(r)$ stands for the relative dielectric permittivity at the position r and $\rho_{\text{o}}f_{\rho}(r)$ corresponds to the spatial distribution of fixed charges carried by the soft biointerphase with $f_{\rho}(r>r_{\text{o}})=0$. $f_{\rho}(r)$ may be formulated according to[1]

$$f_{\rho}(r) = \left\{1 - \tanh\left[(r-r_{\text{o}})/\tilde{\alpha}\right]\right\}/2, \tag{S34}$$

with $\tilde{\alpha}$ the characteristics decay length of the density of soft material and fixed charges across the biointerphase. In the limit $\tilde{\alpha}\to 0$, the case of uniform charge distribution across the soft microbial surface layer is recovered. By the same token, we may write $\varepsilon(r) = \varepsilon_{\text{r}}f_{\varepsilon}(r)$ where ε_{r} is the relative dielectric permittivity of the bulk medium and $f_{\varepsilon}(r)$ the function defined by

$$f_{\varepsilon}(r) = (\Im-1)f_{\rho}(r) + f_{\rho}(r+r_{\text{o}}-r_{\text{c}}), \tag{S35}$$

with $\Im = \varepsilon_{\text{s}}/\varepsilon_{\text{r}}$, as defined in the main text. In the limit $\tilde{\alpha}\to 0$, eqn (S35) leads to $\varepsilon(a\le r\le r_{\text{o}}) = \varepsilon_{\text{s}}$ and $\varepsilon(r_{\text{o}}\le r\le r_{\text{c}}) = \varepsilon_{\text{r}}$. Combining eqns (S33)-(S35) provides after some arrangements

$$\nabla_r^2 y(r) = -\frac{1}{f_{\varepsilon}(r)}\frac{\text{d}f_{\varepsilon}(r)}{\text{d}r}\frac{\text{d}y(r)}{\text{d}r} + \frac{\kappa^2\sinh y(r)}{f_{\varepsilon}(r)} - \frac{\kappa^2\rho_{\text{o}}f_{\rho}(r)}{2zFc^{\infty}f_{\varepsilon}(r)}, \tag{S36}$$

which simplifies into eqn (20) for $\tilde{\alpha}\to 0$ *i.e.* for uniform distribution of charge and dielectric permittivity within the soft surface layer. Equation (S36) and boundaries (21), (23) may be solved numerically by means of the COLSYS procedure detailed elsewhere.[2] It is stressed that the formulation of diffuse distributions for the density of fixed charges and for the dielectric permittivity across the biointerphase (eqn (S34) and (S35),

respectively) as subsumed into eqn (S36), automatically verifies the boundaries given by eqn (22) for the continuity of electrostatic potential and electric field displacement at the position $r = r_o$.

2. Solution of the Nernst-Planck equation (4)-(5) for non-uniform distribution of metal diffusion coefficient across the microorganism soft surface layer.

Following the strategy given in the preceding section, the spatial distribution of the diffusion coefficient $D_M(r)$ across the whole biointerphase may be written $D_M(r) = D_{M,out} f_D(r)$ with $f_D(r)$ defined by

$$f_D(r) = (\varepsilon - 1) f_\rho(r) + f_\rho(r + r_o - r_c). \tag{S37}$$

and $\varepsilon = D_{M,in}/D_{M,out}$. After some developments and using this continuous dependence of the metal diffusion coefficient on radial position, the Nernst-Planck equation governing the spatial distribution of metal concentration across the biointerphase is given in steady-state by

$$\nabla_r^2 c_M(r) = -\frac{d c_M(r)}{dr}\left[\frac{1}{f_D(r)}\frac{d f_D(r)}{dr} + \frac{z_M}{z}\frac{d y(r)}{dr}\right] - \frac{z_M}{z}c_M(r)\left[\nabla_r^2 y(r) + \frac{1}{f_D(r)}\frac{d f_D(r)}{dr}\frac{d y(r)}{dr}\right]. \tag{S38}$$

Equation (S38) with boundaries (6)-(7) may be solved numerically using the same collocation algorithm than that employed for the electrostatic problem.[2] Under the condition $\tilde{\alpha} \to 0$, eqn (S38) reduces to eqns (4) and (5) in the main text. It is further emphasized that eqn (S38) necessarily satisfies the requirements of continuity for the metal concentration and for the metal flux at $r = r_o$ (eqns (8) and (9), respectively). Finally, in view of the different magnitudes for the key electrostatic and diffusion length scales relevant for the problem, it is judicious to replace in the numerical scheme the far-field boundary condition expressed by eqn (6) by the following relationship

$$c_M(r = r^*)/c_M^* = 1 + r^{*2}\frac{d c_M(r)}{dr}\bigg|_{r=r^*}\left[1/r_c - 1/r^*\right] \tag{S39}$$

where $r^* = r_o + n/\kappa$ ($n \gg 1$) is a position just outside the extra-particulate electric double layer, *i.e.*

$$y(r^*) = dy(r)/dr\big|_{r^*} = \nabla_{r=r^*}^2 y(r) = 0. \tag{S40}$$

Equation (S39) is obtained upon solving eqn (S38) outside the extra-particulate electric double layer where eqn (S40) is applicable.

References.

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2. U. Ascher, J. Christiansen and R. D. Russel, *ACM Trans. Math. Software*, 1981, **7**, 209-222.