

On aspects of the dynamic behavior of persistent chemicals in a multimedia environment related to exposure-based hazard assessment

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Abstract The present research study focuses on the analysis and characterization of certain aspects of the dynamic behavior displayed by persistent chemicals in a multimedia environment (chemodynamics), which is jointly determined by the inherent physicochemical properties of the chemical substance under consideration, as well as underlying environmental processes such as degradation in different phases/media (soil, water and air) coupled with intermedia transport (interphase mass transfer). In particular, dynamic multimedia environmental models are considered with constant source terms describing steady chemical release/discharge rates into various environmental media of interest, and key risk-related aspects of the dynamic behavior of persistent chemicals are analyzed using perturbation theory techniques under conditions where degradation rates in different media are considerably slower than intermedia transport rates. Under the above conditions, the problem of defining physically meaningful and practical quantitative measures of overall persistence of chemicals in a multimedia environment is revisited, given its role as a key exposure-based indicator within all major chemical risk assessment frameworks, and a proof is provided

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that rigorously establishes equivalence between two important and popular persistence measures, namely the characteristic time at steady state and the inverse of the associated chemodynamics overall decay rate (slowest chemodynamic mode).

Keywords Chemical dynamics · Multimedia environmental models · Persistence · Exposure-based hazard assessment · Perturbation theory

1 Introduction

The analysis and characterization of the dynamic behavior of chemicals released into the environment (chemodynamics) assumes a central role and significance in a variety of scientific fields such as theoretical and computational chemistry, environmental chemistry, chemical process safety, chemical risk assessment, regulation of chemicals and environmental health [1–6]. Even though the methodologically traditional line of research enquiry into the environmental behavior of chemical substances places its focus on their inherent physicochemical properties and the establishment of correlations (mostly empirical in the form of qualitative or quantitative structure-to-activity relationships) with hazard-based indicators such as persistence, spatial range, bioaccumulation potential, toxicity, etc (often known as PBT assessment), the research community soon recognized that the effect of environmental factors and processes on the environmental fate, behavior and distribution of a chemical substance is equally significant and has to be explicitly taken into account in pertinent studies [1, 2, 4–6]. The study of the aforementioned combined effect of both the inherent physicochemical properties and underlying environmental processes on the chemical's behavior after its (natural, accidental or intentional) release into the environment can be undertaken within a framework of analysis that relies on an appropriate level of mathematical modeling with a varying degree of complexity and sophistication. These modeling approaches range from quantum-mechanically determined inherent key physicochemical properties and their interactions with external environmentally determined fields, to thermodynamic equilibrium models describing the chemical's partition into various environmental media/phases at equilibrium conditions, to explicit macroscopic chemodynamic models realized by compartmentalized mass-balance equations, to risk-relevant pharmacokinetic models [1–6]. It should be emphasized that the development and availability of powerful conceptual, mathematical and computational tools [1–3, 5–8] enabled the wide use of these modeling approaches not only for the advancement of purely scientific objectives, but also to inform decision-making on the policy and regulation levels. In the present study we consider multimedia environmental models as mathematical representations of the behavior of chemicals in multiple environmental media/phases (such as soil, water, air). Originally structured and introduced in a systematic and insightful manner in the pioneering work of Baughman and Lassiter [9] and Mackay [4], multimedia environmental models are typically realized through a system of mass-balance equations applied to a number of environmental compartments (referred to as “boxes”) that are often considered as well-mixed, thus simplifying their structure and enhancing their computational appeal. Multimedia environmental mod-

els explicitly capture the combined effect of the chemical's inherent physicochemical properties and environmental processes on its overall environmental behavior, distribution and fate in the presence of multiple phases by taking into account not only the degradation mechanisms of the chemical in various media, but also its intermedia transport and partitioning potential into all possible media/phases. Multimedia environmental models typically exhibit linearity due to the underlying assumption of relatively low-concentration levels of the chemicals involved, but they could vary in terms of complexity and desired accuracy ranging from purely thermodynamic equilibrium models (described by a system of coupled linear algebraic equations) to dynamic ones (known as Level IV) that capture the dynamic changes of the concentration profile of the chemical induced by the underlying coupled dynamics of degradation in different media with intermedia transport processes and partitioning [4–6]. As such, they retain a desirable element of fidelity while remaining computationally tractable for the calculation of exposure-based and effect-based indicators such as persistence, spatial range and bioaccumulation, toxicity respectively. In the present research study in particular, the model-based quantification and calculation of appropriately defined persistence measures is considered. Persistence, as the temporal extent of the presence of a chemical in the environment, is justifiably one of the most significant exposure-based hazard indicators, and represents a necessary condition for potentially adverse health and ecological effects [3,5,6]. Persistence has also been strongly correlated with the intake fraction of a chemical (the amount that enters the human body through food, air and drinking water for a given exposure level), as well as the effective dose received by the population at a given region [3,5,6]. Furthermore, persistence is often positively correlated with considerable spatial ranges, and therefore, global pollution potential [4,6]. Therefore, it is not surprising, that persistence figures eminently in all international efforts to develop scientifically sound criteria and regulatory standards based on reliable and practical methods that allow its quantitative characterization [10,11]. Using persistence as the basic criterion, chemicals have been traditionally classified, screened and often regulated on the basis of a multiple half-life approach where a chemical substance is characterized as persistent if any one of its half-lives in different media (soil, surface water, sediment, air) exceeds a certain threshold value [6,10–14]. This approach however frequently leads to a misclassification of chemicals by solely focusing on half-lives in media into which the chemical rarely partitions, while unnecessarily overlooking intermedia transport processes and partitioning patterns that significantly contribute to the chemical's fate, dynamic environmental behavior, overall decay rate and persistence [10,11]. In order to overcome the above difficulties, a multimedia environmental model could be employed in order to calculate an appropriately defined quantity that is meaningfully associated with the notion of overall persistence of a chemical in a multimedia environment and serves as a quantitative measure or index [6]. Indeed, the idea of using a multimedia environmental model to readily compute the value of a specific persistence index/measure has been pursued in a number of recent and very interesting pieces of research work (finding its way towards full adoption by the OECD and incorporation into its most recent guidelines related to risk assessment for persistent organic pollutants [6]). Recognizing the fact that using the total chemical clearance-time (the time required for the chemical's total concentration to drop below a prespecified level defined as a

percentage of its initial level at the moment of the chemical's release) as a measure of overall persistence could lead to a gross underestimation of the true persistence by failing to take into account relatively low concentration levels in a medium into which partitioning took place and degradation is fairly slow (the "tail" in the chemical clearance profile), Müller-Herold [15] rigorously derived an explicit formula for the overall decay rate of a chemical in a multimedia environment (slowest chemodynamic mode) in the limiting case where intermedia transport rates are considerably faster than the chemical's degradation rates in individual media. It should be pointed out that in this particular study, the homogeneous source-free case of chemodynamics is considered, where it is implicitly assumed that the chemical's release into the environment occurs in a pulse-like manner, and from a mathematical standpoint, there are no source-terms (or input terms) in the associated chemical dynamic equations [15]. Under the assumption of a pulse-type chemical release, the notion of equivalence width was introduced as a meaningful persistence measure and computed with the aid of source-free multimedia environmental models (the homogeneous case) with various degrees of complexity [16]. In another interesting, yet fundamentally different from a physical point of view, line of research activity, Bennett et al. [17] considered a distributed constant-source term in the multimedia model's dynamic equations (a constant input term that introduces a non-homogeneous mathematical structure) to represent a chemical release scenario under constant/steady rate into possibly multiple media, and considered the characteristic time at steady state as an appropriate measure of overall persistence under the particular conditions considered. In light of the above considerations, the present research study examines the problem of analyzing and characterizing aspects of the dynamic behavior of a persistent chemical that is steadily released into a multimedia environment (or within a certain time-interval considerably larger than the underlying slowest time-constant or dynamic mode) using a dynamic (Level IV) N -dimensional multimedia environmental modeling framework with a constant source-term and non-homogeneous structure similar to the 2- and 3-dimensional ones presented in [17]. Motivated by the analytical perturbatory framework developed in the homogeneous case [15], the dynamic behavior of a persistent chemical is examined in the above non-homogeneous case under similar conditions, namely degradation rates in different media being considerably slower than intermedia transport rates (an assumption that conforms well with the focus being placed on persistent chemicals). Within this framework, the intuitively expected displacement from the thermodynamic equilibrium concentration values displayed by the chemical's concentration profiles in the various environmental media due to the constant source-terms in the non-homogeneous case is explicitly derived. Furthermore, equivalence is rigorously established between the two important and popular persistence measures mentioned earlier, namely the characteristic time at steady state and the inverse of the associated chemodynamics overall decay rate (slowest chemodynamic mode).

The present paper is organized as follows: Sect. 2 contains the requisite conceptual and mathematical preliminaries, followed by Sect. 3 where the paper's main results are presented. Finally, a few concluding remarks are provided in Sect. 4.

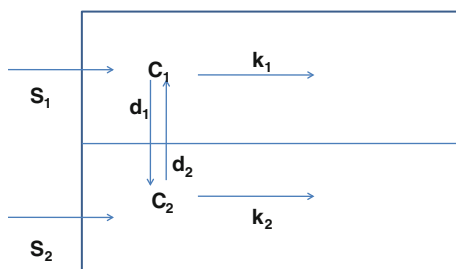
2 Conceptual and mathematical preliminaries

Before proceeding with the presentation of the paper's main results associated with the dynamic behavior of persistent chemicals in a generic multimedia environment comprised of N media/phases/compartments, it would be methodologically appropriate to first consider the dynamic behavior of a chemical substance in a two-compartment or two-box (2-dimensional) environmental model using a mathematically simpler framework of analysis. In particular, a non-homogeneous 2-dimensional dynamic environmental model is considered, that is realized through standard unsteady state mass-balance equations for two phases/compartments/boxes of equal volume (this assumption is made solely for simplicity reasons and will be relaxed in the sequel) resulting in the following mathematical representation:

$$\begin{aligned} \frac{dc_1}{dt} &= -k_1c_1 - d_1c_1 + d_2c_2 + S_1 \\ \frac{dc_2}{dt} &= -k_2c_2 - d_2c_2 + d_1c_1 + S_2 \end{aligned} \quad (1)$$

where (adopting a similar notational framework to the one presented in the homogeneous case [15]) c_1, c_2 denote the chemical's concentration in compartments/boxes 1 and 2 respectively, t is the time variable, k_1, k_2 are the respective degradation rate constants, d_1, d_2 the associated intermedia transport rates (also known as material exchange parameters) and S_1, S_2 constant source (or input) terms in the dynamic Eq. (1) representing the steady state rate of the chemical's release into media 1 and 2, respectively (a simple illustrative schematic is provided in Fig. 1). Let $K_{12} = \frac{d_1}{d_2} = \frac{c_{2,eq}}{c_{1,eq}}$ be the partition constant and $c_{1,eq}, c_{2,eq}$ the equilibrium concentrations due to intermedia transport and mass transfer between the two media. Please notice that the latter represent concentrations at thermodynamic equilibrium conditions in the absence of degradation and constant release rates of the chemical into the two media under consideration. As in the homogeneous case [15], let us also introduce a mathematically convenient scalar parameter: $d \equiv d_2 = \frac{d_1}{K_{12}}$ which represents a measure of the speed of material exchange between the two environmental compartments. Under the above notation, the chemodynamic model (1) takes the following compact form:

Fig. 1 Structure of the two-compartment model (1) encompassing intermedia transport and material exchange, degradation, as well as steady chemical release rates into two environmental media



$$\frac{dc}{dt} = Ac + S \tag{2}$$

where $c = [c_1, c_2]^T$ is the vector of concentrations of the chemical in the two environmental compartments (we use the superscript T to denote the transpose of a vector or matrix throughout the paper), t is the time variable, $S = [S_1, S_2]^T$ the constant source terms input vector associated with the chemical’s steady release rates into the two compartments and

$$A = \begin{bmatrix} -(k_1 + K_{12}d) & d \\ K_{12}d & -(k_2 + d) \end{bmatrix}$$

It can be easily shown, that the above characteristic matrix A of the non-homogeneous chemodynamics (1) is Hurwitz, i.e., has two stable (negative) eigenvalues [18, 19]. As a result, the concentrations of the chemical in media 1 and 2 will asymptotically attain their respective steady state values $c_s = [c_{1,s}, c_{2,s}]^T$ computed as follows:

$$0 = Ac_s + S \implies c_s = -A^{-1}S \tag{3}$$

Notice, that since A is Hurwitz, A^{-1} always exists and $c_s = [c_{1,s}, c_{2,s}]^T$ is uniquely defined through (3). Omitting the intermediate algebraic steps for economy of space, the following explicit expressions for the chemical’s steady state concentration values in media 1 and 2 can be readily derived:

$$\begin{aligned} c_{1,s} &= \frac{d + k_2}{(K_{12}k_2 + k_1)d + k_1k_2} S_1 + \frac{d}{(K_{12}k_2 + k_1)d + k_1k_2} S_2 \\ c_{2,s} &= \frac{K_{12}d}{(K_{12}k_2 + k_1)d + k_1k_2} S_1 + \frac{K_{12}d + k_1}{(K_{12}k_2 + k_1)d + k_1k_2} S_2 \end{aligned} \tag{4}$$

Let us now restrict the analysis within the class of persistent chemicals, and mathematically within the regime of rather fast intermedia transport rates ($d \rightarrow \infty$) compared to degradation rates in individual media. Under the above conditions, as $d \rightarrow \infty$, Eq. (4) give:

$$\begin{aligned} c_{1,s} &= \frac{S_1}{K_{12}k_2 + k_1} + \frac{S_2}{K_{12}k_2 + k_1} = \frac{S_1 + S_2}{\left(\frac{c_{2,eq}}{c_{1,eq}}\right)k_2 + k_1} = \frac{(S_1 + S_2)c_{1,eq}}{k_1c_{1,eq} + k_2c_{2,eq}} \\ c_{2,s} &= \frac{K_{12}S_1}{K_{12}k_2 + k_1} + \frac{K_{12}S_2}{K_{12}k_2 + k_1} = \frac{\left(\frac{c_{2,eq}}{c_{1,eq}}\right)(S_1 + S_2)}{\left(\frac{c_{2,eq}}{c_{1,eq}}\right)k_2 + k_1} = \frac{(S_1 + S_2)c_{2,eq}}{k_1c_{1,eq} + k_2c_{2,eq}} \end{aligned} \tag{5}$$

Please notice that Eq. (5) explicitly capture the intuitively expected displacement of the chemical’s concentration values from equilibrium due to the constant source terms

appearing in the non-homogeneous chemodynamics (1). Furthermore, the steady state concentration values in (5) are critically related to the exposure potential of human populations and/or ecosystems to the chemical under consideration, and thus, to potentially adverse public health and environmental effects [17]. Indeed, within current regulatory frameworks for the management of chemical risk, model-based predicted environmental concentrations (PECs) play a key role in exposure assessment and risk characterization [3, 5, 6]. Equations (5) also enable the explicit calculation of the characteristic time τ_{ss} and the associated decay rate r_{ss} at steady state originally introduced in [17]:

$$\begin{aligned} r_{ss} &\equiv \frac{k_1 c_{1,s} + k_2 c_{2,s}}{c_{1,s} + c_{2,s}} \\ \tau_{ss} &\equiv \frac{1}{r_{ss}} = \frac{c_{1,s} + c_{2,s}}{k_1 c_{1,s} + k_2 c_{2,s}} \end{aligned} \quad (6)$$

Notice that τ_{ss} is a quantity that is amenable to an easy calculation since it explicitly involves the chemical's degradation rates in the two media as well as the corresponding steady state concentration values (that are in principle measurable or amenable to model-based calculation). It should be pointed out that τ_{ss} represents a quite reliable measure of persistence of chemicals in a multimedia environment [17], and, along with spatial range, represent the key exposure-based hazard indicators in all major chemical risk assessment frameworks and management protocols [6]. In light of Eq. (5), τ_{ss} and r_{ss} can be rewritten as follows:

$$\begin{aligned} r_{ss} &= \frac{\frac{(S_1 + S_2)c_{1,eq}}{c_{1,eq}k_1 + c_{2,eq}k_2}k_1 + \frac{(S_1 + S_2)c_{2,eq}}{c_{1,eq}k_1 + c_{2,eq}k_2}k_2}{\frac{(S_1 + S_2)(c_{1,eq} + c_{2,eq})}{c_{1,eq}k_1 + c_{2,eq}k_2}} = \frac{k_1 c_{1,eq} + k_2 c_{2,eq}}{c_{1,eq} + c_{2,eq}} \\ \tau_{ss} &= \frac{c_{1,eq} + c_{2,eq}}{k_1 c_{1,eq} + k_2 c_{2,eq}} \end{aligned} \quad (7)$$

Following a technically different path of analysis, the notion of the slowest eigenmode r_{sl} which is mathematically represented by the eigenvalue of the chemodynamics characteristic matrix A with the numerically smallest modulus (frequently used as a measure of the system's characteristic time inverse in dynamic systems theory [18, 20]) was introduced as another reliable measure of persistence of chemicals in a multimedia environment [15]. In particular, it was rigorously calculated in the $d \rightarrow \infty$ case and found to be given by the following expression [15]:

$$\begin{aligned} r_{sl} &\equiv \frac{k_1 c_{1,eq} + k_2 c_{2,eq}}{c_{1,eq} + c_{2,eq}} \\ \tau_{sl} &\equiv \frac{1}{r_{sl}} = \frac{c_{1,eq} + c_{2,eq}}{k_1 c_{1,eq} + k_2 c_{2,eq}} \end{aligned} \quad (8)$$

where τ_{sl} is the associated time-constant proposed as a reliable persistence measure [15]. Besides its theoretically rigorous roots, please notice the intuitive appeal and practical usefulness of r_{sl} which can be viewed as an “effective” decay rate that represents a weighted-average of the chemical’s decay rates in the two environmental compartments with weights related to the respective equilibrium concentration values. Finally, notice the equivalence of the two measures of persistence $\tau_{ss} = \tau_{sl}$ (Eqs. 7, 8) under the stated conditions, namely relatively fast intermedia transport rates compared to natural degradation rates in various environmental media, that characterize broad classes of persistent chemicals [15].

3 Main results

Let us now consider generic N -dimensional dynamic non-homogeneous (with constant source/input terms) multimedia environmental models comprised of a system of N linear differential equations representing standard unsteady state mass-balance equations for the presence of the chemical under consideration in N well-mixed environmental compartments/boxes of unequal volumes (adopting a similar notational framework to the one presented in the homogeneous case [15]):

$$\frac{dc}{dt} = Ac + S = -\left(K - \tilde{D}\right)c + S \quad (9)$$

where $c = [c_1, \dots, c_N]^T$ is the vector of concentrations of the chemical in the N environmental compartments, t is the time variable, $S = [S_1, \dots, S_N]^T$ the constant source terms input vector associated with the chemical’s steady release rates into the N compartments, $A = -K + \tilde{D}$ is the $N \times N$ system’s characteristic matrix comprised of the diagonal matrix

$$K = \text{diag}\{k_1, \dots, k_N\} = \begin{bmatrix} k_1 & 0 & \dots & 0 \\ 0 & k_2 & \dots & 0 \\ \cdot & \cdot & \dots & \cdot \\ 0 & 0 & \dots & k_N \end{bmatrix}$$

whose diagonal elements are the individual degradation rate constants k_i ($i = 1, \dots, N$) in the N compartments under consideration, and a matrix

$$\tilde{D} = \begin{bmatrix} \tilde{d}_{11} & \tilde{d}_{12} & \dots & \tilde{d}_{1N} \\ \cdot & \cdot & \dots & \cdot \\ \tilde{d}_{N1} & \tilde{d}_{N2} & \dots & \tilde{d}_{NN} \end{bmatrix}$$

whose entries \tilde{d}_{ij} ($i, j = 1, \dots, N$) describe the intermedia transport processes (material exchange between the various media/phases) and uniquely determine the thermodynamic equilibrium concentrations between the various compartments in the absence of degradation and steady release rates of the chemical into them [15]. It can be shown, that in the case of first-order chemodynamics (9), matrix \tilde{D} is endowed with a specific

mathematical structure reminiscent of the Peron-Frobenius one [15, 19]. In particular, A is a Hurwitz matrix (one with stable eigenvalues; [18, 19]) and \tilde{D} has negative diagonal elements, non-negative off-diagonal elements as well as the following properties [15]:

1. \tilde{D} has only non-positive eigenvalues
2. Zero is a non-degenerate eigenvalue of \tilde{D} with corresponding eigenvector the vector of equilibrium concentration values $c_{eq} = [c_{1,eq}, \dots, c_{N,eq}]^T$:

$$\tilde{D}c_{eq} = 0 \quad (10)$$

3. \tilde{D} satisfies the following “balance condition”:

$$\tilde{d}_{ij}c_{j,eq}V_i = \tilde{d}_{ji}c_{i,eq}V_j \quad (11)$$

with respect to the above equilibrium eigenvector c_{eq} , where V_i is the volume of media/compartment i and \tilde{d}_{ij} the (i, j) th element of matrix \tilde{D} ($i, j = 1, \dots, N$).

Finally, as in the two-dimensional case discussed earlier, an analogous mathematically convenient scalar parameter d can be defined that represents a measure of the speed (or rate) of intermedia material exchanges compared to degradation taking place in the various environmental media [15]:

$$d \equiv \|\tilde{D}\| \quad (12)$$

where $\|\cdot\|$ is any appropriately defined matrix norm. Furthermore, a new matrix D can be defined:

$$D \equiv \frac{1}{d}\tilde{D} = \frac{1}{\|\tilde{D}\|}\tilde{D} \quad (13)$$

whose norm is obviously 1: $\|D\| = 1$. Notice that matrices D, \tilde{D} have the same equilibrium eigenvector: $\tilde{D}c_{eq} = Dc_{eq} = 0$ (however, they have, in general, different eigenspectra). Given the non-homogeneous chemodynamics (9) and its specific mathematical structure presented above, we are now in a position to present the paper's main results.

Aiming at a mathematically convenient symmetrization of matrix \tilde{D} as in the homogeneous case [15], the following diagonal transformation matrix \mathcal{C} is introduced:

$$\mathcal{C} = \text{diag} \left\{ \left(\frac{c_{1,eq}}{V_1} \right)^{1/2}, \dots, \left(\frac{c_{N,eq}}{V_N} \right)^{1/2} \right\}$$

$$= \begin{bmatrix} \left(\frac{c_{1,eq}}{V_1}\right)^{1/2} & 0 & \dots & 0 \\ 0 & \left(\frac{c_{2,eq}}{V_2}\right)^{1/2} & \dots & 0 \\ \cdot & \cdot & \dots & \cdot \\ 0 & 0 & \dots & \left(\frac{c_{N,eq}}{V_N}\right)^{1/2} \end{bmatrix} \tag{14}$$

under which the original concentration vector c is transformed as follows:

$$\bar{c} = C^{-1}c \implies c = C\bar{c} \tag{15}$$

and the associated non-homogeneous chemodynamic equations (9) are transformed as shown below:

$$\frac{dC\bar{c}}{dt} = AC\bar{c} + S \implies \frac{d\bar{c}}{dt} = (C^{-1}AC)\bar{c} + C^{-1}S = \bar{A}\bar{c} + \bar{S} \tag{16}$$

where $\bar{A} = C^{-1}AC$ and $\bar{S} = C^{-1}S$. Furthermore, one easily obtains:

$$\bar{A} = C^{-1}AC = -C^{-1}(K - \tilde{D})C = -C^{-1}KC + C^{-1}\tilde{D}C = -K + \tilde{\Delta} \tag{17}$$

with $\tilde{\Delta} = C^{-1}\tilde{D}C$. Notice that K remains invariant under the above transformation and $\tilde{\Delta}$ becomes symmetrical due to the balance condition (11). Notice also that:

$$\bar{A} = -K + \tilde{\Delta} = -K + C^{-1}\tilde{D}C = -K + dC^{-1}DC = -K + d\Delta \tag{18}$$

where $\Delta = \frac{1}{d}\tilde{\Delta} = C^{-1}DC$. The non-homogeneous chemodynamics (16) expressed in the new transformed coordinates \bar{c} can be rewritten as follows:

$$\frac{d\bar{c}}{dt} = -(K - d\Delta)\bar{c} + \bar{S} \tag{19}$$

with the transformed equilibrium concentration vector now given by:

$$\bar{c}_{eq} = C^{-1}c_{eq} = \begin{bmatrix} (c_{1,eq}V_1)^{1/2} & 0 & \dots & 0 \\ 0 & (c_{2,eq}V_2)^{1/2} & \dots & 0 \\ \cdot & \cdot & \dots & \cdot \\ 0 & 0 & \dots & (c_{N,eq}V_N)^{1/2} \end{bmatrix} \tag{20}$$

Let us denote the symmetric positive-definite matrices: $\Lambda \equiv K - d\Delta$ and $\Lambda' \equiv -\Delta + \frac{1}{d}K$. Notice that matrices Λ, Λ' share the same set of eigenvectors $\{\gamma_i\}$

($i = 1, \dots, N$), and eigenspectra $\{\lambda_i\}, \{\lambda'_i\}$ respectively that are related through a multiplicative constant: $\lambda'_i = \frac{1}{d}\lambda_i$. Therefore:

$$\begin{aligned}\Lambda \gamma_i &= \lambda_i \gamma_i \\ \Lambda' \gamma_i &= \lambda'_i \gamma_i\end{aligned}\quad (21)$$

for $i = 1, \dots, N$. Furthermore, there is a unique vector Γ_s such that:

$$\Lambda \Gamma_s = \bar{S} \quad (22)$$

Notice that the transformed vector $\bar{c}_s = C^{-1}c_s$ of the steady state concentration values satisfies: $\bar{A}\bar{c}_s + \bar{S} = 0 = -\Lambda\bar{c}_s + \bar{S} \Rightarrow \Lambda\bar{c}_s = \bar{S}$, and therefore it coincides with $\Gamma_s : \bar{c}_s = \Gamma_s$ (Notice that Λ is an invertible matrix). Since Λ is symmetric and positive-definite, the set of eigenvectors $\{\gamma_i\}$ ($i = 1, \dots, N$) represent a basis in the associated R^N vector space, and therefore, the following expansions are uniquely defined:

$$\begin{aligned}\bar{c}_s = \Gamma_s &= \sum_{i=1}^N \frac{\langle \gamma_i | \Gamma_s \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i = \sum_{i=1}^N \frac{\langle \gamma_i | \bar{c}_s \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i \\ \bar{S} &= \sum_{i=1}^N \frac{\langle \gamma_i | \bar{S} \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i\end{aligned}\quad (23)$$

where $\langle \cdot | \cdot \rangle$ represents the Dirac-notation used for the standard inner product operation associated with the R^N vector space. In light of the above equations one obtains:

$$\begin{aligned}\Lambda \bar{c}_s = \Lambda \Gamma_s = \bar{S} &\implies \sum_{i=1}^N \frac{\langle \gamma_i | \bar{c}_s \rangle}{\langle \gamma_i | \gamma_i \rangle} \Lambda \gamma_i = \sum_{i=1}^N \frac{\langle \gamma_i | \bar{S} \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i \\ &\implies \langle \gamma_i | \bar{c}_s \rangle \lambda_i \gamma_i = \langle \gamma_i | \bar{S} \rangle \gamma_i \\ &\implies \langle \gamma_i | \bar{c}_s \rangle d \lambda'_i = \langle \gamma_i | \bar{S} \rangle\end{aligned}\quad (24)$$

Let us now focus on matrix $\Lambda' = \frac{1}{d}\Lambda = -\Delta + \frac{1}{d}K$, and consider the case where $d \rightarrow \infty$, namely cases where intermedia transport rates of the chemical under consideration are much faster compared to degradation rates in different media, i.e. cases of chemical persistence. As $d \rightarrow \infty$, Λ' may be viewed as a perturbed matrix comprised of an unperturbed nominal term $-\Delta$ and a perturbation term $\frac{1}{d}K$, where $\frac{1}{d}$ is a small perturbation parameter. Standard arguments from perturbation theory yield the following expansions of the eigenvectors $\{\gamma_i\}$ ($i = 1, \dots, N$) and eigenvalues $\{\lambda'_i\}$ of matrix Λ' :

$$\begin{aligned}
 \gamma_i &= \gamma_i^{(0)} + \frac{1}{d}\gamma_i^{(1)} + \frac{1}{d^2}\gamma_i^{(2)} + \dots \\
 \lambda'_i &= \lambda_i^{(0)} + \frac{1}{d}\lambda_i^{(1)} + \frac{1}{d^2}\lambda_i^{(2)} + \dots
 \end{aligned}
 \tag{25}$$

where $\gamma_i^{(0)}$ and $\lambda_i^{(0)}$ are the i th eigenvector and eigenvalue of the unperturbed part $-\Delta$, and $\gamma_i^{(n)}, \lambda_i^{(n)}$ the corresponding n th order (higher order) perturbatory corrections. Without loss of generality, let's order the eigenspectrum $\{\lambda_i^{(0)}\}(i = 1, \dots, N)$ of the unperturbed part $-\Delta$ (its properties were presented in Sect. 2) as follows: $\{\lambda_1^{(0)}, \lambda_2^{(0)}, \dots, \lambda_N^{(0)}\} = \{0, \lambda_2^{(0)}, \dots, \lambda_N^{(0)}\}$, where $\lambda_1^{(0)} = 0$ is (as shown in Sect. 2) the non-degenerate zero eigenvalue associated with the equilibrium concentration eigenvector: $\gamma_1^{(0)} = \bar{c}_{eq}$, and $\lambda_1^{(0)} > 0$ for $i \geq 2$. The corresponding eigenspectrum of the perturbed matrix Λ' is: $\{\lambda'_1, \lambda'_2, \dots, \lambda'_N\}$. In light of the above, Eq. (24) yields:

$$\begin{aligned}
 &\left\langle \gamma_i^{(0)} + \frac{1}{d}\gamma_i^{(1)} + \frac{1}{d^2}\gamma_i^{(2)} + \dots | \bar{c}_s \right\rangle d \left\{ \lambda_i^{(0)} + \frac{1}{d}\lambda_i^{(1)} + \frac{1}{d^2}\lambda_i^{(2)} + \dots \right\} \\
 &= \left\langle \gamma_i^{(0)} + \frac{1}{d}\gamma_i^{(1)} + \frac{1}{d^2}\gamma_i^{(2)} + \dots | \bar{S} \right\rangle \implies \\
 &\left\langle \gamma_i^{(0)} + \frac{1}{d}\gamma_i^{(1)} + \frac{1}{d^2}\gamma_i^{(2)} + \dots | \bar{c}_s \right\rangle \left\{ \lambda_i^{(0)} + \frac{1}{d}\lambda_i^{(1)} + \frac{1}{d^2}\lambda_i^{(2)} + \dots \right\} \\
 &= \frac{1}{d} \left\langle \gamma_i^{(0)} + \frac{1}{d}\gamma_i^{(1)} + \frac{1}{d^2}\gamma_i^{(2)} + \dots | \bar{S} \right\rangle
 \end{aligned}
 \tag{26}$$

When $d \rightarrow \infty$ and $i > 1$, notice that:

$$\langle \gamma_i^{(0)} | \bar{c}_s \rangle \lambda_i^{(0)} = 0 \implies \langle \gamma_i^{(0)} | \bar{c}_s \rangle = 0
 \tag{27}$$

since $\lambda_1^{(0)} > 0$ for $i > 1$. For $i = 1$ however, $\lambda_1^{(0)} = 0$, and therefore, as $d \rightarrow \infty$, Eq. (26) gives:

$$\langle \gamma_1^{(0)} | \bar{c}_s \rangle \lambda_1^{(1)} = \langle \gamma_1^{(0)} | \bar{S} \rangle \implies \langle \bar{c}_{eq} | \bar{c}_s \rangle \lambda_1^{(1)} = \langle \bar{c}_{eq} | \bar{S} \rangle
 \tag{28}$$

Furthermore, using Rayleigh–Schrödinger perturbation theory, the $\lambda_1^{(1)}$ eigenvalue can be explicitly calculated [15]:

$$\lambda_1^{(1)} = \frac{\langle \bar{c}_{eq} | K \bar{c}_{eq} \rangle}{\langle \bar{c}_{eq} | \bar{c}_{eq} \rangle}
 \tag{29}$$

In light of the above Eq. (27), and as $d \rightarrow \infty$, the transformed concentration vector at steady state $\bar{c}_s = \Gamma_s$ can be rewritten as follows:

$$\begin{aligned}\bar{c}_s = \Gamma_s &= \sum_{i=1}^N \frac{\langle \gamma_i | \Gamma_s \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i = \sum_{i=1}^N \frac{\langle \gamma_i | \bar{c}_s \rangle}{\langle \gamma_i | \gamma_i \rangle} \gamma_i \\ &= \sum_{i=1}^N \frac{\langle \gamma_i^{(0)} | \bar{c}_s \rangle}{\langle \gamma_i^{(0)} | \gamma_i^{(0)} \rangle} \gamma_i^{(0)} = \frac{\langle \gamma_1^{(0)} | \bar{c}_s \rangle}{\langle \gamma_1^{(0)} | \gamma_1^{(0)} \rangle} \gamma_1^{(0)} = \frac{\langle \bar{c}_{eq} | \bar{c}_s \rangle}{\langle \bar{c}_{eq} | \bar{c}_{eq} \rangle} \bar{c}_{eq}\end{aligned}\quad (30)$$

Using Eqs. (28–30) becomes:

$$\bar{c}_s = \Gamma_s = \frac{\langle \bar{c}_{eq} | \bar{S} \rangle}{\langle \bar{c}_{eq} | K \bar{c}_{eq} \rangle} \bar{c}_{eq}\quad (31)$$

Transforming back to the original coordinates, namely the actual concentrations c , an explicit expression for the corresponding steady state concentration vector c_s can be derived on the basis of (31) and (20):

$$\bar{c}_s = C^{-1} c_s = \frac{\langle \bar{c}_{eq} | C^{-1} S \rangle}{\langle \bar{c}_{eq} | K \bar{c}_{eq} \rangle} C^{-1} c_{eq} \implies c_s = \frac{\sum_{i=1}^N V_i S_i}{\sum_{i=1}^N V_i k_i c_{i,eq}} c_{eq}\quad (32)$$

Please notice that the above expression provides explicitly the displacement from the thermodynamic equilibrium concentration values that is intuitively expected and attributed to the steady rate of release of the chemical under consideration into the environment. Notice also, that the displacement is expressed in terms of the chemical's degradation rates in various environmental media/phases, their respective volumes as well as the thermodynamically determined equilibrium concentrations. As noted in Sect. 2, the steady state concentration values in (32) are critically related to the exposure potential of human populations and/or ecosystems to the chemical under consideration, and consequently, to potentially adverse public health and environmental effects [17]. For these reasons, model-based predicted environmental concentrations play a key role in exposure assessment and risk characterization within current frameworks for the management of chemical risk [3, 5, 6].

Let us now revisit the two persistence measures and key exposure-based hazard indicators presented in the previous Section, and establish their equivalence in the generic N -dimensional case using the results presented in the present Section. The reader is reminded that the first persistence measure is the characteristic time at steady state τ_{ss} (and the associated effective decay rate r_{ss}), which in the N -dimensional case with N compartments of unequal volumes is defined as follows:

$$\begin{aligned}r_{ss} &\equiv \frac{\sum_{i=1}^N V_i k_i c_{i,s}}{\sum_{i=1}^N V_i c_{i,s}} \\ \tau_{ss} &\equiv \frac{1}{r_{ss}} = \frac{\sum_{i=1}^N V_i c_{i,s}}{\sum_{i=1}^N V_i k_i c_{i,s}}\end{aligned}\quad (33)$$

The second persistence measure represents the slowest dynamic mode r_{sl} (the eigenvalue with the numerically smallest modulus) of the associated chemodynamics, which, as $d \rightarrow \infty$, was found to be given by the following expression in the N -dimensional multimedia case [15]:

$$r_{sl} \equiv \frac{\sum_{i=1}^N V_i k_i c_{i,eq}}{\sum_{i=1}^N V_i c_{i,eq}} \tag{34}$$

$$\tau_{sl} \equiv \frac{1}{r_{sl}} = \frac{\sum_{i=1}^N V_i c_{i,eq}}{\sum_{i=1}^N V_i k_i c_{i,eq}}$$

where τ_{sl} is the associated time-constant. Using the result of Eq. (32), one readily obtains:

$$r_{ss} = \frac{\sum_{i=1}^N V_i k_i c_{i,s}}{\sum_{i=1}^N V_i c_{i,s}} = \frac{\sum_{i=1}^N V_i k_i \left(\frac{\sum_{j=1}^N V_j S_j}{\sum_{j=1}^N V_j k_j c_{j,eq}} \right) c_{i,eq}}{\sum_{i=1}^N V_i \left(\frac{\sum_{j=1}^N V_j S_j}{\sum_{j=1}^N V_j k_j c_{j,eq}} \right) c_{i,eq}}$$

$$= \frac{\sum_{i=1}^N V_i k_i c_{i,eq}}{\sum_{i=1}^N V_i c_{i,eq}} = r_{sl} \tag{35}$$

and consequently, equivalence of the two persistence measures is established under the stated conditions : $\tau_{ss} = \tau_{sl}$. Finally, it should be pointed out, that the earlier results obtained in the 2-dimensional equal-volume case can be easily reproduced using the above results derived within the more generic framework of analysis presented in the present Section.

4 Concluding remarks

Aspects of the dynamic behavior of persistent chemicals in a multimedia environment were studied that are related to exposure-based hazard assessment efforts. In particular, non-homogeneous dynamic multimedia environmental models were considered with constant source terms associated with steady chemical release rates into various environmental media of interest, and risk-relevant aspects of the dynamic behavior of persistent chemicals were analyzed using perturbation theory and matrix theory techniques under conditions where degradation rates in different media are considerably slower than intermedia transport rates. Furthermore, under the aforementioned conditions, a proof was provided that rigorously establishes equivalence between two important and popular persistence measures, namely the characteristic time at steady state and the inverse of the overall decay rate (slowest dynamic mode) of the associated chemodynamics.

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