

A SIMPLE MODEL OF REPRODUCTIVE MASS SPREADING

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ABSTRACT. In this paper a simple model of reproductive toxic mass spreading in a slender trough is investigated. The objectives of the study are to describe the periodic retreat and advance of the toxic front and to show the bistability of the model when the system is driven by a weak periodic forcing. This periodic forcing models two situations of interest: (i) periodic injection of toxic chemical at one end of the trough, and (ii) periodically varying surrounding temperature. Through multiple scales analysis, oscillations of the toxic front are determined. A slope stability theorem for stationary oscillations of the toxic front is proved. This theorem assures the existence of two bifurcation points, at which an infinitesimal change of the forcing term may cause a large jump in the oscillation amplitude of the toxic front.

1. Introduction. Shen and Perry [12] studied a problem of reproductive toxic mass spreading in one spatial dimension. They made the following assumptions:

- (a) the spreading of toxic mass from the region of higher concentration to the one of lower concentration is solely due to diffusion;
- (b) the toxic mass is reproductive if its concentration is higher than a critical value; and
- (c) there is no external disturbance.

The assumption (b) shows a nonlinear dependence of the reproduction rate on the concentration and represents a positive feedback. Under assumptions (a)–(c), the conservation of mass led to a reaction-diffusion equation of I with positive feedback. Here

$$I = I(x, t), \quad 0 \leq x \leq L, \quad 0 \leq t < \infty$$

is the concentration of the toxic mass (see Figure 1). The function $I(x, t)$ is monotonically decreasing in x . Let I_c be the critical concen-

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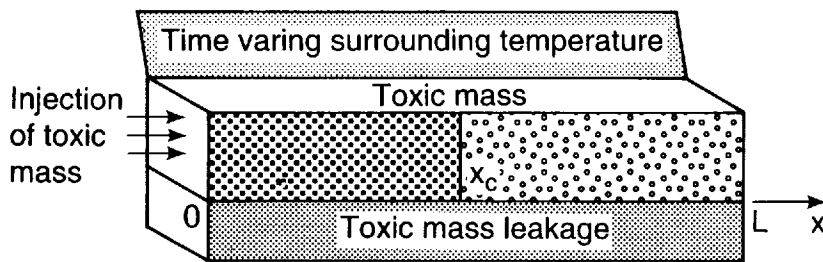


FIGURE 1. Configuration of the toxic mass spreading.

tration. For simplicity, in this paper I_c is taken as the standard of the toxic level. Namely, if $I(x, t) > I_c$, then the toxicity at the point x and the time t is unacceptable. The set $\mathbf{T} = \{x \mid x \in [0, L], I(x, t) > I_c\}$ is called the *toxic region*. The set $[0, L] \setminus \mathbf{T}$ is called the *nontoxic region*. Since $I(x, t)$ is a decreasing function of x , we thus have $x_1 < x_2$ for any x_1 in \mathbf{T} and x_2 in $([0, L] \setminus \mathbf{T})$. We denote this relation by $\mathbf{T} < ([0, L] \setminus \mathbf{T})$.

Shen and Perry [12] used the condition $I(x, t) = I_c$ to determine the position $x_c(t)$ which separates the toxic and nontoxic regions. This position $x_c(t)$ is referred to as the *toxic front*. They considered both steady and unsteady states. For the steady state, multiple solutions are found and a slope stability theorem was proved. Due to the instability, there exist two bifurcation points, around which the solutions do not continuously depend on all parameters. An infinitesimal change in the reaction rate may cause a large jump of the toxic front.

The jump type of bifurcation in a reaction-diffusion system for a fixed boundary was also studied by Cohen [2], Parter [11] and Pao et al. [10], among others. For the unsteady state, Shen and Perry derived an integral equation for the toxic front $x_c(t)$ and found numerical solutions of $x_c(t)$ for different parameters. Hence, Shen and Perry's major contributions are: (i) proof of the slope stability theorem of the multiple steady state solutions, (ii) derivation of the integral equation for the toxic front, and (iii) report of a concrete value of waiting time at which the toxic front starts to retreat.

The new contribution included in the present paper is on the bistability of our previous model (the model as described above [12]) when

a periodic forcing is introduced into the system. We study an interfacial free boundary value problem of the parabolic type with a time periodic forcing. This external forcing is introduced to model the following two cases. The first case is that the reproduction of the toxic mass through chemical reactions depends on surrounding temperature, while this temperature varies periodically in time. However, it is assumed that the amplitude of the variation is small compared with the mean temperature. An example of this is the seasonal change of the weather (if the temperature is measured in degrees of Kelvin). The second case is that there is a periodic injection of toxic mass at one end of the slender trough. An example of this is the daily release of chemical waste into a river (see Figure 1).

It is difficult to solve the feedback reaction-diffusion equation to get the function $I(x, t)$ since the interface is moving. So it does not seem easy to use $I(x, t) = I_c$ to determine $x_c(t)$. Nevertheless, for most cases of toxic mass spreading the global average $\bar{I}(t)$ of $I(x, t)$ for x in $[0, L]$ is related to the position of the toxic front $x_c(t)$. When $\bar{I}(t)$ is large, so is $x_c(t)$, and vice versa. But $\bar{I}(t)$ and $x_c(t)$ do not move at the same pace. Actually the response of $x_c(t)$ slightly lags behind the variation of $\bar{I}(t)$ (see Figure 2). If $x_c(t)$ and $\bar{I}(t)$ are both periodic, then there is a time lag between $x_c(t)$ and $\bar{I}(t)$. By this argument it is plausible to assume a relationship between $x_c(t)$ and $\bar{I}(t)$ as follows (Flügge [4]):

$$(1) \quad x_c(t) = \alpha \int_{t_0}^t \exp(\beta(\tau - t)) \frac{d\bar{I}}{d\tau} d\tau + \frac{\gamma}{\beta}$$

where t_0 is determined by

$$(2) \quad x_c(0) = \alpha \int_{t_0}^0 \exp(\beta t) \frac{d\bar{I}}{dt} dt + \frac{\gamma}{\beta}.$$

Here $x_c(0)$ is the initial position of the toxic front. A detailed analysis will be given in Section 2 to show how (1) exhibits this time lag.

The objectives of the study are to describe the periodic retreat and advance of the toxic front and to show the bistability of the model when the system is driven by a weak periodic forcing which has a component near the resonant state. This system is a new concrete example of birhythmicity (coexistence of two stable stationary oscillation regimes). The novel conclusions included in this paper are: (i) there exist two

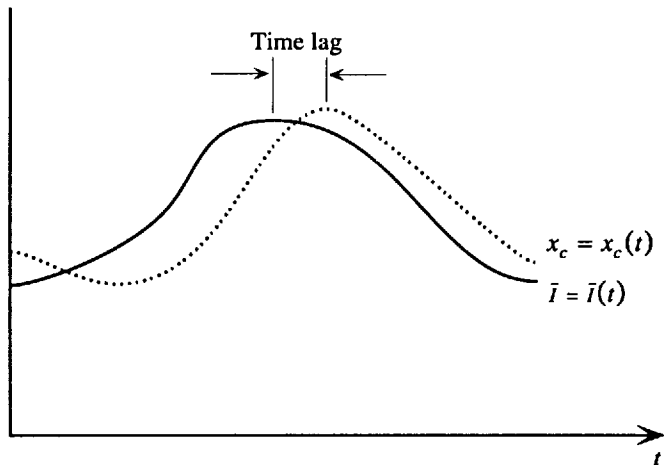


FIGURE 2. Time lag between the toxic front oscillation and the oscillatory external forcing.

stable oscillatory states which exhibit that the system has a memory, i.e., that the system reaches which stable state depends on the past history of the system; (ii) a multiple scales analysis implies that there exist two bifurcation points at which an infinitesimal perturbation of the external forcing may cause a very large jump in the amplitude of the toxic front oscillation; and (iii) our theory of bistability for the system under investigation qualitatively agree with the measurement results from some experiments in continuous-flow stirred tank reactors (CSTR). A CSTR can be used to demonstrate chemical oscillations, and interested readers are referred to references [3, 1] and the references therein.

The context of this paper is arranged as follows. In Section 2 we formulate the mathematical problem, where the plausibility of toxic front condition (1) is analyzed and a globally averaged mass balance equation is derived. A multiple scales analysis of the formulated problem is presented in Section 3. In the same section a slope stability theorem is proved, and two bifurcation points are analytically found. Some discussions and concluding remarks are given in Section 4.

2. Formulation of the problem. This section includes two subsections. The first subsection describes the condition of the toxic front and the second subsection includes the derivation of the ordinary differential equation that is satisfied by the toxic front.

2.1. The condition of the toxic front. In this subsection we will show that condition (1) exhibits a time lag between the oscillation of the external forcing and the toxic front. Let $T(t)$ be a continuously differentiable function of period p . So dT/dt is a periodic function of the same period. By

$$\int_{t_0}^t \exp(\beta(\tau - t)) \begin{cases} \sin b\tau \\ \cos b\tau \end{cases} d\tau = \frac{1}{(\beta^2 + b^2)^{3/2}} \begin{cases} \sin(bt - \varphi) \\ \cos(bt - \varphi) \end{cases} + \text{transient term}$$

where

$$\varphi = \arccos(\beta/\sqrt{\beta^2 + b^2}), \quad 0 \leq \varphi \leq \pi,$$

we see that φ/b is the time lag. The transient term exponentially decays to zero when $|t - t_0| \rightarrow \infty$. If $\bar{I}(t)$ is a sum of finitely many harmonics, then $x_c(t)$ determined by a relation (1) is an asymptotically periodic function composed of the same harmonics with a delay for each harmonic. This delay (i.e., time lag) is determined by properties of the toxic mass (i.e., β) and the frequencies of the harmonic components (i.e., b) of the external forcing. For the reason of convenience, later on in this paper condition (1) is written as the differential relation

$$(3) \quad \frac{dx_c}{dt} = \alpha \frac{d\bar{I}}{dt} - \beta x_c + \gamma.$$

2.2. The conservation of mass. Let $I(x, t)$ be the concentration of the toxic mass, $\partial I/\partial t$ the increasing rate of the concentration, $(\partial/\partial x)(D(x)\partial I/\partial x)$ the diffusion effect and $D(x)$ the diffusion coefficient. The quantity $A + BI$ represents the mass loss due to the leakage of the container or due to the radiation of the toxic chemicals. The mass reproduction is represented by $(R + \Theta - \varepsilon T(t))f(x, x_c)$, where R is the temperature equivalent reactive rate, $R + \Theta - \varepsilon T(t)$ is the modified reaction rate by the temperature field $\Theta - \varepsilon T(t)$, and $0 < \varepsilon \ll 1$ is a small

positive number which characterizes the variation of the surrounding temperature field. The function $T(t)$ is periodic in t as follows:

$$(4) \quad T(t) = \sum_{n=0}^{\infty} r_n \cos(\omega_n t - \theta_n)$$

with $0 = \omega_0 < \omega_1 < \omega_2 < \omega_3 < \dots$. And $f(x; x_c)$ has its dimension as reaction rate per unit temperature and is assumed to be

$$(5) \quad f(x; x_c) = (\bar{a} + \varepsilon a^* x^2) \begin{cases} w, & \text{if } x > x_c, \\ s, & \text{if } x < x_c. \end{cases}$$

In (5), $\bar{a} > 0$, $a^* < 0$ and $s > w \geq 0$ (cf. North et al. [9]). Hence, w and s signify weak and strong reactions, respectively. The injection of toxic mass at the left end is represented as

$$(6) \quad S(t) = S_0 + \varepsilon \sum_{n=0}^{\infty} s_n \cos(\omega_n t - \psi_n).$$

For simplicity of the analysis, we assume that $\psi_n = \theta_n$, $n = 0, 1, 2, \dots$.

Then the conservation of mass yields

$$(7) \quad \frac{\partial I}{\partial t} - \frac{\partial}{\partial x} \left(D(x) \frac{\partial I}{\partial x} \right) + A + BI = (R + \Theta - \varepsilon T(t)) f(x; x_c).$$

The boundary conditions for I at $x = 0$ and $x = L$ are

$$(8) \quad \left. \frac{\partial I}{\partial x} \right|_{x=0} = S(t),$$

$$(9) \quad \left. \frac{\partial I}{\partial x} \right|_{x=L} = 0.$$

Condition (9) implies that the right end of the slender trough is completely blocked.

Integrating (7) with respect to x from 0 to L and dividing the resulting equation by L , we obtain an averaged mass balance equation

$$(10) \quad \frac{d\bar{I}}{dt} + A + B\bar{I} = (R + \Theta - \varepsilon T(t))(a_0 + a_1 x_c - \varepsilon a_3 x_c^3) - D(0)S(t)$$

where

$$\bar{I} = \frac{1}{L} \int_0^L I(x, t) dx,$$

$$a_0 + a_1 x_c - \varepsilon a_3 x_c^3 = \frac{1}{L} \int_0^L f(x, x_c) dx.$$

Here a_0, a_1 and a_3 are all positive and related to \bar{a}, a^*, w and s in equation (5).

Define

$$(11) \quad Q = R + \Theta$$

as the *major reaction rate*. The critical major reaction rate is defined as

$$(12) \quad Q_c = (\beta + B)/(\alpha a_1).$$

We will show the existence of the interesting bistability in our system when the major reaction rate Q is near its critical value, i.e.,

$$(13) \quad \alpha a_1 Q - (\beta + B) = \lambda \varepsilon + O(\varepsilon^2).$$

If $\lambda > 0$ ($\lambda < 0$), then the system is called *supercritical* (*subcritical*).

So far, we have established two coupled first order ordinary differential equations for \bar{I} and \bar{x}_c , which are equations (3) and (10). The quantity \bar{I} can be eliminated from those two equations and a single second order ordinary differential equation for x_c can be obtained as follows:

$$(14) \quad \begin{aligned} \ddot{x}_c + \omega^2 x_c &= d_1 + \varepsilon(d_2 + d_3 x_c^2) \dot{x}_c \\ &+ \varepsilon \dot{x}_c \sum_{n=0}^{\infty} e_n \cos(\omega_n t - \theta_n) \\ &+ \varepsilon x_c \sum_{n=0}^{\infty} g_n \cos(\omega_n t - \bar{\varphi}_n) \\ &+ \varepsilon \sum_{n=0}^{\infty} h_n \cos(\omega_n t - \bar{\psi}_n) \end{aligned}$$

where

$$\begin{aligned} \dot{x}_c &= \frac{dx_c}{dt}, & \ddot{x}_c &= \frac{d^2x_c}{dt^2}, & \omega^2 &= \beta B, \\ d_1 &= \gamma B, & d_2 &= \alpha(\lambda - a_1 r_0), & d_3 &= -3\alpha Q a_3, \\ e_n &= -\alpha a_1 r_n, & g_n &= \alpha a_1 r_n \omega_n, & h_n &= \alpha \omega_n / \sqrt{a_0^2 r_n^2 + D^2(0) s_n^2}, \\ \bar{\varphi}_n &= \theta_n + \pi/2, & \bar{\psi}_n &= \arccos\left(a_0 r_n / \sqrt{a_0^2 r_n^2 + D^2(0) s_n^2}\right) + \theta_n + \pi/2. \end{aligned}$$

The problem (14) is a weakly forced nonlinear oscillation problem (Guckenheimer and Holmes [5]). Our main effort next is to study the solution behavior of equation (14) when

$$(15) \quad \omega_k - \omega = \sigma \varepsilon + O(\varepsilon^2)$$

for some integer k . If condition (15) is satisfied, then we say that the system (14) is at the *near resonant state*. It is this resonance of the system driven by the external forcing of the harmonic $\cos(\omega_k t - \theta_k)$ that yields an instability. This instability in turn implies that the solution does not always continuously depend on the parameter of the external forcing.

3. Oscillatory solution of (14) and its stability. In this section we will use the multiple scales method (Nayfeh [7, 8]) to find an approximate oscillatory solution of equation (14). Let

$$T_0 = t, \quad T_1 = \varepsilon t, \quad x_c = x_c(T_0, T_1, \varepsilon).$$

Then

$$\begin{aligned} \dot{x}_c &= x_{cT_0} + \varepsilon x_{cT_1}, & \ddot{x}_c &= x_{cT_0T_0} + 2\varepsilon x_{cT_0T_1} + \varepsilon^2 x_{cT_1T_1}, \\ \omega_k t &= (\omega + \sigma \varepsilon)t = \omega T_0 + \sigma T_1 \end{aligned}$$

where $x_{cT_0} = \partial x_c / \partial T_0, x_{cT_0T_1} = \partial^2 x_c / (\partial T_0 \partial T_1)$, etc.

Assume that x_c has an asymptotic expansion of the form

$$(16) \quad x_c = x^{(0)}(T_0, T_1) + \varepsilon x^{(1)}(T_0, T_1) + \varepsilon^2 x^{(2)}(T_0, T_1) + \dots$$

Substituting (16) into (14) and assembling the terms according to the powers of ε , we obtain a differential equation for each order.

Order ε^0 :

$$(17) \quad x_{T_0 T_0}^{(0)} + \omega^2 x^{(0)} = d_1.$$

Order ε^1 :

$$(18) \quad \begin{aligned} x_{T_0 T_0}^{(1)} + \omega^2 x^{(1)} = & -2x_{T_0 T_1}^{(0)} + (d_2 + d_3(x^{(0)})^2)x_{T_0}^{(0)} \\ & + x_{T_0}^{(0)} \sum_{n=0}^{\infty} e_n \cos(\omega_n t - \theta_n) \\ & + x^{(0)} \sum_{n=0}^{\infty} g_n \cos(\omega_n t - \bar{\varphi}_n) \\ & + \sum_{n=0}^{\infty} h_n \cos(\omega_n t - \bar{\psi}_n). \end{aligned}$$

The order ε^2 and the other higher order terms are omitted.

The general solution of (17) is

$$(19) \quad x^{(0)} = A(T_1) \exp(i\omega T_0) + d_1/\omega^2 + \text{c.c.}$$

where A is a complex valued function of T_1 and c.c. stands for complex conjugate. By (19), equation (18) can be written as

$$\begin{aligned} x_{T_0 T_0}^{(1)} + \omega^2 x^{(1)} = & [-2i\omega A' + id_2\omega A + i\omega A(|A|^2 + d_1^2/\omega^4) d_3 \\ & + g_0 A \cos \bar{\varphi}_0 + \frac{1}{2} h_k \exp(i\sigma T_1 - i\bar{\psi}_k)] \exp(i\omega T_0) \\ & + \text{nonresonant terms} + \text{higher order terms} + \text{c.c.} \end{aligned}$$

where $A' = dA/dT_1$. To eliminate the secular term, the coefficient of $\exp(i\omega T_0)$ must be set to zero. This yields a differential equation for the complex valued function A :

$$(20) \quad \begin{aligned} A' + (-d_2/2 - d_3 d_1^2/\omega^4 + ig_0 \cos \varphi_0/(2\omega))A - (d_3/2)|A|^2 A \\ = -(i/4\omega)h_k \exp(i\sigma T_1 - i\bar{\psi}_k). \end{aligned}$$

Let A be expressed in exponential form

$$(21) \quad A(T_1) = \rho(T_1) \exp(i\varphi(T_1))$$

where $\rho(T_1)$ and $\varphi(T_1)$ are real valued functions of T_1 , and ρ is nonnegative. Then

$$A'(T_1) = [\rho'(T_1) + i\varphi'(T_1)\rho(T_1)] \exp(i\varphi(T_1)).$$

Substitution of this formula and equation (21) into equation (20) results in

$$(22) \quad \rho' + i\varphi'\rho + (-d_2/2 - d_3d_1^2/\omega^4 + ig_0 \cos \bar{\varphi}_0/(2\omega))\rho - (d_3/2)\rho^3 \\ = -(i/4\omega)h_k \exp(i(\sigma T_1 - \bar{\psi}_k - \varphi)).$$

We separate the complex valued equation (22) into its real and imaginary parts and obtain two real valued coupled differential equations for ρ and φ

$$(23) \quad \rho' - (d_2/2 + d_3d_1^2/\omega^4)\rho - (d_3/2)\rho^3 = (h_k/4\omega) \sin(\sigma T_1 - \bar{\psi}_k - \varphi),$$

$$(24) \quad \rho\varphi' + (g_0 \cos \bar{\varphi}_0/2\omega)\rho = -(1/4\omega)h_k \cos(\sigma T_1 - \bar{\psi}_k - \varphi).$$

Actually equations (23) and (24) can be changed into an autonomous system by the following transform

$$(25) \quad \rho = \rho,$$

$$(26) \quad \theta = \sigma T_1 - \bar{\psi}_k - \varphi.$$

Then equations (23) and (24) become

$$(27) \quad \rho' - (d_2/2 + d_3d_1^2/\omega^4)\rho - (d_3/2)\rho^3 = (h_k/4\omega) \sin \theta,$$

$$(28) \quad \rho\theta' - (g_0 \cos \bar{\varphi}_0/2\omega)\rho - \sigma\rho = (h_k/4\omega) \cos \theta.$$

If the oscillatory solution (19) is steady (i.e., the amplitude of the oscillatory solution (12) does not depend on T_1), then $\rho' = \theta' = 0$. Hence, for the case of the steady state,

$$(29) \quad (d_2/2 + d_3d_1^2/\omega^4)\rho + (d_3/2)\rho^3 = -(h_k/4\omega) \sin \theta,$$

$$(30) \quad (g_0 \cos \bar{\varphi}_0/2\omega)\rho + \sigma\rho = -(h_k/4\omega) \cos \theta.$$

To obtain a relation between the oscillation amplitude ρ of the toxic front and the amplitude of the external forcing h_k , we square (29) and (30) and add the resulting equations together. The sum is

$$(31) \quad \left[\left(\frac{d_2}{2} + \frac{d_3 d_1^2}{\omega^4} + \frac{d_3}{2} \rho^2 \right)^2 + \left(\frac{g_0 \cos \bar{\varphi}_0}{2\omega} + \sigma \right)^2 \right] \rho^2 = \left(\frac{h_k}{4\omega} \right)^2.$$

From (31), we see that ρ is a multiple valued function of h_k . This implies that for a given external forcing the toxic front may have more than one steady oscillation state, each of which is of different amplitude. The relation between ρ and h_k given by (31) is represented by Figure 3. The curve ρ versus h_k is called an *operating curve*, denoted by Γ . Every point on the operating curve Γ corresponds to an approximate solution of (14):

$$(32) \quad x_c(t) = d_1/\omega^2 + 2\rho \cos(\omega t + \varepsilon\sigma t - \bar{\psi}_k - c) + O(\varepsilon)$$

where ρ is determined by (31), and $\bar{\psi}_k$ and θ are constants.

Next we consider the stability of the solution (32). This is a question of whether a small perturbation of h_k will cause a large change in ρ . If it does, this solution is unstable. Otherwise, the solution is stable.

Let ρ_0 and α_0 be a steady state solution of equations (27) and (28). Then $\rho = \rho_0$ and $\theta = \theta_0$ satisfy (29) and (30). Suppose that small perturbations $\delta\rho$ and $\delta\theta$ are added to ρ_0 and θ_0 , respectively. Namely, in equations (27) and (28), let

$$(33) \quad \rho = \rho_0 + \delta\rho,$$

$$(34) \quad \theta = \theta_0 + \delta\theta.$$

Substituting equations (33) and (34) into equations (27) and (28) and linearizing the resulting equations about (ρ_0, θ_0) , we obtain that

$$(35) \quad \begin{pmatrix} \delta\rho \\ \delta\theta \end{pmatrix}' = M \begin{pmatrix} \delta\rho \\ \delta\theta \end{pmatrix}$$

where

$$(36) \quad M = \begin{pmatrix} d_2/2 + d_3 d_1^2/\omega^4 + 3d_3 \rho_0^2/2 & h_k \cos \theta_0/(4\omega) \\ g_0 \cos \bar{\varphi}_0/(2\omega) + \sigma & -h_k \sin \theta_0/(4\omega) \end{pmatrix}$$

and $(\sin \theta_0, \cos \theta_0)$ in the matrix M is determined by (29) and (30). Since d_2 and d_3 are both negative, by the Hurwitz method (Leipholz [6]) on a dynamical system of two freedoms (35) is linearly unstable if and only if

$$(37) \quad \det(M) < 0.$$

In this case, if we let $\delta\rho \propto e^{\lambda t}$, $\delta\theta \propto e^{\lambda t}$, then $\operatorname{Re}(\lambda) > 0$. Otherwise, ($\det(M) \geq 0$), the system (35) is linearly stable (i.e., $\operatorname{Re}(\lambda) \leq 0$).

By using (29) and (30), $\det(M)$ can be easily evaluated as

$$(38) \quad \det(M) = \left[\left(\frac{d_2}{2} + \frac{d_3 d_1^2}{\omega^4} + \frac{3d_3}{2} \rho_0^2 \right) \left(\frac{d_2}{2} + \frac{d_3 d_1^2}{\omega^4} + \frac{d_3}{2} \rho_0^2 \right) + \left(\frac{g_0 \cos \bar{\varphi}_0}{2\omega} + \sigma \right)^2 \right] \rho.$$

Now let us go back to equation (31) and consider the structure of the operating curve $\Gamma: \rho$ versus h_k . It turns out that the slope of the curve Γ is closely related to $\det(M)$. Actually, this is what we expected in order to establish the slope stability theorem mentioned in Section 1.

The quantity h_k^2 is a single valued smooth function of ρ^2 determined by (31). Taking a derivative of both sides of (31) with respect to ρ^2 and letting $\rho = \rho_0$, we obtain a surprisingly nice relationship

$$(39) \quad \rho \frac{d(h_k^2)}{d(\rho^2)} = (4\omega)^2 \det(M).$$

Thus $d(h_k^2)/d(\rho^2)$ and $\det(M)$ are of the same sign. This crucial relationship implies the slope stability theorem:

Theorem. *If $d\rho/dh_k \geq 0$ (< 0), then the primary oscillatory toxic front given by (32) is linearly stable (unstable).*

Referring to Figure 3, the BC section corresponds to unstable solutions since the BC section has negative slope. However, the AB section and the CD section correspond to stable solutions since those two sections have positive slope. By this operating curve and due to the

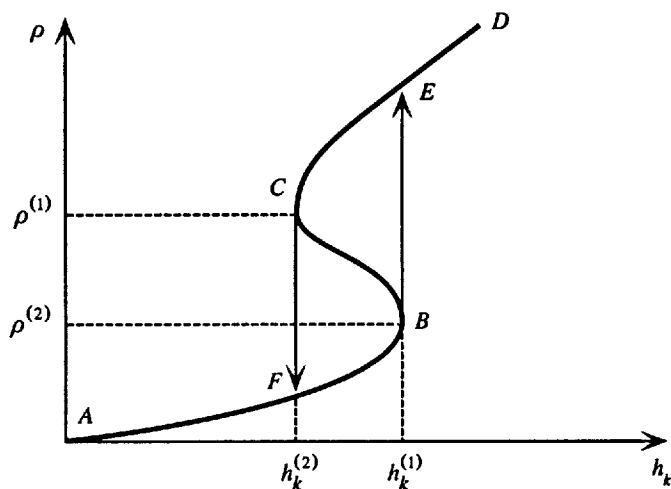


FIGURE 3. Operating curve Γ determined by equation (31):

$$h_k^{(1,2)} = 4|\omega| \left(\frac{g_0 \cos \bar{\varphi}_0}{2\omega} + \sigma \right) \left[- \left(\frac{d_2}{2} + \frac{d_3 d_1^2}{\omega^4} \right) \pm \left(\frac{g_0 \cos \bar{\varphi}_0}{2\omega} + \sigma \right) \right]^{1/2},$$

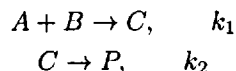
$$\rho^{(1,2)} = \left[- \left(\frac{d_2}{2} + \frac{d_3 d_1^2}{\omega^4} \right) \pm \left(\frac{g_0 \cos \bar{\varphi}_0}{2\omega} + \sigma \right) \right]^{1/2}.$$

unstable section BC , a jump in the oscillation amplitude ρ will occur if we change h_k around the bifurcation points B and C . If the present state is on the section AB and h_k increases gradually beyond B , then the oscillation amplitude ρ will jump up to point E . Conversely, if the present state is on the section CD and h_k decreases gradually beyond C , then the oscillation amplitude will jump down to point F .

4. Discussions and concluding remarks. Chemical oscillations—oscillations of electrical potential or color of the solution in a tank while the reaction conditions remain unchanged—were first reported in 1921 and met with skepticism. Nowadays, chemical oscillations can be demonstrated in classrooms for students. The theory of nonequilib-

rium thermodynamics shows that chemical oscillations are consistent with physical laws.

The more interesting phenomenon is the birhythmicity (coexistence of two stable stationary states) of the chemical oscillations. This phenomenon can be observed in a continuous-flow stirred tank reactor, called CSTR for short, as shown in Figure 4. When conducting the experiment, the chemical contents and surrounding temperature in the reactor are maintained unchanged. The only change is the flow rate from tanks A, B and C. As described in [3], if we consider a simple reaction



in a CSTR, the reaction rate equations in the CSTR can be described by

$$\begin{aligned} dA/dt &= -k_1AB + k_0(A_0 - A) + D_A\Delta A, \\ dB/dt &= -k_1AB + k_0(B_0 - B) + D_B\Delta B, \\ dC/dt &= k_1AB - k_2C + k_0(C_0 - C) + D_C\Delta C. \end{aligned}$$

Here A , B and C are the concentrations of the chemical solutions A , B , and C in the reactor, and A_0 , B_0 and C_0 are the concentrations of these fluids in the reservoirs, D_A , D_B and D_C are the diffusion coefficients in the reactor, Δ is the three-dimensional Laplacian operator, and k_0 is referred to as the flow rate.

Figure 5 shows the experimental birhythmicity results in a chlorite-bromate-iodide system due to Alamgir and Epstein reported in [3, 1]. At the times indicated by the arrows, the flow rate k_0 is changed. In Figure 5, the horizontal axis time [4 min.] and the vertical axis is electrical potential (Pt electrode vs. Hg/Hg₂SO₄ reference electrode) [100 mv]. The flow rate k_0 is changed from 6.58×10^3 to 7.14×10^3 , to 7.26×10^3 , back to 7.14×10^3 , and finally to 6.09×10^3 [sec⁻¹]. The reaction temperature $T = 25^\circ\text{C}$ is maintained constant. The four chemical concentrations in the reservoirs are also maintained constants: $[\text{I}^-]_0 = 6.5 \times 10^{-4}$, $[\text{BrO}_3^-]_0 = 2.5 \times 10^{-3}$, $[\text{ClO}_2^-]_0 = 1.0 \times 10^{-4}$, $[\text{H}_2\text{SO}_4]_0 = 0.75$ [mole]. We note that both oscillatory states A and B are stable and correspond to the same parameters, $[\text{I}^-]_0$, $[\text{BrO}_3^-]_0$, $[\text{ClO}_2^-]_0$, $[\text{H}_2\text{SO}_4]_0$, k_0 and T . This is the birhythmicity (co-existence of two stable stationary oscillation states). At any given moment, as for what state the system is at depends on the past history of the

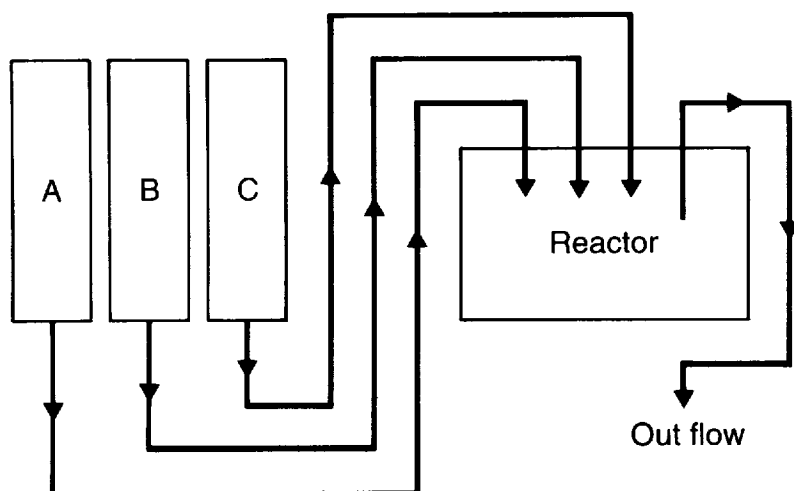


FIGURE 4. Continuous-flow stirred tank reactor.

experiment. To make the transition of the system from one state to the other is subtle and varies from system to system. For the chlorite-bromate-iodide system presented in Figure 5, the transition was made by changing the flow rate and a one-time perturbation with oxidants (e.g., bromate, chlorite and permanganate).

The nature of the above chemical oscillations are reflected in the toxic front motion in our model. The advance and retreat of the toxic front of reproductive chemicals in a slender trough under a periodic external disturbance exhibit the birhythmicity. This external disturbance models periodic variation in the surrounding temperature or periodic injection of the toxic mass into the trough. The governing equation of the problem is the equation of conservation of the toxic mass. The condition of the toxic front is a differential delay equation which exhibits a time lag in the response of the toxic front to the variation of the external disturbance. Nonlinearity is introduced into the system by the reproduction mechanism of the toxic chemical. The globally averaged governing equation over the spatial dimension and the condition of the toxic front result in a second order nonlinear ordinary differential equation for $x_c(t)$ with a weak forcing (cf. equation (14)). When conditions put the system near critical (cf. equation (13)) and near resonant (cf. equation (15)), asymptotic oscillatory solutions of

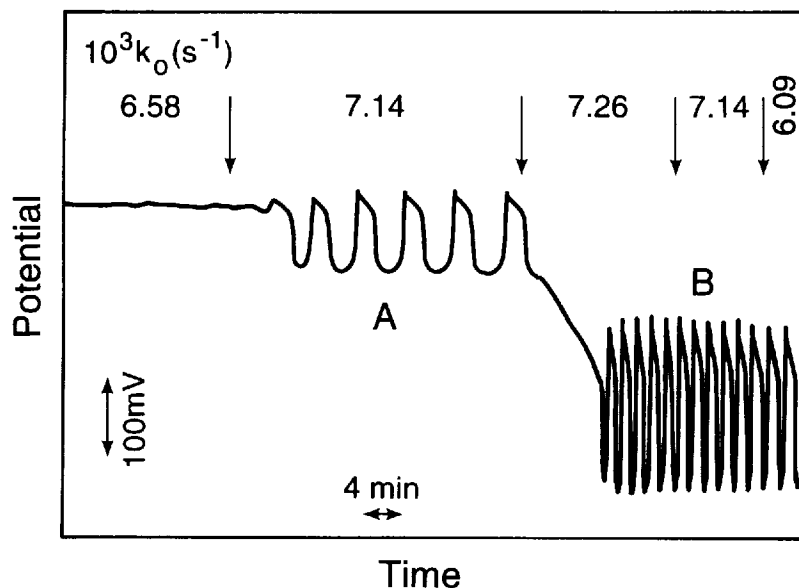


FIGURE 5. Birhythmicity in the chlorite-bromate-iodide system. The horizontal axis is time [4 minutes] and the vertical axis is electrical potential (Pt electrode versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode) [100 mv]. At the times indicated by the arrows, the flow rate k_0 is changed. The flow rate k_0 is changed from 6.58×10^3 , to 7.14×10^3 , to 7.26×10^3 , back to 7.14×10^3 , and finally to 6.09×10^3 [sec^{-1}]. The reaction temperature $T = 25^\circ \text{C}$ is maintained constant. The four chemical concentrations in the reservoirs are also maintained constants: $[\text{I}^-]_0 = 6.5 \times 10^{-4}$, $[\text{BrO}_3^-]_0 = 2.5 \times 10^{-3}$, $[\text{ClO}_2^-]_0 = 1.0 \times 10^{-4}$, $[\text{H}_2\text{SO}_4]_0 = 0.75$ [mole]. [Reproduced with permission from the American Chemical Society.]

(14) have been found by the multiple scales method (cf. equation (32)). A slope stability theorem has been proved. Due to the instability, there exist two bifurcation points. At those points, an infinitesimal perturbation of the amplitude of the near resonant harmonic forcing can result in a large jump in the oscillation amplitude of the toxic front. Because of the birhythmicity, it is desirable to keep the toxic front at the smaller stable oscillation state in order to reduce the pollution effect. Therefore, for the same amount of chemical waste dump, different chemical plants may cause tremendously different pollution

results because one may happen to be at the smaller oscillation state and the other at the larger oscillation state. Thus, in theory, our results reveal a possibility to control the spreading of reactive toxic mass.

Our current model is zero dimensional (averaged one-dimensional model) and simple. Nevertheless, it provides some very interesting qualitative features. Hence, our present theory may be a guide in the study of other complex systems. Based upon this point of view, further research should be conducted on the oscillation of the toxic front in one, two or three dimensional models.

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