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Guidance on the selection of efficient computational methods for multimedia fate models

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Complete List of Authors:	Semplice, Matteo; University of Insubria, Dep. of Science and High Technology Ghirardello, Davide; University of Insubria, Dep. of Science and High Technology Morselli, Melissa; University of Insubria, Dep. of Science and High Technology Di Guardo, Antonio; University of Insubria, Dep. of Science and High Technology

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Guidance on the selection of efficient computational methods for multimedia fate models

M. Semplice,* D. Ghirardello, M. Morselli, and A. Di Guardo

Dep. of Science and High Technology

University of Insubria – Via Valleggio, 11 – Como (Italy)

E-mail: matteo.semplice@uninsubria.it

Abstract

Dynamic Multimedia fate models (MFMs) have to deal with the temporal and spatial variation of physical-chemical properties, environmental scenarios and chemical emissions. In such complex simulation tools, an analytical solution is not practically feasible and even a numerical approach requires a suitable choice of the method in order to obtain satisfying speed and reliability, particularly when certain combinations of modelling scenarios and chemical properties occur. In this paper, considering some examples of a wide range of realistic chemical and scenario properties, some sources of stiffness in MFM equations are pinpointed. Next, a comparison of the performances of several numerical schemes (chosen as representatives of three wide classes) is performed. The accuracy and the computational effort required by each method is evaluated, illustrating the general effectiveness of automatically adapted timesteps in numerical algorithms and the pros and cons of implicit timestepping. The results show that automatic error control methods can significantly improve the quality of the computed solutions and most often lead to relevant savings in computing time. Additionally, explicit and implicit methods are compared, indicating that an implicit method of medium order (around 5) is the best choice as a general purpose MFM computing engine.

*To whom correspondence should be addressed

Introduction

MFMs are nowadays standard tools to evaluate ecosystem exposure and to assess the indirect exposure of humans. Most of the initial MFMs^{1,2} were based on the definition of well mixed standard compartments, such as air, soil, water and sediment, and were simple steady state partitioning models with a fixed environmental scenario.³⁻⁶ Many MFMs then evolved towards unsteady state or dynamic systems,⁷ also used to study the behaviour of persistent organic pollutants at a global level.^{8,9} The number of compartments also increased as the original four were often subdivided into a number of boxes (e.g. layered soil compartments) in order to gain a more accurate description of chemical movement.¹⁰⁻¹³ Spatial variability of emissions and environmental scenarios was later introduced and handled in a variety of ways, from site specific models, to GIS/spatially explicit approaches.¹⁴⁻¹⁶ More recently, a lot of effort was devoted to incorporating the influence of environmental scenario and chemical changes in the models:¹⁷ from seasonal changes, such as vegetation cycles, to monthly/daily/hourly¹⁸ variations of compartment properties, meteorological conditions, and physical-chemical properties.

Among MFMs, compartmental models are the most used in environmental fate studies and are usually composed by boxes that exchange chemicals with each other and in which various processes (partitioning, transformation, etc) occur.⁶ The focus of the present paper is on numerical solution techniques suitable for MFMs representing real-world systems that can be simplified to one spatial dimension (e.g. depth in soil, position along a river, etc).

In a MFM, the time evolution of the amount $Y_i(t)$ of a substance in the i^{th} compartment at time t is described by an Ordinary Differential Equation (ODE) that takes the environmental behaviour of the substance and considering all the processes mentioned above. There is an ODE per compartment and, as the equations are intertwined by the exchange/transport terms, they must be solved as a system. This system is often too large or too complex in order to allow the computation of an analytic solution and thus one resorts to numerical methods to compute an approximation. While MFMs become more and more complex, the choice of a numerical method is crucial in order to obtain a good approximation of the solution (with respect to its accuracy, absence of spurious drifts,

oscillations, etc.) in a reasonable computational time.

More in details, the discrepancy between the computed result and the true value (accuracy) can be split into two parts: the modelling error, that is to say the difference of the true value of a variable from the exact solution of the ODE, and the numerical error, that is to say the difference between the exact and the computed solution of the ODE. The modelling error is due, for example, to the approximations of chemical and physical processes in the MFM, to the uncertainty in the input data, etc., and it can be reduced only by changing the model or its parameters. However, once these are fixed, the numerical error can be controlled by employing a numerical algorithm that is suitable for the task at hand. Thus, for the purpose of this paper, the quality of the solution is defined as the relative numerical error: a numerical method is better than another one if it can compute a solution with comparable numerical error, using less computing time.

Any numerical method requires the selection of a timestep Δt and computes the amounts Y_i at time $t_{n+1} = t_n + \Delta t$ from the known amounts at time t_n . An appropriate choice of Δt is crucial for the quality of the computed solution. Obviously, one has to take into account the stability requirement of the methods (see TextSI-1 in the Supporting Information), but this is not sufficient to guarantee the accuracy of the computed results: the latter is controlled by a combination of the method (especially its order) and of the choice of timesteps.

The majority of numerical methods for ODEs can be conveniently subdivided according to the following criteria:¹⁹⁻²¹

(a) choice of timestep length

- *fixed timestep*: it is chosen a-priori by the user
- *automatic timesteps*: an error tolerance is set by the user and the algorithm takes care of choosing Δt in order to meet the requirement

(b) time advancement, i.e. the computation of $\mathbf{Y}(t_{n+1})$ from the value $\mathbf{Y}(t_n)$ at the previous timestep

- *explicit methods*: it is achieved simply by evaluating some formula

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3 - *implicit methods* it requires the solution of a system of equations
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6 (3) *order*, a positive integer number (see TextSI-1).
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9 Automatic and implicit methods are more delicate and difficult to implement than fixed timestep
10 and explicit ones, but can have significant advantages: in (a) the reliability of the results deriving
11 from the embedded error control mechanism and in (b) the possibility of taking longer (even though
12 more computationally demanding) timesteps. Higher order methods are expected to give lower er-
13 rors at a given timestep length, but the evaluation of a numerical method should be performed from
14 a slightly different point of view. In fact, each step of a higher order method will cost more CPU
15 time than a step of a low order; thus, the computational efficiency of a method is a balance of the
16 cost of each step and the Δt needed to ensure a fixed relative numerical error.
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19 The difficulty encountered by numerical methods in approximating the solution of an ODE sys-
20 tem is related to the so-called *stiffness* of the ODE. In brief, an ODE is *stiff* if its solution changes
21 abruptly in a timescale which is much shorter than the time span of interest.²¹ For an ODE sys-
22 tem describing the environmental fate of a chemical, stiffness may arise from all the processes
23 that imply rapid and large changes of the amount of chemical, which could be related to envi-
24 ronmental conditions (e.g. high winds, rapidly changing compartment volumes) and particularly
25 extreme physical-chemical properties (e.g. solubility). Degradation processes are also supposed
26 to cause stiffness, because a very degradable chemical could be lost in a few hours, requiring very
27 short time-steps to track accurately its rapidly varying concentrations. Unless a suitable numerical
28 method is employed, the numerical solution of a stiff system requires an unreasonable number of
29 very short timesteps, resulting in long computational times and enhancing the risk of “pollution”
30 of the results by floating point approximation errors.
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33 Additionally, a careful choice and implementation of the numerical scheme becomes vital when
34 computing resources are put under stress, like for spatially explicit situations (e.g. GIS-based ap-
35 proaches) or when considerable time frames must be considered in a highly dynamic situation. The
36 aim of this paper is to provide a guidance for the choice of efficient and reliable numerical meth-
37 ods by enlightening the relationship between environmental/chemical facts and the performance of
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3 methods of different types, with regard to their ease of use, implementation, accuracy, robustness
4 and efficiency.
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7 The example developed in the main article is a MFM with one spatial dimensions, while a
8 description of a solver for more general situation (e.g. more space dimensions) can be found in
9 TextSI-4.
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13 14 15 16 **Materials and methods**

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19 **Mathematical description of MFMs** A rather general mathematical description of a MFM with
20 N compartments is given by the *system of linear ODEs*
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$$23 \frac{d}{dt} \mathbf{Y}(t) = M(t) \cdot \mathbf{Y}(t) + \mathbf{s}(t) \quad (1)$$

24 where \cdot denotes the matrix-vector product. The column vector \mathbf{Y} collects the amounts (e.g. mol)
25 $Y_j(t)$ of chemical present in compartment j at time t . In the formula M represents an $N \times N$ matrix,
26 whose entries may change with time (e.g. hourly, in response to environmental parameters). Each
27 matrix entry M_{ij} is the transport rate (e.g. mol/h) from compartment j to compartment i , with
28 diagonal entries M_{ii} representing loss terms from the i^{th} compartment (e.g. degradation). For
29 example, in a soil compartment, there will be contributions to M due to biodegradation, advection,
30 runoff, infiltration, etc. The column vector \mathbf{s} collects source terms (e.g. emission rates).
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43 When the boxes of the MFM are ordered so that each box exchanges substances only with two
44 other ones (e.g. layers in air/soil, segments of a river) most M_{ij} will be zero and matrix M will take
45 the *tridiagonal* form
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$$49 M = \begin{bmatrix} -d_1 & u_1 & 0 & \dots & \dots & 0 \\ l_2 & -d_2 & u_2 & 0 & \dots & 0 \\ 0 & \ddots & \ddots & \ddots & & \\ \vdots & & & & & \\ 0 & \dots & 0 & l_N & -d_N \end{bmatrix}. \quad (2)$$

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3 **Numerical methods for ODEs** In this paper, as prototypes of the methods of the different kinds
4 mentioned in the Introduction, several methods of the Runge-Kutta (RK) class are tested (see
5 TextSI-1 for background information). However, the relative performance of an implicit versus an
6 explicit method or of a fixed versus automatic timestepping is largely maintained across the various
7 implementations and thus the results also represent a guide for the choice of a routine in one of the
8 publicly available libraries mentioned below.
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16 The first method is the classic fourth-order Runge-Kutta method,^{19,20} which is explicit and
17 uses a fixed timestep that has to be chosen at the beginning of the computation (see TextSI-2).
18 There is no straightforward way to make a good choice of the timestep length based only on the
19 chemical and environmental characteristics for a given simulation run, but formula (SI.4) in TextSI-
20 1 provides a safe choice computed from the coefficients of the matrix M . When this formula is used
21 to analyse the matrix $M(t)$ and to select a timestep which is used for the whole computation, the
22 numerical method will be called RK4. When the timestep is changed at fixed intervals (e.g. every
23 hour, every day, every month) and estimated each time by applying the formula to this smaller time
24 span, the method will be named RK4a.
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35 The other two methods employ the technique of automatic timestepping. These methods vary
36 the timestep during the computation of the solution in order, taking automatically into account
37 the variations in the model coefficients, like those arising from variations of internal transfer and
38 degradation processes as well as those depending on the variations of the advective fluxes that cross
39 the boundaries of the region described by the MFM. As a representative of explicit automatic meth-
40 ods, the Runge-Kutta of order five DOPRI5(4),^{19,20} introduced by Dormand and Prince, is used.
41 Finally, the implicit method of order five ESDIRK5(4),²² introduced by Kværno, was considered.
42 These algorithms choose a trial timestep length according to formula (SI.4) at the beginning of
43 each simulation hour and compute a final timestep together with an estimate of the approximation
44 error committed (see formulas (SI.8) and (SI.9) in TextSI-3). The computed values are accepted
45 only if the error is lower than a tolerance set by the user and rejected otherwise. In both cases
46 a better guess for the timestep is derived and either the rejected step is recomputed with the new
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4 (shorter) timestep length or the values are accepted and the next timestep is computed with the
5 new (possibly longer) timestep length. The most common way to choose the error tolerance is to
6 set a parameter, called RTOL , to 10^{-q} , where q is the number of leading significant digits that the
7 user wants to be correct in the computed values. For the timestep control mechanism to be reli-
8 able, $q \geq 3$ must be used; in the following numerical tests $q = 6$ was employed, corresponding to
9 numerical results correct within one part per million. A thorough description of the two methods
10 is given in TextSI-3 and TextSI-4.
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18 For a MFM with N compartments, the computational cost of a single timestep of these methods
19 is approximately $19N$ for RK4 and RK4a, $48N$ for DOPRI5(4) and $69N$ for ESDIRK5(4), as
20 detailed in the Supporting Information. The overall computational time listed in TableSI-1 is of
21 course the result of the balance between the cost of each step and the timestep length employed.
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27 **Implementation of the methods** RK4 and ESDIRK5(4) are used in the most recent codes for
28 SoilPlus¹² and AirFug,¹³ but for this paper all the methods were implemented in a C++ library, in
29 order to perform a fair comparison. Since the scenario properties in the tests are constant within
30 each hour but change from one hour to the next, loss and transport coefficients for each air and
31 soil box are computed by the MFM and the coefficients of the matrix M and the vector s are
32 saved to disk for each simulation hour. The coefficients are then loaded from disk, the numerical
33 solution is computed and the results of the simulations are saved, including statistics on the num-
34 ber of accepted, rejected and total timesteps employed, which allow the evaluation of the overall
35 performance of the methods.
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46 In order to evaluate the errors of the computed solutions, an *exact* solution would be needed.
47 As this is not available analytically, following the tradition in the evaluation of numerical methods
48 for ODEs, the approximation calculated by the *fixed timestep* RK4 using 10^6 steps per hour was
49 regarded as being exact. This choice rules out errors coming from the automatic timestep selection.
50 The runs for the reference solutions took 2 hours each on an Intel Xeon running at 2.80 GHz. All
51 the other simulations and CPU times were recorded with an Intel Core2 running at 1.2 GHz and
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3 using binaries compiled with the same optimisation flags (`-O2` in `gcc`).

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5 The choice to employ methods of the Runge-Kutta type was guided by the ease of imple-
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7 mentation of the automatic timestepping version: sample pseudo-codes are provided in TextSI-2,
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9 TextSI-3 and TextSI-4. One should also be aware that many free libraries are available to compute
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11 numerical solutions of an ODE system, for example the rather complete collection `odepack`²³
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13 for linear multistep methods and the `GSL` library²⁴ for Runge-Kutta methods. In this respect, it
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15 can be observed that these routines are tailored for nonlinear ODEs and that, in order to achieve
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17 high performances on linear equations like Eq. (1), they must be called with $M\mathbf{Y} + \mathbf{s}$ as the function
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19 defining the ODE and specifying explicitly that M is the derivative function.
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23 **Eigenvalues and stiffness** The *eigenvalues* of a $N \times N$ matrix are N scalar values associated to
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25 the matrix and they can be used to characterise the matrix.²⁵ Let $\max E$ denote the largest absolute
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27 value of these N numbers. The study of $\max E$ for the tridiagonal matrix M will show the link
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29 between the chemical/environmental properties and the behaviour of the different algorithms, thus
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31 providing a guide to the choice of a reliable and time-efficient method for computing the solution
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33 of Eq. (1).
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36 In fact, in the presence of large values of $\max E$ (which is controlled by the elements of the
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38 matrix M and thus by the environmental scenario and chemical properties of the substance) or
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40 large emission rates in \mathbf{s} , explicit methods are usually forced to take very short timesteps due to the
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42 very stringent stability requirement, while implicit ones are free to choose Δt basing only on `RTOL`
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44 (see TextSI-1). Thus, the knowledge of the largest eigenvalue is needed in order to choose a stable
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46 timestep length, or otherwise to predict what timesteps will be chosen by an automatic timestepping
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48 procedure. On the one hand, the computation of the eigenvalues is a time consuming and delicate
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50 task if $N > 4$. On the other hand, in order to compute a stable Δt , only an approximation of $\max E$ is
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52 required. The maximum row-sum of the absolute values of the matrix entries (Λ in formula (SI.5))
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54 estimates $\max E$ from above and thus it can replace $\max E$ in formula (SI.4) in order to get a stable
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56 timestep length (see TextSI-1).
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3 **Environmental model and test-case scenarios** The numerical methods described above were
4 compared on a number of simulations performed using the SoilPlus model.¹² This is a site-specific,
5 dynamic model of the fate of organic chemicals, composed by two air compartments (named upper
6 air (UA) and lower air (LA)) and a variable number of litter and soil boxes. An illustration of the
7 MFM is provided in FigureSI-1.
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13 The air compartments,¹³ are characterised by hourly changing heights and wind speeds. In the
14 simulations, realistic meteorological conditions of a semi-urban area nearby Milan (Italy) for the
15 period between May and August 2007 (2232 hours) were employed, in order to provide a reason-
16 able range of values for such environmental parameters: UA height (10–2270 m), LA height (10–
17 4000 m), UA wind speed (0.29–35 m/s), LA wind speed (0.26–26 m/s), rainfall (0–24 mm/day),
18 minimum (7.5–21 °C) and maximum (13.5–35 °C) daily temperature and global solar radiation
19 (3–29 MJ/day).
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28 In order to distinguish between the numerical difficulties (stiffness) arising from the meteo-
29 rological scenario and those arising from the physical-chemical properties of the chemicals, all
30 simulations were performed in the scenario described above (named *dynamic-air scenario*), and in
31 a static one (named *still-air scenario*), which is identical to the previous one, except for UA and LA
32 heights (fixed at 500 m) and wind speed (constant at 0.1 m/s), corresponding to a rather immobile
33 air compartment.
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40 In this work, a 0.3 m thick loamy soil, according to the USDA classification,²⁶ with an organic
41 carbon fraction in soil set to 0.02, is subdivided into 60 boxes, with two additional ones for the air
42 compartments. This results in an ODE system of the form of Eq. (1) with 62 ODEs and coefficients,
43 changing hourly but kept constant within each hour.
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48 Several chemicals, characterised by different physical and chemical properties, and thus envi-
49 ronmental behaviour, were simulated in both scenarios. The selected chemicals are not intended to
50 be representative of the range of property variations, but rather to illustrate some specific real chem-
51 ical property features that may change the model response and induce stiffness. Their physical-
52 chemical properties are reported in Table 1. Dodine and benomyl, albeit present in ionised form,
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Table 1: Properties of the simulated chemicals at 25 °C.^{27–29}

Chemical	MW (g mol ⁻¹)	log K _{ow}	log K _{aw}	log K _{oa}	HL _{air} (days)	HL _{soil} (days)
PHE phenantrene	178.2	4.57	-2.88	7.45	2	230
CHR chrysene	228.3	5.86	-4.58	10.44	7	710
COR coronene	300.4	6.75	-6.76	13.51	7	2300
HCB hexachlorobenzene	284.8	5.5	-1.28	6.78	710	2300
CB chlorobenzene	112.6	2.8	1.18	1.62	7	230
DCM dichloromethane	89.94	1.25	-1.15	2.40	81	230
MET metolachlor	283.8	3.13	-6.04	9.17	7	23
BEN benomyl	290.6	2.3	-9.11	11.41	0.21	71
DOD dodine	287.4	1.25	-9.00	10.25	7	13.25

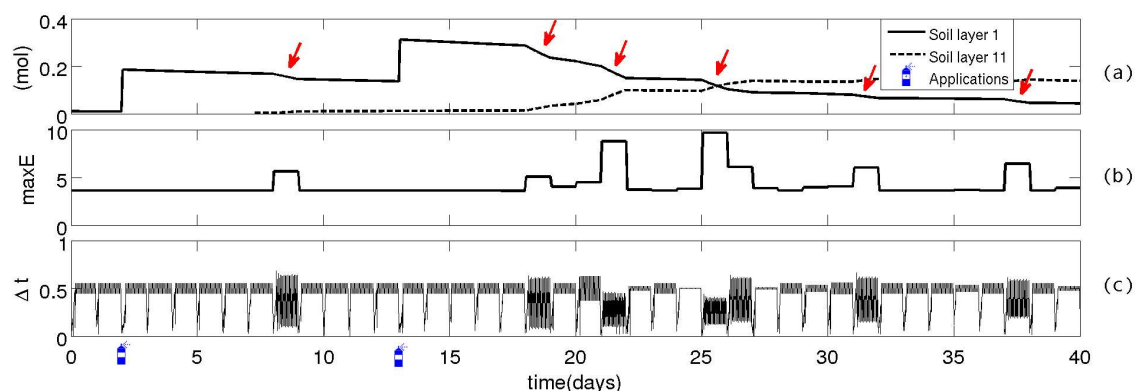
were considered as non-ionic chemicals, characterised by the properties listed in Table 1. The chemicals can be grouped as follows:³⁰

- (a) scarcely intermedia mobile hydrophobic chemicals, with relatively high octanol-water partition coefficient ($\log K_{ow} > 4$) and air-water partition coefficients ($\log K_{aw}$) ranging between -6.76 and -2.88 : phenanthrene (PHE), chrysene (CHR) and coronene (COR).
- (b) multimedia semivolatile chemicals, with $\log K_{aw}$ between -1.28 and 1.18 and $\log K_{ow}$ between 1.25 and 5.5 : hexachlorobenzene (HCB), dichloromethane (DCM), chlorobenzene (CB). These chemicals, given their range of properties, show a relative volatility.
- (c) multimedia soluble chemicals, with $\log K_{aw}$ comprised between -9.00 and -6.00 and $\log K_{ow}$ in the $1.25 - -3.13$ range: metolachlor (MET), benomyl (BEN) and dodine (DOD). Such chemicals, given the range of their partition coefficients, are relatively involatile and tend to partition, to a large extent, to the water phase.
- (d) half-life driven chemicals: in order to evaluate the stiffness introduced by biodegradation, MET was simulated using decreasing half-lives, progressively reducing the reference value provided in Table 1 (23 days) by one order of magnitude at a time (2.3, 0.2, 0.02 days).

The chemicals were homogeneously applied in the first 10 soil boxes (total application depth of 0.05 m) during the first hour of each simulation performed, with an application rate of 1 kg/ha.

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4 However, series (a) chemicals, given their very scarce intermedia transfer, resulted in simulations
5 where no rapid changes of the mass balance of the substance in the compartments were observed:
6 this produced no appreciable differences in the performance of the numerical methods. On the
7 other hand, when these chemicals were applied to air, significant and rapid transport processes
8 towards the soil compartments (due to deposition) are shown; this, in turn, magnifies the different
9 behaviour of the MFM with respect to the numerical integration. Therefore the results reported for
10 series (a) refer to the application of chemicals in LA with a constant emission of 0.001 mol/h.
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23 Results and discussion



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38 Figure 1: 40 days of a still-air MET simulation. Application days are marked on the bottom time
39 line. Top: MET content (mol) in the first soil layer (arrows indicate rainy days). Middle: maximum
40 eigenvalue. Bottom: timestep used by DOPRI54 (hour).
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44 **Environmental unsteadiness and automatic time stepping** Figure 1 illustrates the relation be-
45 tween environmental events, eigenvalues and timesteps. In the simulation shown, performed in the
46 still air scenario, an herbicide (MET) was applied twice (day 3 and 14) in the top 5 cm of soil (first
47 10 soil boxes in SoilPlus). For the sake of clarity, only the content of the first and the eleventh
48 soil boxes is shown in Figure 1a. Rainy days cause a decrease in the MET amount in the first
49 soil box due to leaching (arrows in Figure 1a). Mathematically, this shows up with maxE being
50 2-3 times higher than in dry days (Figure 1b). Correspondingly, during these events, the explicit
51 method DOPRI5(4) had to take shorter timesteps for the whole day (Figure 1c). Analogously,
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shorter timesteps were used during the application hours. It is also clear that short timesteps are needed at the beginning of each simulation day, in response to the updated coefficients. Obviously, a fixed timestep algorithm would have needed short timesteps for all the simulation, increasing the computational cost.

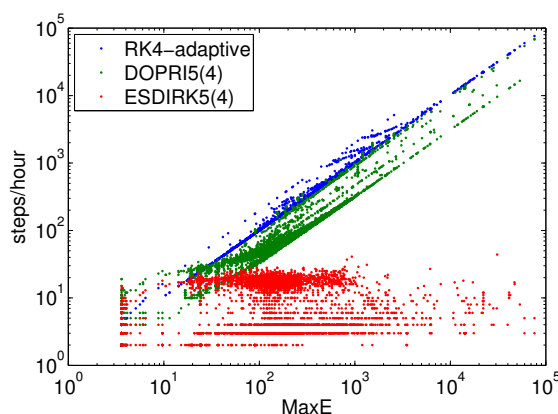


Figure 2: Correlation between maxE and number of steps per hour employed by RK4a and the two automatic algorithms. (Data from MET and DOD, still-air and dynamic-air scenarios)

Figure 2 is the scatter-plot of maxE and the number of timesteps taken by RK4a and the two automatic algorithms in the 2232 hours for four representative simulations. The linear relationship between maxE and the timesteps for the two explicit schemes is evident: up to 10⁵ steps per hour are required, when maxE is of the same order of magnitude. On the other hand, ESDIRK5(4) never needed more than 100 steps per hour. This is due to the fact that ESDIRK5(4), being implicit, is not subject to the stability requirement and can take longer timesteps even when maxE is very high (see TextSI-1 and TextSI-4).

Eigenvalues dependence on environmental and physical-chemical properties Environmental properties may rule maxE in some circumstances. For example, when volatility and solubility are not extreme (e.g. unusually involatile or insoluble chemicals), maxE is mainly controlled by rain in the still-air scenario and by wind speed in the dynamic-air scenario. This is evident from Figures 3a–c, where the scatter plot of maxE in the MET simulations versus the hourly rainfall and the average of the UA and LA wind speed is shown. However, for highly volatile or soluble

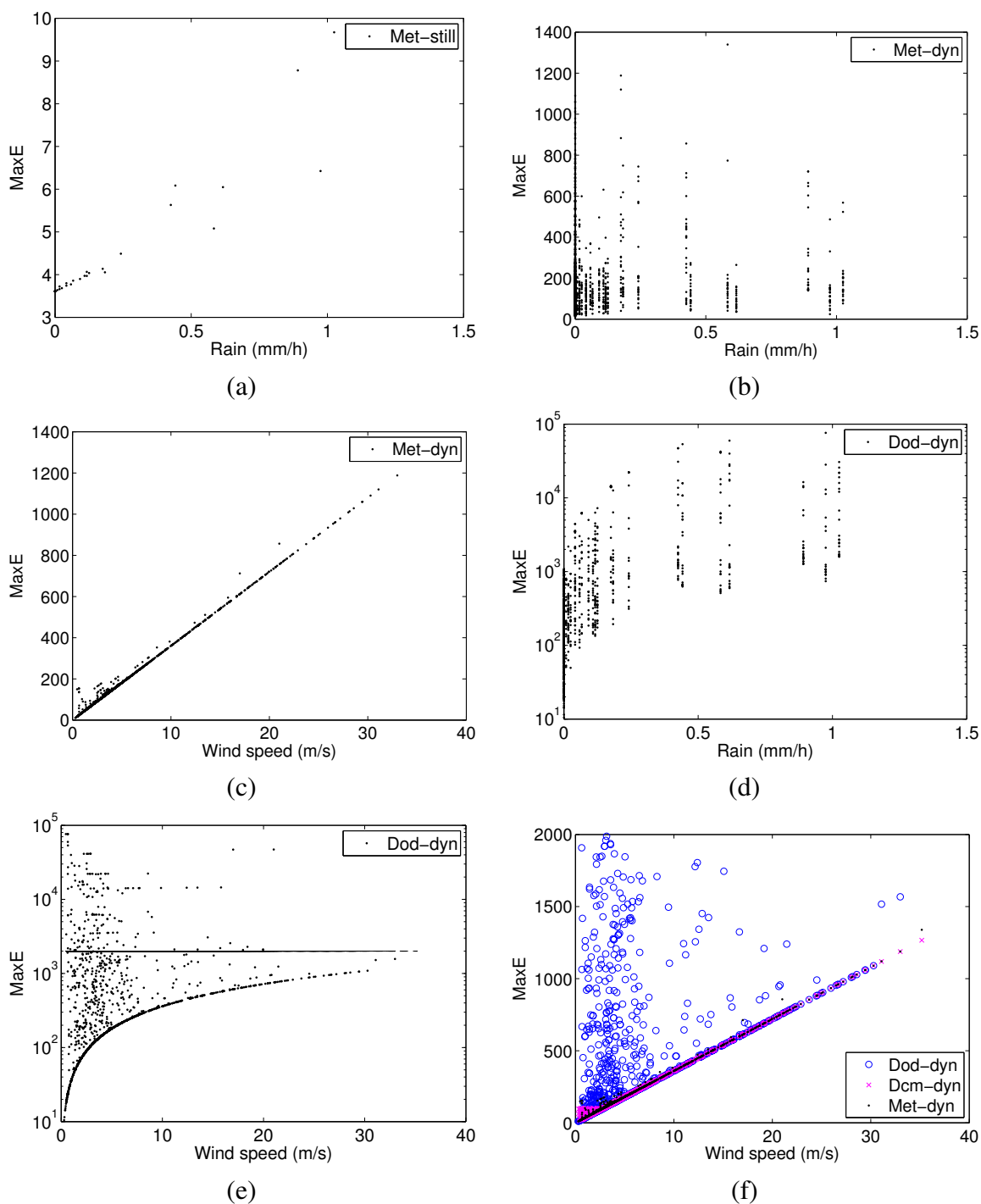


Figure 3: Correlation between rain rate, wind speed and maxE. a) MET in the still-air scenario. b,c) MET in the dynamic-air scenario. d,e) DOD in the dynamic-air scenario, with logarithmic scale on the vertical axis. f) A comparison of 3 chemicals (DOD values above the horizontal line in (b) are out of scale and not shown).

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chemicals, this simple relationship is lost. For example, Figures 3d,e show the scatter plots of $\max E$ versus the hourly rainfall and the average wind speed in the case of DOD. Figure 3d shows that increasing rainfall sharply enlarges $\max E$, even if there is not a strict correlation between $\max E$ and rainfall (note the different vertical scale with respect to Figure 3b). The variability in $\max E$ that is not explained by the rainfall amount could in principle be explained by the wind speed. However, Figure 3e clearly depicts that wind speed determines a minimum value for $\max E$ without being able to explain all its variance. Such variability in $\max E$ is not even explained by some linear combination of the two controlling variables: in fact, a multivariate linear regression fit (not shown) has an R^2 value of only 0.2, evidencing no correlation of $\max E$ with rainfall and wind speed. Finally, Figure 3f shows that the lower bound on $\max E$ determined by the wind speed is linear and largely independent on the molecule, whereas the upper limit of $\max E$ strongly depends on the chemical under consideration.

This is a very strong indication that simulation efficiency can be greatly improved by using algorithms that are capable to automatically choose the timestep and adapt it during the simulation, since a good value of the timestep h cannot be easily predicted *a priori* by examining the properties of the chemicals and of the modelled environment.

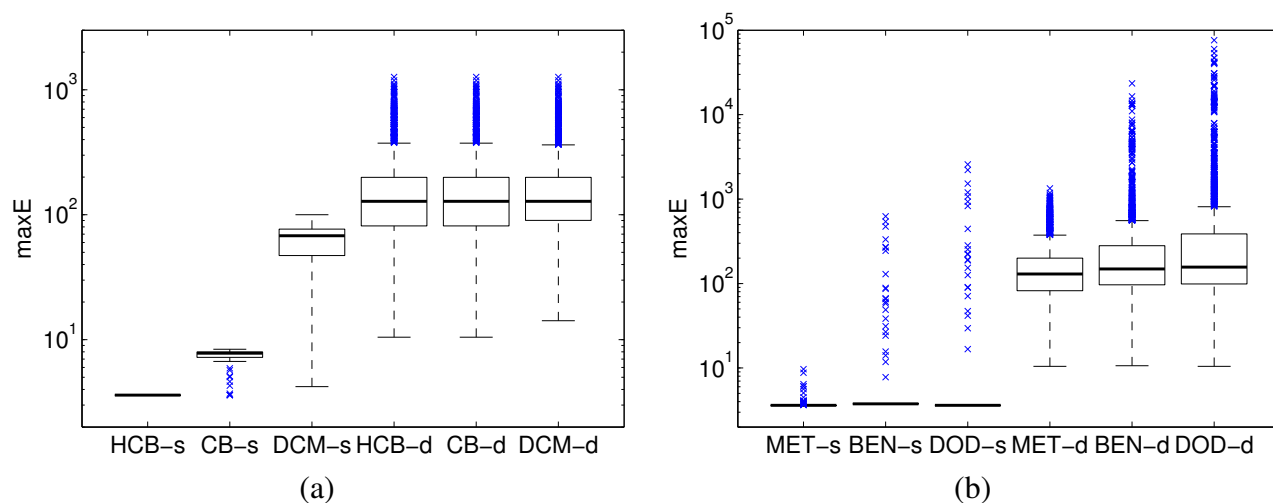


Figure 4: Box-plot of the maximum eigenvalue occurring during the 2232 hours of various simulations (whiskers indicate 3/2 of the interquartile range and the crosses represent outliers). (a): increasing volatility (b): increasing solubility. (Note the different vertical scale)

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4 The effect of the chemical properties on $\max E$ (and consequently on the number of timesteps
5 per hour) was further examined by analysing the distribution of $\max E$ during the 2232 simulation.
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7 In particular, one can observe that stiffness increases with very high or very low volatility and
8 solubility, whereas $\log K_{ow}$ and the half-lives have a comparably smaller effect (complete results
9 may be found in TableSI-1).
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13 Figure 4 shows the box-plots of $\max E$ occurring during each simulation. Increasing volatility
14 in the still-air scenario causes an increase in the median of the maximum eigenvalue (4a): when
15 $\log K_{aw}$ changes from -1.28 to 1.18 , the median of $\max E$ is increased by two orders of magnitude.
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17 Introducing a realistic wind greatly increases the eigenvalues, but reduces the above mentioned
18 difference among the chemicals: this shows that wind is the dominant source of stiffness.
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24 On the other hand, the increase of solubility (from MET to DOD) in the still-air scenario does
25 not affect the median of $\max E$, but produces a wider distribution with very large outliers (4b), with
26 $\max E$ becoming as large as in the dynamic scenario for other series. This makes the employment
27 of a fixed timestep method very unfeasible, whereas an automatic one is at its best.
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32 When the dynamic-air scenario is considered, both median and outliers of the $\max E$ distribution
33 move up by a factor of 10^2 , so that the spread of $\max E$ in a simulation may now reach 4 orders
34 of magnitude, with the higher values reaching 10^5 . In these extreme cases, only an automatic
35 algorithm based on an implicit method, like ESDIRK5(4), can perform the job of computing the
36 solution efficiently.
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44 **CPU times, error and performance comparison** In order to evaluate the numerical methods,
45 their relative performance in terms of computational times and errors has to be taken into account.
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47 On the one hand, each timestep of an higher order method will require more CPU time than a
48 step of a low order method; on the other hand, an higher order method can usually guarantee
49 the same tolerance taking longer steps. Similarly, each timestep of an implicit method is more
50 computationally demanding than an explicit one; this is counterbalanced by the fact that implicit
51 methods can guarantee the same precision with longer timesteps and thus less steps are taken to
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3 complete the simulation. TableSI-1 collects the data on the performance of the algorithms on all
4 the scenarios considered and the simulations performed.
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8 The RK4a tests show that some degree of adaptivity in the timestep choice helps in lowering
9 the computing time. However, setting a criterion for the choice of Δt based only on stability yields
10 unpredictable results in terms of the relative error of the computed solution. For example, errors up
11 to 10^{-2} in the nonstiff cases of CHR and COR in the still-air scenario were produced. Moreover,
12 unexpected variability of the relative error (10^{-3} – 10^{-7}) was observed for series (b) chemicals
13 in the dynamic scenario. DOPRI5(4) and ESDIRK5(4) automatically choose the length of each
14 timestep in order to satisfy a desired (set by the user) relative tolerance. RTol was set to 10^{-6} ,
15 which ensures that the numerical errors are at least 4–5 orders of magnitude smaller than those
16 deriving from parameter uncertainties. All simulations reveal a relative error lower than 10^{-8}
17 (see TableSI-2). The little computational overhead introduced by the adaption algorithm is well
18 compensated by the reliability of the computed solution.
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30 In evaluating the data on the number of steps, it has to be kept in mind that each simulation
31 hour has a different matrix M and thus, no method can employ less than 2232 steps. The fastest
32 CPU times of the implicit method reflect the lack of stability requirement: the algorithm is free
33 to choose Δt based on RTol only. For example, in the case of PHE in still air, both methods
34 use roughly 2 steps per hour to compute a numerical solution within tolerance while the explicit
35 method is slightly faster, since its cost per timestep is lower. In dynamic air, the MFM system is
36 much stiffer and stability forces DOPRI5(4) to take 10^5 steps, but ESDIRK5(4) can reach RTol
37 using just one fifth of steps, being therefore much faster. Additionally, ESDIRK5(4) saves CPU
38 time thanks to the very low ratio of rejected steps, since almost all of the CPU time is employed
39 in computing accepted steps. No rejections due to negative values in the solution were observed,
40 showing the robustness of the method. As a result, time savings can be striking: DOD in the
41 dynamic-air scenario is simulated in 32 seconds by DOPRI5(4) and in 1.7 seconds by ESDIRK5(4)
42 (see TableSI-1 for details).
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4 **Selection of methods for MFM applications** A good method for general purpose MFM inte-
5 gration should yield results with predictable errors and in a reasonably short computational time,
6 so that the modeller can concentrate on the MFM code, without worrying about the numerical
7 part. Additionally, CPU time savings can become crucial for longer simulations or when spatially
8 explicit models, such as those requiring a large discretization of an environmental scenario, are
9 employed. Based on the framework shown, the following guidance can be provided

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16 **order** The most convenient order for a numerical method is around 4 or 5. In fact lower order
17 methods need too many timesteps to achieve the required accuracy and higher order ones
18 usually cannot deploy their potential due to the non-smoothness of the solution. TableSI-2
19 contains a comparison with methods of order 2 and 8.

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26 **automatic timestep choice** This is highly recommended, since it frees the modeller from having
27 to worry about stability issues and the need to estimate the degree of stiffness of the MFM's
28 equation. Given the degree of uncertainty of many input properties (physical and chemical
29 properties, compartment composition, etc) the value suggested for $RTol$ is 10^{-6} . This a
30 reasonable choice to ensure that the errors introduced in the results by the numerical integra-
31 tion procedure are orders of magnitude smaller than those caused by the uncertainty in the
32 parameters.

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41 **implicit methods** They are a very convenient choice, since their extra cost is mitigated by the lin-
42 earity of the ODE to be solved and they can achieve high accuracy while take comparatively
43 long timesteps, even when rapid changes of the MFM variables occur in short times. In most
44 of the tests, the implicit method outperformed the explicit ones. They are thus suggested for
45 a general purpose MFM integrator. Only for low stiffness MFMs can explicit methods be
46 considered.

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54 **implementation** To the best of our knowledge, all ready-made implementations of implicit meth-
55 ods for ODEs assume that the ODE is non-linear. An ad-hoc implementation that takes into
56 account the linearity of the MFM equation can lead to extra time saving.

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Finally, it can be pointed out that, by examining a graph of the timestep length used by an explicit automatic algorithm during the simulation, the troublesome events for the numerical methods can be unveiled. As an example, these peculiarly short timesteps reveal when extreme changes in the value of a variable are present, which can be due to the normal variation of an environmental condition (e.g. a sudden rise or fall in temperature, high wind speeds or heavy rainfall as in Figure 1) or the wrong compilation of the environmental dataset (such as merging datasets of an environmental variable deriving by two non intercalibrated instruments).

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Supporting Information Available

An overview of Runge-Kutta methods, pseudo-codes for the methods employed, complete data on the tests performed and a pictorial representation of the SoilPlus MFM are included in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

A library with an implementation of the algorithms considered is available in source code format by contacting the corresponding author.

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Graphical TOC Entry

