GIS BASED CHEMICAL FATE MODELING
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Principles and Applications

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Preface

Ever since I was a young boy, I have been charmed by maps. They were one of the favorite subjects in my drawings. What I especially enjoyed was to draw maps of Europe, Italy, and the world, where I could give borders shapes I found logical, or interesting for some purpose, or simply bizarre. Giving regions a name and inventing empires or kingdoms or fierce independent republics, like Switzerland, or city-states or maybe lands with no patron, run by pirates or Robin Hood, was the start of meandering fantasy travels and a way to look at the world as a set of possibilities. Borders in the world change at a pace sometimes faster than our capacity to draw political maps: they fade as new communities find an identity, a common project. And the more a state expands, the more regions find reasons for their specificity: so, for instance, the continent of Europe, where I live, might turn into a federation where old national states become less and less compact and regions become more and more autonomous. And the whole world, with our globalized economy, is to some extent becoming a sort of federation with regions interacting in unforeseen ways. But a world of disappearing borders is more and more a world of continua—just as we see from satellites that detect temperature, or clouds, or ocean colors, or vegetation—and also a single runway for contaminants, which makes our world particularly united, where problems affect everybody and call for coordinated efforts. The perception of Earth as a single system is the door through which geography joined chemistry, not so long ago after all: an unexpected molecule found thousands of kilometers away from where it was used, in animal tissue or in food where it should not be. The study of molecules in the environment has been undertaken during the last decades using either unit world models, considering the Earth (or a large region therein) as a well mixed box, or through complex multidimensional models developed by oceanographers and meteorologists for the study of global dynamics. Only in the last decade have geographic information systems (GIS) started to be used extensively as tools not just for handling and displaying maps, but also for the analysis of chemical fate and transport in the environment. GIS and the “spatial thinking” of geographic disciplines have stimulated developing a third kind of models that combines the use of simple equations, as with unit world models, but with large use of spatially distributed data, as with complex models. Besides helping in the management of data used in all kinds of models, GIS provides a family of analytical techniques (such as overlaying and map calculations, spatial statistics, distance calculations, and hydrological processing) that may be of help to the environmental chemist and the modeler.

Chemical fate and transport modeling is a highly uncertain endeavor, in which we have to decipher and represent what may happen to molecules in the environment, grounding often on relatively weak evidence: a few points where concentrations are measured, some information on the quantities emitted, and little else. Many modeling exercises have been considered successful, insofar as they have produced a representation that is compatible with data and helped in the search for remedies to pollution. Models do not differ substantially from one another, as they all rely on the same fundamental principles of environmental chemical fate and transport; what does make models different is the data they
use for model parameterization. While in the past there was much discussion on the choice of an appropriate model, we are now at a point where we may take models for granted. Any model may work well for our purposes—once we have assigned appropriate model parameters: transport patterns (water or wind velocity), soil properties, climate, vegetation, the spatial distribution of emissions, and so on. Simple calculations with complex spatial data, which can be visualized as maps and checked immediately, facilitate the identification of critical factors driving chemical fate and transport, and enable more transparent and effective communication of model assumptions to decision makers who need to rely on them.

GIS is not an alternative to traditional models: rather it calls for revisiting modeling practice by putting more emphasis on data and reviving simple and transparent calculations whenever possible. In most cases, our modeling problems may actually be addressed with simple mass balances, along with limited use of transport simulations entailing numerical solution of complex flow fields. When such simulations are required, GIS helps to manage the data and provides visualization of results that can later be combined with other evidence in support of decisions. GIS and models are more and more ubiquitous in environmental assessment, and boundaries between GIS and models tend to disappear. Even software packages are becoming more open, to the point where parts of their functionalities can be used from within other packages and the whole GIS business is migrating to the cloud. This will hopefully bring more emphasis on “what to model” instead of “how to model” it.

This book introduces the fundamental concepts of GIS for use in chemical fate and transport modeling. For practical reasons, we develop several examples throughout the book, which are conducted using the popular ArcGIS software by ESRI, but the reader is constantly warned about the fact that functionalities of a software may be found in other software as well, and the same reasoning proposed with one single package can be extended to many other packages. Even the version of ArcGIS used here for the examples is not the most recent commercially available: software evolves, and the reader is invited to think about the implementation of the proposed methods directly in the software with which he/she is familiar. This book assumes the reader has a basic familiarity with GIS (several “quick start” tutorials are available for a plethora of both commercial and free software, a selection of which are suggested in the book). The reader should also be familiar with the basic concepts of chemical fate and transport. Both GIS and chemical fate and transport modeling fundamentals are presented in this book, with the purpose of establishing an interface between the two domains. Nevertheless, the book is about the link of these two areas of environmental science, and is not a specialized textbook on either of the two independently.

Several references are made to traditional literature, but also to websites, data repositories, online reports, and so on. Although much attention has been devoted to verifying the accuracy and update of links, these should be considered as last checked at the time of delivering this book to the publisher. Data available for modeling evolve, and so do models: for this reason the book is accompanied by a website (www.gecosistema.eu/gis_em_book) where all online material is kept up to date: links, datasets used for the examples and exercises, and other material such as reports.

This book presents ideas stemming from my research experience at the European Commission JRC during 2004–2010, and my professional experience in environmental assessment since 1998. I am indebted to several people I met during those years, who stimulated me through discussion, constructive criticism, and collaboration in analyses and projects. Looking back at my years at the
JRC. I would like to thank unit head Giovanni Bidoglio for encouraging and supporting the ideas behind the MAPPE modeling strategy. Dimitar Marinov at the European Commission JRC has been working extensively on the MAPPE modeling concepts applied to European continental scale assessment of contaminants and has contributed to Chapters 14, 18, and 19. Davide Geneletti at the University of Trento, Italy, has contributed to Chapter 11 by writing on general concepts of spatial decision support systems. Stefano Bagli at GECOsistema srl, Italy, has contributed to Chapter 17 on human health risk assessment; Paolo Mazzoli, also from GECOsistema, has contributed to Chapters 5 and 11. Christof Weissteiner and Pilar Vizcaino, former colleagues at the JRC, have contributed to Chapter 12, while Chapter 20 partly stems from research conducted together with Christof and others. Finally, Chapter 10 was entirely and generously written by Ezio Crestar at GIScience, Italy. My old friend, Simone Taioli, from Fondazione Bruno Kessler, Trento, made useful comments on selected parts of this book. Countless discussions, suggestions, and tips came from several other friends and colleagues that I would like to acknowledge here collectively and one by one, but I am sure I would miss to mention too many of them. On the other hand, all mistakes in this book are under my sole responsibility.

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In this book, we discuss concepts and algorithms for the analysis of environmental data and the development of chemical fate and transport models, which can easily be applied using a number of different geographic information systems (GIS) packages having conceptually similar structure and functionality. Most of these packages are freely available as open software, while a few are upmarket, commercial software broadly used in industry, government, and academia.

This chapter introduces some fundamental concepts that are subsequently dealt with in specific chapters. After identifying certain open issues in developing and using spatially explicit models, a tiered approach is proposed for chemical fate and transport modeling, examining separately absolute quantities, temporal dynamics, and spatial patterns. Finally, we will discuss the strengths and weaknesses, along with the opportunities and limitations of using simple GIS based models for different chemical modeling problems. The issue of choosing an optimal model complexity level, in light of the model scope and data availability, is a common thread that is considered throughout the book.

1.1 CHEMISTRY, MODELING, AND GEOGRAPHY

The title of this book recalls three distinct subjects: chemicals, environmental modeling, and geographic information systems (GIS). These may sound like they go well together but, if we examine them in more detail, we must admit there is something odd in this triplet.

Geography is about what one can see in the world out there. It is a discipline often associated with the humanities, descriptive in nature, that only in relatively recent times has introduced the use of quantitative tools [1, 2]. GIS technology and software are not just tools for geographers: their use is widespread in everyday life, and everyone has some experience of it (e.g., optimal routing or place finding using web-GIS applications such as Google Maps). In this book, however, we do not introduce the use of GIS technology and software as a mere ancillary tool for the handling of spatial data: rather, we describe how spatial analysis supported by GIS may help in setting up chemical fate and transport models that...
are simple, transparent, and at the same time spatially explicit and geographically meaningful, and enable us to make decisions on chemicals at a level that could only be addressed traditionally through complex numerical models.

In contrast with geography, chemistry has always been a science of the hardly visible, dealing with mysterious objects beyond common perception and only accessible through knowledge perceived by the layman as closer to magic than to geographic descriptions, or to the geometric clarity of Galilean physics. Not by chance, the word to denote this discipline is a minor variation on the original alchemy. Contemporary environmental chemistry was born because of the concerns of humankind for the consequences of a number of types of molecules—something like $10^5$—that were deliberately created by the industry, partly in response to societal needs, and released into the environment, often without questioning their possible consequences. Chemicals cannot be seen, but their effects have been noted and are sometimes worrying. Environmental chemistry appears extremely complex because the phenomena with which it deals involve an overwhelming number of variables: the behavior of chemicals in the environment is difficult to predict from laboratory tests, as environmental drivers of fate and transport vary in space and time, and their comprehensive description is still a challenge.

Environmental chemistry is inherently a multidisciplinary arena, where causal relationships between observed chemical concentrations or fluxes in the environment, human activities, and environmental processes are continuously examined by scientists using necessarily limited data.

In such an arena, however, cultural attitudes are rather varied, and the modeling of chemical fate and transport has always been to some extent a story of misunderstanding. On the one hand, mathematicians and system engineers seem convinced, following Galileo’s claim of mathematics as the language in which the book of the world is written [3], that good equations with a sufficient number of parameters will lead us to accurate predictions of chemical fate and transport; on the other hand, chemists with a precise understanding of the complexity of chemicals, but often with limited critical expertise with models, are eager to see their experience-based beliefs reflected in nice, smooth, but still realistic graphs or maps of chemical concentrations in air, soil, water, or vegetation. Traditionally, and obviously with several exceptions, chemists tend to be “experiment oriented” and to reason by examples capitalizing on their direct experience in measurements; they regard models as “tools” that may be useful or even essential but should not be questioned in too much detail about their grounds, merits, and limitations. And, most importantly, they should not be taken too seriously until robust evidence of agreement with observations is available. There is some truth in the old saying that “everybody believes in data except the one who measured them, nobody believes in models except the modeler”.

1-2 MR. PALOMAR AND MODELS

The original challenge of modeling is to describe reality as exactly and comprehensively as possible, and the last few decades have witnessed significant advances toward this goal, especially in such fields as meteorology and oceanography, paving the way for a generation of Earth system models [4].

Models of the Earth as a single (albeit extremely complex) system tend to be in line with the Digital Earth concept [5, 6], that is, a single repository of information on whatever can be observed on Earth. Earth system modelers would like to see this huge amount of information actually used in their models, which should tend
to be more and more reliable so they could be used to make critical decisions for "what-if" type scenario simulations.

This greed for modeling has not spared the domain of chemical fate and transport in the environment, despite the apparent complexity of environmental chemistry. It was noted long ago that simple phenomena easily observed in practice—such as the dilution of a drop of dye in a pond, or the transport of a spill of oil over the sea, or the plume of smoke from an isolated industrial chimney—lend themselves to be interpreted through a neat mathematical scheme—a Gaussian plume or puff, for example—suggesting that complex environmental systems might obey, if not analytical solutions, at least numerical solutions of elegant governing equations.

Modelers, often coming from nonchemical disciplines such as meteorology, oceanography, or hydrology, tend to use their traditional interpretive schemes, implicitly assuming that models are basically adequate and problems are mostly in the input data, which will be resolved as soon as new data are available. They tend to confront discrepancies between model predictions and field measurements by making models more comprehensive: a frequent temptation of modelers is to overemphasize the needs of a detailed and accurate description of reality, for example, by including more process equations in models.

Novelist Italo Calvino reflects on the use of models to describe reality in a collection of stories having as the main character a man with a capacity for observation that recalls a telescope: Mr. Palomar.

In Mr. Palomar’s life there was a period when his rule was this: first, to construct in his mind a model, the most perfect, logical, geometrical model possible; second, to see if the model is adapted to the practical situations observed in experience; third, to make the corrections necessary for model and reality to coincide. The procedure, developed by physicists and astronomers, who investigate the structure of matter and of the universe, seemed to Palomar the only way to tackle the most entangled human problems, those involving society, first of all, and the best way to govern [7].

Although not easy to admit, many modelers still live in something like Mr. Palomar’s first period. Our mathematical models still fall short of being able to accurately predict the spatiotemporal environmental distribution of chemicals in many cases of practical interest, even when they include a very fine description of virtually all known relevant processes.

But when comparing the sublime geometric harmony of the first period’s ideal model, with the contorted and deformed lines of reality, Palomar obviously perceives the need of continuous and gradual adjustments to both the model and reality: “if the model can’t change reality, reality may change the model” [7]. Palomar is an icon of what Donald Schön calls the “reflective practitioner” [8], who continuously questions the body of knowledge he/she refers to in action and recognizes the need to zoom out of the perspective of simply “applying tools” when tackling problems that require a combination of intuition, experience, creativity, and technical skills. A reflective practitioner soon realizes that a single line of modeling cannot be suitable for all purposes. Again Calvino’s point:

Mr. Palomar’s rule had gradually altered: now he needed a great variety of models, perhaps interchangeable, in a combining process, in order to find the one that would best fit a reality that, for its own part, was always made of many different realities, in time and in space [7].

Palomar’s enquiry turns to what would be a just use of just models to bridge the expanding abyss between reality and theory. A model is considered robust if
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it can be applied under a broad range of conditions. Then if the success of a model is based on its robustness, models may become fortresses that shield from what is outside—from reality. On the other hand, what really matters is what happens in reality despite models. Palomar concludes that a “model of models” should be “transparent, diaphanous, thin as cobwebs” [7].

Robustness, that is, the capacity of a model to provide consistent responses to smoothly varying input, may often be a desirable feature; however, when phenomena are not well understood, it may be desirable to explore the significant variations that arise from small perturbations of the input, and robustness turns into a limitation. This is especially true when a model’s use is to support decisions about solutions: that, as Calvino reminds, may be designed by wise and enlightened reformers, but implemented by the unfit, the dishonest, or both. Palomar’s/Calvino’s conclusion is that reality cannot be handled by models; answers can only stem from “the memory of fragments of experience” [7]. In the last year, many in the domain of environmental chemistry have raised a call for abandoning excessive attention for model calibration in favor of jointly interpreting model and measurement results, considering the limitations of both, as the only reasonable means to provide descriptions of the distribution of chemicals in the environment. Such descriptions would be narratives rather than accurately simulated fields of environmental concentrations: the latter would be just one among several possible pieces of evidence in support of these narratives. Examples of narratives based on this approach are the UNEP Chemicals global and regional reports on persistent toxic substances [9], in which a description of chemicals is only partly (and very flexibly) based on model output.

1-3 WHAT MAKES A MODEL DIFFERENT?

In light of these considerations, there may be limited agreement, or even confusion, about the scope of a chemical fate and transport model, its role in understanding chemical processes, and consequently the degree of complexity it needs to include.

The development of GIS in the last decades has definitely contributed to bringing chemistry and modeling closer to each other: solving equations in space and time is more and more comfortable, and model results may be represented in maps that can in turn be overlaid with other environmental information. This makes the reading of model output easier, but it also stimulates comparison between models and other spatial patterns: emission sources, atmospheric circulation, soil organic matter, and so on. It makes modelers more sensitive to the complexity of the geographic distribution of environmental drivers of processes that they want to include in their descriptions. Finally, it recalls continuously that the lines of reality are contorted, and the patterns arising from mathematical models are, in the best case, only approximating “trends” (the macrovariations of phenomena in space) and leave “residuals” (properties and processes acting locally) unresolved.

Environmental chemists, trying to visualize data and define the relationship with landscape and climate variables, should consider data not just as points but as samples of spatially distributed phenomena. GIS stimulates one to think about what is between two points. For instance, how continuous in space is a given chemical pollution and what is the shape of a contaminated area downstream of a pollution release? We need to use models to answer questions like these.

Also based on GIS and maps, we have started to develop and apply models of chemical fate and transport in the environment, in order to answer questions such
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as “Where do chemicals go once released into the environment?” and “Where can a certain observed concentration come from?” These two general questions correspond to what we could term the direct and the inverse problem of chemical modeling, respectively (for a general introduction to, and discussion of, inverse problems, see Tarantola [10]), and provide the motivation for this book, where we illustrate the use of GIS for data representation and analysis also through the use of simple models to test hypotheses on the source and potential evolution of contaminants in the environment.

Born in the mainstream of the digital revolution of the 1980s, environmental modeling (and particularly the modeling of chemicals in the environment) has witnessed an exponential growth in the toolbox available to scientists and practitioners who need to simulate environmental processes. Indeed, one might say that we now have more models available than practical problems in need of a model.

But what do we mean by “models”? Although most of the time practitioners use the word to denote software that implements algorithms for the solution of certain equations, in a general context a scientific model is meant as an interpretation scheme that enables drawing predictions on the behavior of a system.

In this more general sense, are we sure we have that many models ready for use? What are the reasons for the variety of chemical models available?

Actually, chemical modeling is based on a limited number of commonly accepted schemes, which may be implemented in several ways in a plethora of numerical codes and software platforms. At the basis of any such schemes is the mass balance of a substance, which simply states that the net sum of all its mass fluxes incoming or outgoing of a given “control volume” needs to equal the velocity of variation of mass inside the volume. The general principle of mass balance, or Lavoisier’s law, is accepted as the foundation of chemistry and, consequently, chemical modeling.

However, when using this simple, general principle to make practically useful predictions, additional assumptions have to be made. From the variety of possible and a priori all valid assumptions stems the variety of available models.

We focus first on the case of a substance in a single environmental medium, such as water or air; that is, we consider a control volume of a single medium over a given region, for which we estimate a mass balance.

The fluxes of a chemical in or out of that control volume are of three types: fluxes due to the transport of molecules by currents, that is, water or air passing through the boundary of the control volume (advection or convection); fluxes due to diffusion, that is, a trend that we observe in chemicals to move from high to low concentration regions; and fluxes of mass due to the transformation of molecules, which may correspond to a chemical reaction (e.g., the substance is decomposed into reaction products), a biological life cycle (the substance—e.g., bacteria—becomes inactive or dies), or a physical reaction (e.g., radioactive decay of a radionuclide or—most relevant for environmental chemistry—movement of the substance to other phases, e.g., sorption of a water-dissolved chemical to suspended solids).

Fluxes due to advection or convection may be defined as the volumetric flux of water or air times the mass of chemical per unit volume, or concentration, and are relatively simple to understand: if a material moves, it conveys all chemicals attached to it or dissolved in it. On the contrary, fluxes due to diffusion are much more difficult to understand: we do not have good explanations of why we observe that molecules move from high to low concentration regions. In all chemical models, we simply assume that diffusion fluxes are proportional to the gradient of concentrations (Fick’s law). The proportionality constant is
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small when the air or water is still or very slowly moving (molecular diffusion), while it is larger when the air or water is moving fast (turbulent diffusion or dispersion).

Finally, fluxes due to transformation are the most difficult to describe: often, it is assumed that a given mass of a substance exposed to environmental conditions would be transformed with a speed proportional to the mass itself present in the water or air—that is, it disappears exponentially. Many formulations also account for a nonconstant speed (nonlinear transformation models), giving the disappearance curve a shape other than exponential. But this is inessential for the present discussion.

Combining these assumptions in a continuum (differential) formulation yields the advection–dispersion–reaction equation (ADRE), which is formally presented in Chapter 2. According to the scheme that we have just sketched, mass fluxes of a substance are proportional either to the concentration (advection or, after multiplication by bulk volume to yield chemical mass, transformation) or to the gradient of concentration (diffusion/dispersion).

The ADRE can be integrated over a finite volume or “box” representing an environmental control volume (see Chapter 2). Although the numerical scheme in which the equation is solved may have some impact on the results and should be handled with care (e.g., see the discussion in Warren et al. [11] about the role of resolution in box models), all practically used chemical fate and transport models are based on the same mathematical structure; differences between models are essentially due to the proportionality constants. Therefore, when considering a single medium such as water or air, we might argue that all models are essentially the same and would yield the same results if we assigned the same velocity of water or air currents, the same proportionality constant between concentration gradients and diffusive fluxes, and between mass and transformation speed. These are called altogether model parameters.

Advection and dispersion parameters can be defined in several different ways. In the case of advection, these should be the vector components of the environmental material current velocities. One may theoretically assume that these velocities are well defined at every location in space. However, in reality they come out of a specific (e.g., hydraulic, meteorological) model, affected in turn by a number of debatable assumptions, some of which involve severe and sometimes unrealistic simplifications. Thus velocities are very seldom validated to a point that ensures full realism of these estimates at all scales of space and time.

The dispersion/diffusion proportionality constants usually come from even more questionable sources: molecular diffusion alone could be considered a physical property of a given molecule, but it only assumes relevance in fluids with a laminar flow, which is the exception rather than the rule in environmental modeling. On the contrary, in turbulent media the so-called dispersion coefficients (or dispersivities) are often assumed to be purely empirical constants to be adjusted while fitting models to data, sometimes on the basis of semiempirical schemes derived either from observations (e.g., dispersion coefficients proportional to a power of the dispersion scale or time; e.g., see (Csanady [12]) or from fluid dynamics interpretations (e.g., the field of deformation velocity of the fluid motion [13]), as discussed in Chapter 2.

If we turn our attention to the chemical transformation parameters, in principle these may be measured experimentally in the laboratory; however, the complexity of environmental conditions compared to the controlled ones in the laboratory makes them de facto calibration parameters—that is, quantities to be adjusted on a case-by-case basis in order to improve consistency between observations and model calculations and to close the mass balance.
There is another important element that introduces differences in model results: the ADRE yields defined solutions only when appropriate boundary conditions (BCs) are assigned. For a single medium, BCs consist of specifications on the mass fluxes that may be known to occur at the boundary of the area of interest, most notably chemical emissions. Throughout the book, emissions mean the amount of chemical introduced per unit time in the modeling domain. In principle, emissions are a known model input quantity. However, it is not infrequent that emissions are poorly, if at all, known and therefore can be regarded as an additional model parameter that is adjusted in order to match observations.

If we broaden the scope, we may consider more than one single medium, and allow for substances that do not simply leave one medium to enter another, but can also reenter the medium of origin from the one of destination. This requires one to consider more mass balances simultaneously. In this way, for instance, we consider explicitly volatilization from water to the overlaying atmosphere; atmospheric deposition to surfaces; sorption to and desorption from solids within water and air; and media inherently inhomogeneous or multiphase, such as soil formed by air, water, and solids.

These fluxes at the interface between two media are in practice boundary conditions for the bordering media. The ways in which interfacial flows may be described can be more varied than the assumptions of the mass balance in a single medium, albeit the range of interface models usually adopted is practically rather limited. Often interfacial fluxes require the most complex and questionable assumptions to be made in a model, as very little sound physical knowledge can be invoked to support them. The essential reason for this poor foundation is that the mechanics of continua fail to predict the behavior of discontinuities between two media.

At this point we may summarize that, irrespective of the model structure, the main differences in predictions among different models stem from (1) parameters, (2) BCs (among particular emissions), and (3) interface exchanges among media. The mathematical tools and software currently available to solve equations are probably fully adequate: improvements to models are not likely to come from better mathematical solutions, but rather from better parameters and BCs. Most of the times, paraphrasing an old adage from the hydrological literature, it may be said that our problem is not how to model but rather what to model. We might even argue that a model whose structure is simple, and whose parameters and BCs are easy to inspect and modify, would be an ideal tool for understanding most of the aspects of chemical fate and transport.

1-4 SIMPLE, COMPLEX, OR TIERED?

In the past, the application of models to real world problems has had mixed success. Models are currently not at the peak of their popularity, challenged by histories

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1 In the strict sense, boundary conditions of an equation are a prescribed value of the variable or a prescribed value of its gradient on the border of the domain. Emissions may be mathematically represented in this way, or in the form of a source term at positions inside the integration domain. Sometimes, the former are called external boundary conditions while the latter are internal boundary conditions. Further details may be found in basic fluid dynamics and transport phenomena textbooks such as that by Schiesser and Silebi [14].
of bad predictions and discrepant measurements and observations, in turn often (and mistakenly) regarded as simple reality, overlooking the assumptions and errors associated with measurement itself. Although model comprehensiveness and detail are still being improved, the pledge for joint interpretation of models and observations is now very strong both from the modelers’ side and from the analysts’ side. A more humble paradigm of modeling is evolving, directed more at the final use of a model than at its capacity to reproduce reality. “All models are wrong; the practical question is how wrong they have to be to not be useful” [15]. Yet, more complex, comprehensive, and detailed models continue to be regarded as more accurate and exact, under the implicit assumption that systems combining as much of available knowledge as possible may better account for reality. Although, in principle, this may be true, there are practical limits to the level of detail that can be achieved. For instance, Blöschl and Montanari [16] cite experiments clearly highlighting that the amount of water running off alpine pastures in Austria depends on the state of soil, which is controlled by cattle grazing and earthworm activity. Should we then include cattle and earthworms in a hydrological model of pastures? Even if it is possible to describe a specific phenomenon under controlled experimental conditions, pertinent information that can be practically available in reality might be incomplete or conjectural; hence, its consideration in predictions might bring little improvement or even introduce errors. We must acknowledge that “details” and “complexity” in models do not necessarily mean more explanatory capacity. In the example of alpine pastures, we might simply live with the fact that runoff has a certain range of variability, owing to unpredictable grazing pressure and earthworm activity. Rather than developing models further, we might take this variability into consideration when using models to support decisions. This is a fortiori true when complex models raise concerns about their transparency and practical usability:

What would be the minimal model to describe the fate and transport of chemicals in space and time? Would it actually be simpler than today’s complex models? . . . Indeed, a model that is so detailed and complicated that it cannot be readily comprehended cannot be easily translated into insights or testable hypotheses about the real system [17].

Although physics based models implying the solution of coupled partial differential equations [18, 19] are seen as inherently more reliable than simple semiempirical models, all implementations of models based on fundamental physics include semiempirical assumptions that make them mediating models rather than fully theoretical ones [20]. For instance, a physics based advection–dispersion equation model for ocean chemical transport may describe volatilization to air through a conceptual or semiempirical two-film model (see discussion in Schwarzenbach et al. [21]). Whenever models are sensitive to these semiempirical assumptions, they cannot be safely regarded as benchmarks for simpler models. There is no general reason to prefer a complex physics based model to a simpler one. Often models are used because of contingent reasons, including the modeler’s subjective preference, irrespective of the focused target (e.g., see Beven [36]). We keep using the models we have, with success and failure stories being told equally for complex and simple models.

If we refer not just to the equations coded in our model software but also to the way in which they are used to structure problems, models correspond tightly to what Kuhn [22] calls paradigms: “standard examples of scientific work which embody a set of conceptual, methodological and metaphysical assumptions.” When we develop and apply a model, we necessarily structure a problem to be...
solved. Are current models actually helping us to better understand chemicals? Are our modeling efforts cost effective to get insights on the fate and transport of chemicals in the environment? Are we structuring problems in a useful, progressive way?

Usually, when we study the fate and transport of a chemical in the environment, we may organize our investigation in four steps: (1) the compatibility of assumed emissions, residence times (or, equivalently, removal rates) in the different environmental compartments, and observed concentrations; (2) the spatial and temporal variability of emissions and residence times; (3) the spatial patterns of transport; and (4) the details of local processes.

Each of these aspects can be dealt with using models. But do we need a single model to deal with all these aspects together? Or should we organize our modeling in a tiered approach, focusing on each of the mentioned aspects separately in order to maintain the maximum possible simplicity, without losing capacity to answer the questions specifically raised?

Compatibility of Emissions and Concentrations

The first question a model should answer is about the plausibility of certain assumed emissions, environmental transfer rates (advection, dispersion, transformation: see Chapter 2 for more rigorous definitions), in light of available observed concentrations. A modeling study is based on a reasonably assumed causality relationship. Therefore, the first step is to propose a relationship \( C = f(E, K) \) that reflects correctly at least the orders of magnitude of known \( E \) and measured \( C \). At steady state, the relationship becomes \( C \sim E/K \).

Although it is known that chemical fluxes are seldom, if ever, approximated to steady state, this assumption is useful in the early stages of assessment. Before embarking on a complex model calculation, most of the time a back-of-the-envelope steady-state calculation allows one to compare the range of \( C, K, \) and \( E \), to see if they fit together by orders of magnitude. Emissions are a model input and need to be estimated anyway, but a check on the reasonableness of estimates does not require complex calculations. Environmental transfer rates, \( K \), can be described in a more or less complex way. However, most of the time relatively simple calculations, using the same approaches codified, for example, in popular multimedia box models [23], enable capturing the order of magnitude, which is the level of accuracy required for a consistency check of causal relationships.

A consistency check can be performed in both direct and inverse mode. In the former, the typical approach, in general, proceeding top–down from emission inventories through a fate and transport model calculation followed by a comparison of observed and computed concentrations/fluxes, in turn making adjustments to the emissions and/or model to improve predictions. Recently, inverse modeling (i.e., estimating emissions from observed concentrations) has been proposed as an effective alternative approach for a consistency check [24, 25]. Within this framework, one needs to evaluate whether the emission estimates given by a model from observed concentrations are compatible with available evidence about the production, use, and fate of a chemical. In both modes of calculation, the model can be as simple as a steady-state equation or similar algebraic formulas.

The simple, back-of-the-envelope calculation required by a consistency check can be performed, in spatially distributed form, using GIS functions of map algebra [26], dealt with in Chapter 4. This enables spatial comprehensiveness and, particularly, the consideration of emission and removal rate ranges specific to a certain location, in order to account for phenomena that are inhomogeneous in space.
Spatiotemporal Variability

The second question for models is about spatiotemporal variability. For a reason- able spatially distributed calculation it is important to distinguish what is simple uncertainty in a parameter from what is significant spatial variation. Pistocchi et al. [27] discuss how parameters having random distribution in space, independent of the amplitude of their range of variability, do not help in identifying spatial trends and hot spots in chemical distribution, which is dominated by the interplay between emissions and environmental parameters. As an example, the Authors consider the case of a spatially random emission to soil for a chemical subject to degradation only (Figure 1-1). If a strong trend is present in removal rates, the distribution of predicted mass (ratio of emission to degradation rate) will follow the trend while introducing fluctuations across it. However, if degradation rates are distributed randomly, the distribution of predicted masses will also be random with increased amplitudes of fluctuation. In such a case, no trend in space would be highlighted anyway, and replacing the spatially explicit representation of degradation with the spatial average of removal rates does not dramatically change the spatial mean of predicted masses. Including the variability of the degradation rates would only help to preserve realism in the assessment of the mass variability which does not require a spatially explicit model.

Although we know a priori that environmental phenomena in practice are never spatially homogeneous, some phenomena vary in space in a way that looks random, while others have some form of spatial structure: for instance, they vary with continuity across one region, or they assume an approximately constant value within one area and a different one in other areas. A necessary test for inclusion of a spatially explicit parameter in a model concerns its spatial variability, which can be investigated through the variogram—that is, the plot of the variance of data points at a given spatial distance, as a function of the distance itself [42], as will be further discussed in Chapter 6. It is worth observing that the spatial variability of parameters depends on the scale of interest: for instance, certain soil properties may be spatially continuous and exhibit trends if examined at the field scale (tens to hundreds of meters) but appear random if one aggregates over coarser resolutions (1 km or more). Emissions of chemicals to the environment are a fundamental input to models, and their spatial variability should be particularly considered when setting up a model.

The analysis of spatial variability of parameters, with its implications for chemical modeling, is further dealt with in Chapter 6. Concerning temporal variability, the simplest model of chemical fate and transport assumes steady state, which is often regarded as a first level of assessment, implying that, for reliable predictions, models should always relax this assumption. However, usually the temporal development of chemical fate and transport processes can be described in terms of a limited set of time variation typologies that follow the dynamics of BCs and, in particular, emissions (Figure 1-2). For certain processes, no trend in time appears and a steady-state approximation is fully acceptable. Such cases correspond to situations where emissions and removal rates vary randomly around mean values, so that the net effect is an approximately constant mass of the chemical in the environment (see Figure 1-2A). Another very common situation is when emissions of a chemical have occurred in the past, and the current condition is that of the depletion of a stock (Figure 1-2B). A third, recurring situation is when emissions or removal rates occur cyclically in time and at sufficient time intervals for the chemical not to accumulate in the