Design of localized spatiotemporal pH patterns by means of antagonistic chemical gradients
electronic supplementary information

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Derivation of the numerical model

The simulations were made by the dimensionless equations derived from the Rábai model of the pH oscillators (R1)-(R3)[1] and extended with (R4).

$$\text{A}^- + \text{H}^+ \rightleftharpoons \text{HA} \tag{R1}$$

$$\text{HA} + \text{B} \xrightarrow{\text{H}^+} \text{H}^+ + \text{P} \tag{R2}$$

$$\text{C} + \text{B} + \text{H}^+ \longrightarrow \text{Q} \tag{R3}$$

$$\text{S}^- + \text{H}^+ \rightleftharpoons \text{HS} \tag{R4}$$

The corresponding rate equations are the following:

$$v_1 = k_1[\text{A}^-][\text{H}^+] - k_{-1}[\text{HA}] \tag{1}$$

$$v_2 = (k_2[\text{H}^+] + k_2')[\text{HA}][\text{B}] \tag{2}$$

$$v_3 = k_3[\text{B}][\text{C}][\text{H}^+] \tag{3}$$

$$v_4 = k_4[\text{S}^-][\text{H}^+] - k_{-4}[\text{SH}] \tag{4}$$

The state of Tank A and B can be described by the following set of equations:

$$\frac{d[\text{A}^-]_\text{X}}{dt} = -k_1[\text{A}^-]_\text{X}[\text{H}^+]_\text{X} + k_{-1}[\text{HA}]_\text{X} + k_0([\text{A}^-]_\text{X0} - [\text{A}^-]_\text{X}) \tag{5}$$

$$\frac{d[\text{HA}]_\text{X}}{dt} = k_1[\text{A}^-]_\text{X}[\text{H}^+]_\text{X} - k_{-1}[\text{HA}]_\text{X} - (k_2[\text{H}^+]_\text{X} + k_2')[\text{HA}]_\text{X}[\text{B}]_\text{X}$$

$$+ k_0([\text{HA}]_\text{X0} - \text{HA}]_\text{X}) \tag{6}$$

$$\frac{d[\text{H}^+]_\text{X}}{dt} = -k_1[\text{A}^-]_\text{X}[\text{H}^+]_\text{X} + k_{-1}[\text{HA}]_\text{X} + (k_2[\text{H}^+]_\text{X} + k_2')[\text{HA}]_\text{X}[\text{B}]_\text{X}$$

$$- k_3[\text{B}]_\text{X}[\text{C}]_\text{X}[\text{H}^+]_\text{X} - k_4[\text{S}^-]_\text{X}[\text{H}^+]_\text{X} + k_{-4}([\text{S}]_\text{tot} - [\text{S}^-]_\text{X}) - k_0[\text{H}^+]_\text{X} \tag{7}$$

$$\frac{d[\text{B}]_\text{X}}{dt} = -(k_2[\text{H}^+]_\text{X} + k_2')[\text{HA}]_\text{X}[\text{B}]_\text{X} - k_3[\text{B}]_\text{X}[\text{C}]_\text{X}[\text{H}^+]_\text{X} + k_0([\text{B}]_\text{X0} - [\text{B}]_\text{X}) \tag{8}$$

$$\frac{d[\text{C}]_\text{X}}{dt} = -k_3[\text{B}]_\text{X}[\text{C}]_\text{X}[\text{H}^+]_\text{X} + k_0([\text{C}]_\text{X0} - [\text{C}]_\text{X}) \tag{9}$$

$$\frac{d[\text{S}^-]_\text{X}}{dt} = -k_4[\text{S}^-]_\text{X}[\text{H}^+]_\text{X} + k_{-4}([\text{S}]_\text{tot} - [\text{S}^-]_\text{X}) - k_0[\text{S}^-]_\text{X} \tag{10}$$

where $[\ ]_\text{X}$ and $[\ ]_\text{X0}$ are concentrations in Tank A and B and in their feed. The feedback of the gel content on the state of the tanks is neglected as the volume of the tanks is much larger than that of the gel.

The dynamics of the gel content is governed by the following set of equations:

$$\partial_t[\text{A}^-] = -k_1[\text{A}^-][\text{H}^+] + k_{-1}[\text{HA}] + D_{\text{A}^-}\Delta[\text{A}^-] \tag{11}$$

$$\partial_t[\text{HA}] = k_1[\text{A}^-][\text{H}^+] - k_{-1}[\text{HA}] - (k_2[\text{H}^+] + k_2')[\text{HA}][\text{B}] + D_\text{HA}\Delta[\text{HA}] \tag{12}$$

$$\partial_t[\text{H}^+] = -k_1[\text{A}^-][\text{H}^+] + k_{-1}[\text{HA}] + (k_2[\text{H}^+] + k_2')[\text{HA}][\text{B}] - k_3[\text{B}][\text{C}][\text{H}^+]$$

$$- k_4[\text{S}^-][\text{H}^+] + k_{-4}([\text{S}]_\text{tot} - [\text{S}^-]) + D_{\text{H}^+}\Delta[\text{H}^+] \tag{13}$$

$$\partial_t[\text{B}] = -(k_2[\text{H}^+] + k_2')[\text{HA}][\text{B}] - k_3[\text{B}][\text{C}][\text{H}^+] + D_\text{B}\Delta[\text{B}] \tag{14}$$

$$\partial_t[\text{C}] = -k_3[\text{B}][\text{C}][\text{H}^+] + D_\text{C}\Delta[\text{C}] \tag{15}$$

$$\partial_t[\text{S}^-] = -k_4[\text{S}^-][\text{H}^+] + k_{-4}([\text{S}]_\text{tot} - [\text{S}^-]) + D_{\text{S}^-}\Delta[\text{S}^-] \tag{16}$$

with Dirichlet boundary conditions at the gel/tank surfaces, i.e.: $[\text{A}^-]_{(x=0)} = [\text{A}^-]_\text{A}$ and $[\text{A}^-]_{(x=w)} = [\text{A}^-]_\text{B}$. Here $[\ ]$ denotes the space and time dependent concentration in the gel.

The dimensionless variables are defined as $a_X = [A^-]_X/[A]_{tot}$, $a_{hX} = [HA]_X/[A]_{tot}$, $h_X = [H^+]_X/[A]_{tot}$, $b_X = [B]_X/[A]_{tot}$, $c_X = [C]_X/[A]_{tot}$, $a_{X0} = [A^-]_{X0}/[A]_{tot}$, $a_{hX0} = [HA]_{X0}/[A]_{tot}$, $h_{X0} = [H^+]_{X0}/[A]_{tot}$, $b_{X0} = [B]_{X0}/[A]_{tot}$, $c_{X0} = [C]_{X0}/[A]_{tot}$, $s_{X0} = [S^-]_{X0}/[A]_{tot}$, $a = [A^-]/[A]_{tot}$, $a_h = [HA]/[A]_{tot}$, $h = [H^+]/[A]_{tot}$, $b = [B]/[A]_{tot}$, $c = [C]/[A]_{tot}$, $s = [S^-]/[A]_{tot}$ and $s_{tot} = [S]_{tot}/[A]_{tot}$, where $[A]_{tot} = [A^-]_{X0} + [HA]_{X0}$ and $[S]_{tot} = [S^-]_{X0} + [HS]_{X0}$. The dimensionless space $(\tilde{x}, \tilde{y})$ and time $(\tilde{t})$ coordinates are scaled by $\sqrt{k_0/D}$ and k_0, respectively. Hereafter, dot, ∂_t and Δ denote the time derivatives and Laplacian, respectively.

The equations for the content of Tank A and B can be written as:

$$\dot{a}_X = -\kappa_1 a_X h_X + \kappa_{-1} a_{hX} + a_{X0} - a_X \tag{17}$$

$$\dot{a}_{hX} = \kappa_1 a_X h_X - \kappa_{-1} a_{hX} - (\kappa_2 h_X + \kappa_2') a_{hX} b_X + a_{hX0} - a_{hX} \tag{18}$$

$$\dot{h}_X = -\kappa_1 a_X h_X + \kappa_{-1} a_{hX} + (\kappa_2 h_X + \kappa_2') a_{hX} b_X - \kappa_3 b_X c_X h_X$$
$$- \kappa_4 s_X h_X + \kappa_{-4}(s_{tot} - s_X) - h_X \tag{19}$$

$$\dot{b}_X = -(\kappa_2 h_X + \kappa_2') a_{hX} b_X - \kappa_3 b_X c_X h_X + b_{X0} - b_X \tag{20}$$

$$\dot{c}_X = -\kappa_3 b_X c_X h_X + c_{X0} - c_X \tag{21}$$

$$\dot{s}_X = -\kappa_4 s_X h_X + \kappa_{-4}(s_{tot} - s_X) - s_X \tag{22}$$

where $a_{X0} + a_{hX0} = 1$.

The equations for the content of the gel can be written as:

$$\partial_t a = -\kappa_1 ah + \kappa_{-1} a_h + \Delta a \tag{23}$$

$$\partial_t a_h = \kappa_1 ah - \kappa_{-1} a_h - (\kappa_2 h + \kappa_2')a_h b + \Delta a_h \tag{24}$$

$$\partial_t h = -\kappa_1 ah + \kappa_{-1} a_h + (\kappa_2 h + \kappa_2')a_h b - \kappa_3 bch$$

$$- \kappa_4 sh + \kappa_{-4}(s_{tot} - s) + 4\Delta h \tag{25}$$

$$\partial_t b = -(\kappa_2 h + \kappa_2')a_h b - \kappa_3 bch + \Delta b \tag{26}$$

$$\partial_t c = -\kappa_3 bch + \Delta c \tag{27}$$

$$\partial_t s = -\kappa_4 sh + \kappa_{-4}(s_{tot} - s) + 0.01\Delta s \tag{28}$$

The parameters are defined as: $\kappa_1 = k_1[\text{A}]_{\text{tot}}/k_0$, $\kappa_{-1} = k_{-1}/k_0$, $\kappa_2 = k_2[\text{A}]_{\text{tot}}^2/k_0$, $\kappa_2' = k_2'[\text{A}]_{\text{tot}}/k_0$, $\kappa_3 = k_3[\text{A}]_{\text{tot}}^2/k_0$, $\kappa_4 = k_4[\text{A}]_{\text{tot}}/k_0$, $\kappa_{-4} = k_{-4}/k_0$. The diffusion coefficients are set to be equal for all species ($D_{\text{A}^-} = D_{\text{HA}} = D_{\text{B}} = D_{\text{C}} = D$) except for the hydrogen ions, where $D_{\text{H}^+} = 4D$,[2] and for the polyacrylate, where $D_{\text{S}^-} = 0.01D$.

The value of κ_1 and κ_{-1} are set to 5×10^{10} and 5×10^5 respectively, which are calculated by using the following kinetic parameter values for the protonation of sulfite ions: $k_1 = 10^{10}\,\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$, $k_{-1} = 10^3\,\text{s}^{-1}$ and the typical set of experimental conditions, $k_0 = 2 \times 10^{-3}\,\text{s}^{-1}$, $[\text{A}^-]_{\text{tot}} = 10\,\text{mM}$. The values of κ_2, κ_2', κ_3, κ_4 and κ_{-4} are set to 5×10^5, 5×10^1, 5×10^3, 5×10^{10}, 5×10^7 respectively.

Dependence of the simulated values of the width ($\tilde{d}$) of the middle band of the M state on the width of the gel ($\tilde{w}$)
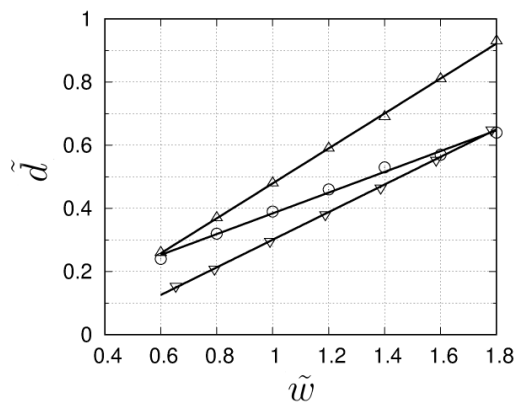

Figure S1: Dependence of $\tilde{d}$ on $\tilde{w}$ at $a_{A0} = 1$, $a_{hA0} = 0$, $a_{B0} = 0.4$, $a_{hB0} = 0.6$, $c_{X0} = 0$, $b_{A0} = 1.5$, $b_{B0} = 0$ (∇), at $a_{A0} = 1$, $a_{hA0} = 0$, $a_{B0} = 0.4$, $a_{hB0} = 0.6$, $c_{X0} = 0$, $b_{A0} = 1.8$, $b_{B0} = 0$ (∇) and at $a_{A0} = 1$, $a_{hA0} = 0$, $a_{B0} = 0.2$, $a_{hB0} = 0.8$, $c_{X0} = 0.3$, $b_{A0} = 1.5$, $b_{B0} = 0$ ($\odot$). The solid lines show the results of fitted linear functions.

Dependence of the limits of the domain of oscillations on the rate of the oxidation steps
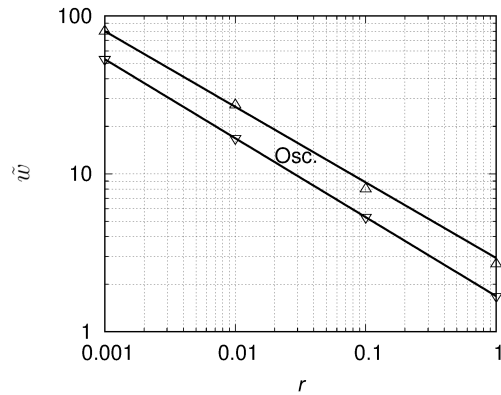

Figure S2: Dependence of the limits of the domain of oscillations on rate of the oxidation steps. The rate constants are scaled by a factor r, as $\kappa_2 = r \times 5 \times 10^5$, $\kappa_2' = r \times 5 \times 10^1$, $\kappa_3 = r \times 5 \times 10^3$. The slope of the solid lines are $-0.50(\pm 0.01)$ and $-0.48(\pm 0.01)$.

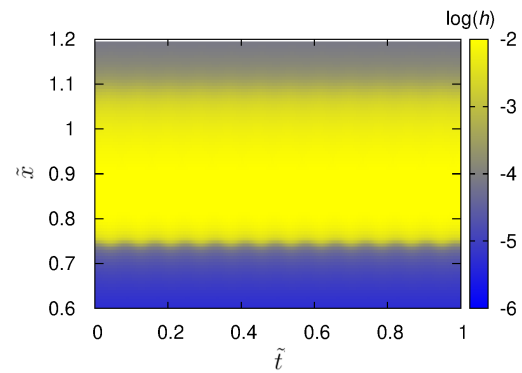# Simulated small amplitude oscillations

Figure S3: Simulated small amplitude oscillations at $a_{A0} = 1$, $a_{hA0} = 0$, $a_{B0} = 0.4$, $a_{hB0} = 0.6$, $c_{X0} = 0.8$, $b_{A0} = 1.5$, $b_{B0} = 0$, $w = 2.76$. The figure shows only the middle part of gel.

References

(1) Rabai, G. Modeling and Designing of pH-Controlled Bistability, Oscillations, and Chaos in a Continuous-Flow Stirred Tank Reactor. *ACH - Models Chem.* **1998**, *135*, 381–392.

(2) Schuszter, G.; Gehér-Herczegh, T.; Szűcs, Á.; Tóth, Á.; Horváth, D. Determination of the diffusion coefficient of hydrogen ion in hydrogels. *Phys. Chem. Chem. Phys.* **2017**, *19*, 12136–12143.