Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for: Reaction-diffusion phenomena in antagonistic bipolar diffusion fields

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1 Supplementary methods

1.1 Derivation of the numerical models

In the 2D simulations Dirichlet boundary conditions were used at the gel/channel surfaces, and no flux boundary conditions were used at the outer surfaces of the gel.

Model A:

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \tag{R1a}$$
$$\mathrm{C} \longrightarrow \mathrm{D} \tag{R2a}$$
$$\mathrm{D} \longrightarrow \mathrm{E} \tag{R3a}$$

The corresponding rate equations are the following:

$$v_{1a} = k_{1a}[\mathrm{A}][\mathrm{B}] \tag{1}$$
$$v_{2a} = k_{2a}[\mathrm{C}] \tag{2}$$
$$v_{3a} = k_{3a}[\mathrm{D}] \tag{3}$$

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

$$\partial_t[\mathrm{A}] = -v_{1a} + D\Delta[\mathrm{A}] \tag{4}$$
$$\partial_t[\mathrm{B}] = -v_{1a} + D\Delta[\mathrm{B}] \tag{5}$$
$$\partial_t[\mathrm{C}] = v_{1a} - v_{2a} + D\Delta[\mathrm{C}] \tag{6}$$
$$\partial_t[\mathrm{D}] = v_{2a} - v_{3a} + D\Delta[\mathrm{D}] \tag{7}$$
$$\partial_t[\mathrm{E}] = v_{3a} + D\Delta[\mathrm{E}] \tag{8}$$

Here [ ] denotes the space and time dependent concentration in the gel and $\Delta = \partial_x^2 + \partial_z^2$.

The dimensionless variables are defined as $a = [\mathrm{A}]/[\mathrm{A}]_0$, $b = [\mathrm{B}]/[\mathrm{A}]_0$, $c = [\mathrm{C}]/[\mathrm{A}]_0$, $d = [\mathrm{D}]/[\mathrm{A}]_0$, $e = [\mathrm{E}]/[\mathrm{A}]_0$.

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

$$\partial_t a = -\kappa_{1a} ab + \Delta a \tag{9}$$
$$\partial_t b = -\kappa_{1a} ab + \Delta b \tag{10}$$
$$\partial_t c = \kappa_{1a} ab - \kappa_{2a} c + \Delta c \tag{11}$$
$$\partial_t d = \kappa_{2a} c - \kappa_{3a} d + \Delta d \tag{12}$$
$$\partial_t e = \kappa_{3a} d + \Delta e \tag{13}$$

The diffusion coefficients are set to be equal for all species. The dimensionless space and time coordinates are scaled by $\sqrt{k_0/D}$ and k_0, respectively. Here, k_0 is a reciprocal residence time in the channels. The parameters are defined as: $\kappa_{1a} = k_{1a}[\mathrm{A}]_0/k_0$, $\kappa_{2a} = k_{2a}/k_0$, $\kappa_{3a} = k_{3a}/k_0$. Parameters used in the simulations: $a = 1.0$ in the "A" channel and $b = 1.0$ in the "B" channel, $\kappa_{1a} = \kappa_{2a} = \kappa_{3a} = 5.0$.

Model B:

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \tag{R1b}$$
$$\mathrm{C} + \mathrm{B} \longrightarrow \mathrm{D} \tag{R2b}$$
$$\mathrm{D} + \mathrm{B} \longrightarrow \mathrm{E} \tag{R3b}$$

The corresponding rate equations are the following:

$$v_{1b} = k_{1b}[\mathrm{A}][\mathrm{B}] \tag{14}$$
$$v_{2b} = k_{2b}[\mathrm{C}][\mathrm{B}] \tag{15}$$
$$v_{3b} = k_{3b}[\mathrm{D}][\mathrm{B}] \tag{16}$$

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

$$\partial_t[\mathrm{A}] = -v_{1b} + D\Delta[\mathrm{A}] \tag{17}$$
$$\partial_t[\mathrm{B}] = -v_{1b} - v_{2b} - v_{3b} + D\Delta[\mathrm{B}] \tag{18}$$
$$\partial_t[\mathrm{C}] = v_{1b} - v_{2b} + D\Delta[\mathrm{C}] \tag{19}$$
$$\partial_t[\mathrm{D}] = v_{2b} - v_{3b} + D\Delta[\mathrm{D}] \tag{20}$$
$$\partial_t[\mathrm{E}] = v_{3b} + D\Delta[\mathrm{E}] \tag{21}$$

Here [ ] denotes the space and time dependent concentration in the gel and $\Delta = \partial_x^2 + \partial_z^2$.

The dimensionless variables are defined as $a = [\mathrm{A}]/[\mathrm{A}]_0$, $b = [\mathrm{B}]/[\mathrm{A}]_0$, $c = [\mathrm{C}]/[\mathrm{A}]_0$, $d = [\mathrm{D}]/[\mathrm{A}]_0$, $e = [\mathrm{E}]/[\mathrm{A}]_0$.

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

$$\partial_t a = -\kappa_{1b} ab + \Delta a \tag{22}$$
$$\partial_t b = -\kappa_{1b} ab - \kappa_{2b} cb - \kappa_{3b} db + \Delta b \tag{23}$$
$$\partial_t c = \kappa_{1b} ab - \kappa_{2b} cb + \Delta c \tag{24}$$
$$\partial_t d = \kappa_{2b} cb - \kappa_{3b} db + \Delta d \tag{25}$$
$$\partial_t e = \kappa_{3b} db + \Delta e \tag{26}$$

The diffusion coefficients are set to be equal for all species. The parameters are defined as: $\kappa_{1b} = k_{1b}[\mathrm{A}]_0/k_0$, $\kappa_{2b} = k_{2b}[\mathrm{A}]_0/k_0$, $\kappa_{3b} = k_{3b}[\mathrm{A}]_0/k_0$. Here, k_0 is a reciprocal residence time in the channels.

Parameters used in the simulations: $a = 1.0$ in the "A" channel and $b = 1.0$ in the "B" channel, $\kappa_{1b} = \kappa_{2b} = \kappa_{3b} = 10.0$.

The simulations of the pH oscillators were made by the dimensionless equations derived from the Rábai model (R1c)-(R3c).[1]

$$\mathrm{A^-} + \mathrm{H^+} \rightleftharpoons \mathrm{HA} \tag{R1c}$$

$$\mathrm{HA} + \mathrm{B} \xrightarrow{H^+} \mathrm{H^+} + \mathrm{P} \tag{R2c}$$

$$\mathrm{C} + \mathrm{B} + \mathrm{H^+} \longrightarrow \mathrm{Q} \tag{R3c}$$

The corresponding rate equations are the following:

$$v_{1c} = k_{1c}[\mathrm{A^-}][\mathrm{H^+}] - k_{-1c}[\mathrm{HA}] \tag{27}$$

$$v_{2c} = (k_{2c}[\mathrm{H^+}] + k'_{2c})[\mathrm{HA}][\mathrm{B}] \tag{28}$$

$$v_{3c} = k_{3c}[\mathrm{B}][\mathrm{C}][\mathrm{H^+}] \tag{29}$$

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

$$\partial_t[\mathrm{A^-}] = -v_{1c} + D_{\mathrm{A^-}}\Delta[\mathrm{A^-}] \tag{30}$$

$$\partial_t[\mathrm{HA}] = v_{1c} - v_{2c} + D_{\mathrm{HA}}\Delta[\mathrm{HA}] \tag{31}$$

$$\partial_t[\mathrm{H^+}] = -v_{1c} + v_{2c} - v_{3c} + D_{\mathrm{H^+}}\Delta[\mathrm{H^+}] \tag{32}$$

$$\partial_t[\mathrm{B}] = -v_{2c} - v_{3c} + D_{\mathrm{B}}\Delta[\mathrm{B}] \tag{33}$$

$$\partial_t[\mathrm{C}] = -v_{3c} + D_{\mathrm{C}}\Delta[\mathrm{C}] \tag{34}$$

The dimensionless variables are defined as $a = [\mathrm{A^-}]/[\mathrm{A}]_{\mathrm{tot}}$, $a_h = [\mathrm{HA}]/[\mathrm{A}]_{\mathrm{tot}}$, $h = [\mathrm{H^+}]/[\mathrm{A}]_{\mathrm{tot}}$, $b = [\mathrm{B}]/[\mathrm{A}]_{\mathrm{tot}}$, $c = [\mathrm{C}]/[\mathrm{A}]_{\mathrm{tot}}$, where $[\mathrm{A}]_{\mathrm{tot}} = [\mathrm{A^-}] + [\mathrm{HA}]$.

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

$$\partial_t a = -\kappa_1 ah + \kappa_{-1} a_h + \Delta a \tag{35}$$

$$\partial_t a_h = \kappa_1 ah - \kappa_{-1} a_h - (\kappa_2 h + \kappa'_2) a_h b + \Delta a_h \tag{36}$$

$$\partial_t h = -\kappa_1 ah + \kappa_{-1} a_h + (\kappa_2 h + \kappa'_2) a_h b - \kappa_3 bch + 4\Delta h \tag{37}$$

$$\partial_t b = -(\kappa_2 h + \kappa'_2) a_h b - \kappa_3 bch + \Delta b \tag{38}$$

$$\partial_t c = -\kappa_3 bch + \Delta c \tag{39}$$

The diffusion coefficients are set to be equal for all species except for the hydrogen ions, which diffuses 4 times faster than the other species.[2]

The parameters are defined as: $\kappa_1 = k_{1c}[\mathrm{A}]_{\mathrm{tot}}/k_0$, $\kappa_{-1c} = k_{-1c}/k_0$, $\kappa_2 = k_{2c}[\mathrm{A}]^2_{\mathrm{tot}}/k_0$, $\kappa'_2 = k'_{2c}[\mathrm{A}]_{\mathrm{tot}}/k_0$, $\kappa_3 = k_{3c}[\mathrm{A}]_{\mathrm{tot}}/k_0$. Here, $k_0 = 2 \times 10^{-3}\,\mathrm{s^{-1}}$ is a reciprocal residence time in the channels. The value of κ_1, κ_{-1}, κ_2, κ'_2, κ_3 are set to 5×10^{10}, 5×10^5, 5×10^5, 5×10^1, 5×10^3, respectively.

Parameters used in the simulations: $b = 1.5$, $a = 1.0$, $c = 1.0$ in the "B" channel and $a = 1.0$, $c = 1.0$ and variable value of h in the "HA" channel.

1.2 Supplementary figures

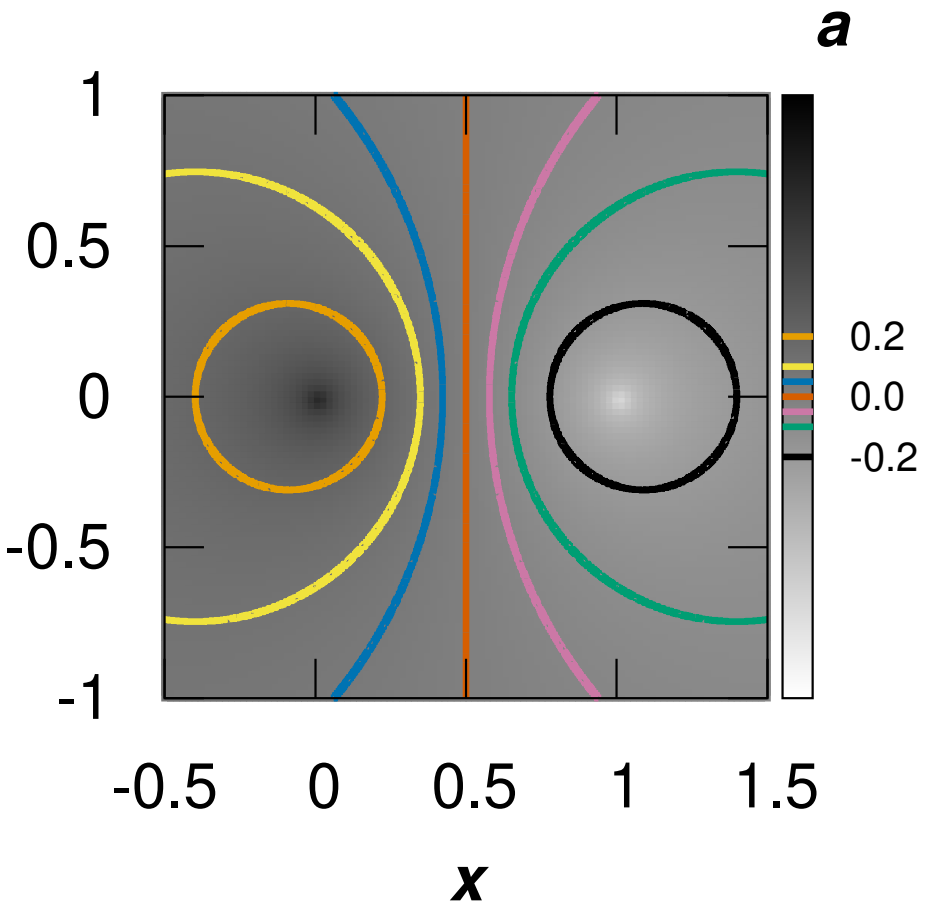

Figure S1 Bipolar field described by equation $a(x,z) = \frac{\sigma}{4\pi} \ln \frac{(x-w)^2 z^2}{x^2+z^2}$. Here, $\sigma = 1$ is the source strength, the source is located at $(0,0)$, and the distance between the sink and the source is $w = 1$.

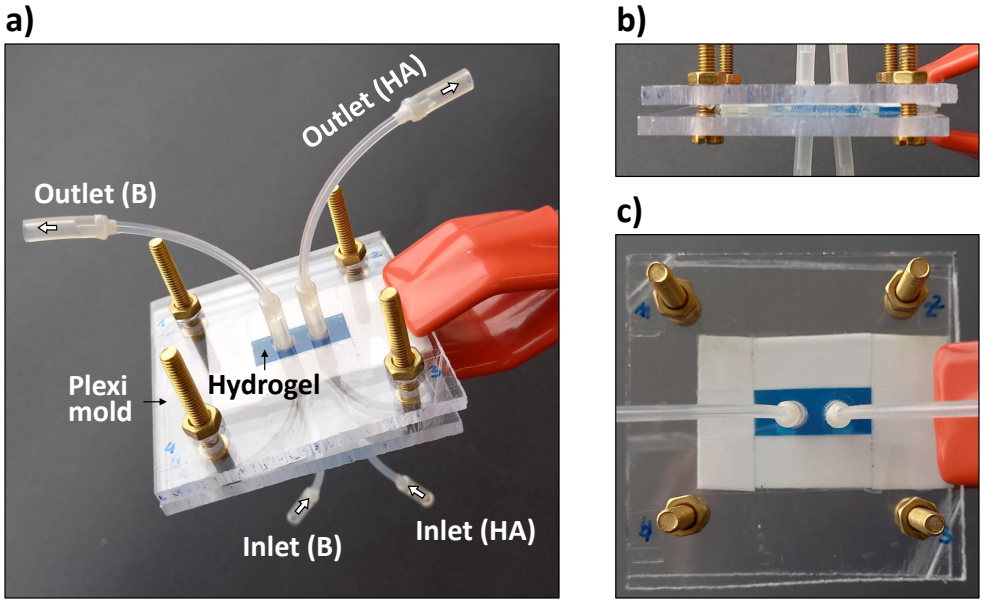

Figure S2 Photos of the home-made two-source-fed gel reactor from different views. The hydrogel is made of 2 m/V% agarose and filled with 0.1 mM bromocresol green sodium salt pH indicator. The mold is made of Plexi, the tubes are made of silicone. The white arrows indicate the direction of the feeding flows of the reactant solutions (B) and (HA).

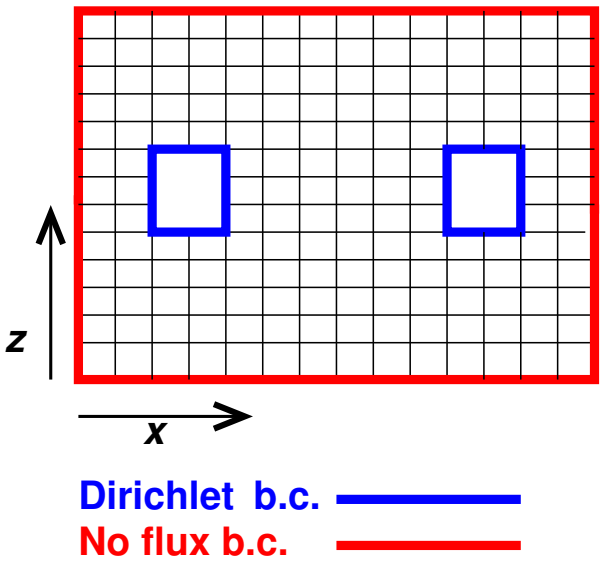

Figure S3 The sketch of the applied mesh in the numerical simulations with boundary conditions.

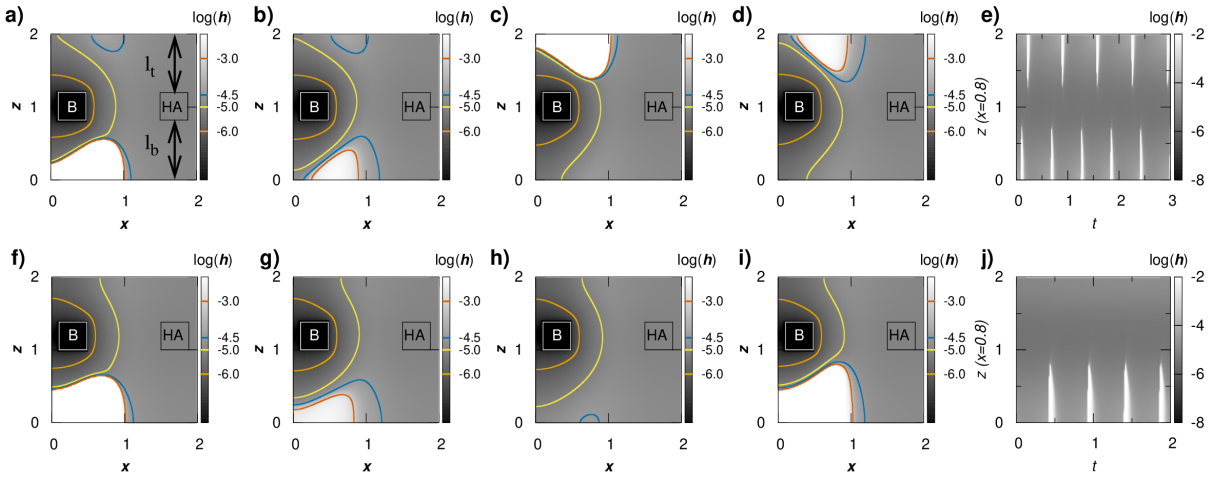

Figure S4 Simulated large amplitude spatiotemporal oscillations observed in the Rábai model of the pH oscillators in a flow-through gel reactor at asymmetric geometry. Snapshots (a-d) and (f-i) and space-time plot (e and j) of oscillations. The distance from the top and bottom walls are different: l_t/l_b is 0.95 (a-e) and 0.6 (f-j). Parameters used in the simulations: $b = 1.5$, $a = 1.0$ and $c = 1.0$ at the source B and $a = 1.0$, $c = 1.0$ and $h = 0.55$ at the source HA. Along the contour lines, the $\log(h)$ has a constant value that is indicated on the palettes.

Notes and references

[1] G. Rabai, *ACH - Models Chem.*, 1998, **135**, 381–392.

[2] G. Schuszter, T. Gehér-Herczegh, Á. Szűcs, Á. Tóth and D. Horváth, *Phys. Chem. Chem. Phys.*, 2017, **19**, 12136–12143.