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CHEMIE der ERDE GEOCHEMISTRY

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Integrated modeling of metals biogeochemistry: Potential and limits

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Received 12 April 2007; accepted 2 December 2008

Abstract

We performed an analysis of a family of models relevant for the integrated modeling in metals biogeochemistry by two approaches: a hierarchical one and a disciplinary one. The hierarchical approach was performed in a theoretical framework accepting the existence of a hierarchy of ecological systems, and split the population of analyzed models into classes based on their relevance for various biological and ecological hierarchical levels. We identified two types of integrated models: between abiotic and biotic components at the same levels, and between biotic components across hierarchical levels. The complementary, disciplinary approach, focused on bioremediation models. The delineation of the class of bioremediation models proved that practically all biogeochemical models are relevant for this class, while only some of the analyzed models have been explicitly declared as 'bioremediation models'. Based on these analyses we identified a set of research directions, and proposed an alternative, complementary theoretical framework for basic research problems. With regard to bioremediation models, we could identify three levels of potential for development. The strategic potential: if correctly evaluated, models in bioremediation are the most useful tools for rational decision making. The tactical potential, of reactive type: internalizing the future knowledge arising from systems biology, and many other fields such as cognitive sciences biogeochemistry, ecotoxicology, soil science or plant science. The tactical potential of proactive type: (a) combining physico-chemical mechanistic "in principle" approach with uncovering the mathematical laws directly at the bio-geo level by empirical research and use of the existing new mathematical tools and (b) empirical research for delineating *in situ* the elementary units of models application and the use of programming in geographic information systems (GIS) and new generation GIS software for up-scaling the models' results from the elementary units of application to the site. And, finally, the operational potential: long-term research network for the study of contaminated sites as basic science experimental areas for implementing the proactive operational potential.

Keywords: Biogeochemistry; Metals; Bioremediation; Systems identification; Ecosystem; Developmental system; Mathematical modeling

1. Introduction

The need for integrating modeling comes at least in three parts: to integrate (models for) different processes (especially abiotic with biotic ones) at the same space–time scale, to integrate processes of the same type across

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doi:10.1016/j.chemer.2008.12.001

space–time scales (e.g. hydrological transport processes from lateral fluxes in upstream catchments to longitudinal buffering in downstream floodplains, or bioaccumulation from small, practically sessile organisms, to large-scale mobile organisms), and most challenging, to integrate processes of different types across scales (e.g. export of metals from upstream mining areas with exposure in mobile organisms in the downstream parts of the river network).

If one equates space–time scale with levels of ecological organization (ecosystems, landscape, macrolandscapes), one can say that an integrated modeling at landscape scale can be seen either at the same hierarchical level, or integrated across hierarchical levels, or both. By macrolandscapes we mean a hierachically structured system including at least two levels: ecosystems and local landscapes. Examples of local landscapes are a river stretch (with its floodplain), or a small catchment. Examples of macrolandscapes are a larger catchment, or an ecoregion. Ecosystems, local landscapes and macrolandscapes are identified based on their emergent properties, structural or functional. An integrated modeling of the functioning of macrolandscapes (in particular of the biogeochemical cycles and effects of metals) should deal with the relevant processes at the scale of that system, *and* of its subsystems (ecosystem, local landscapes). More details about this approach can be found in Iordache and Bodescu (2005).

In this paper, we are concerned more with the strategy of the research for integrated modeling, and less with tactical and operational problems. This is the reason because of which the non-expert will not find in this paper much guidance into the technicalities of this field, but rather an overview of the main conceptual and methodological issues. The assumption which led us to this position is that one needs more coherence in the development of integrated modeling in biogeochemistry. Our objective is to propose several ideas potentially useful for the differentiation of an explicit specific strategy in the scientific community, with consequences for both basic and applied science issues.

2. Method

The limitations of mathematical models could arise from:

- adequacy of the models to represent the phenomena (the main focus of this article)
- the difficulties of allocating values to the parameters
- the computational resources to solve the mathematical model.

The literature in this area is large, heterogeneous, and consequently no single attempt of critical analyses can extract all the patterns relevant for evaluating the potential of integrated modeling. We performed two complementary attempts, after sampling a large number of articles from on-line libraries using key words and citation tracing. At the sampling stage an interesting finding was that the body of articles dealing with modeling of metals is connected with articles about biogeochemical processes involving organic pollutants either by direct citations, or through common citations of articles discussing more general issues of modeling. This is the reason why, while this review focuses on metals, information concerning modeling of organic pollutants and more general aspects of ecosystems conceptualization are also touched, as long as they refer to or have consequences for modeling.

In the first attempt of information processing we classified a sub-sample of about hundred articles based on the following criteria:

- type of problem (abiotic, biotic or mixed);
- biological level of the modeled system (organism, population, trophic–dynamic module – TDM, food web); TDM is a more rigorous concept for communities, grouping species similar from biomass turnover, space–time location and functional niche point of view (Pahl-Wostl, 1995). The classification based on this criterion was frequently our interpretation of the article's position, not explicitly stated by the authors;
- ecological level relevant for the modeled system (infra-ecosystem, ecosystem, and landscape); by ecosystem we mean homogeneous areas referred to by common terms like 'forest', 'lake', by landscapes larger-scale aggregates of ecosystems, and by infra-ecosystem small parts of such ecosystems (like a soil plot in a forest, or an area of benthic sediment in a river). We are aware of the conceptual weaknesses of this criterion and will propose in the second part of the review a more rigorous alternative. However, for a first exploration of the information its application was useful;
- type of solutions (analytical/numerical/hybrid – numerical + analytical);
- space distribution (yes or no);
- type of relationship between parameters (deterministic or stochastic);
- modeling principle (deductive, inductive, other aspects).

A short description of the problem and of the model has been made for each article. Appendix 1–3 present in table format the result of this screening.

A second way to cross the set of articles was by the scientific disciplines in the frame of which they have been developed. The focus was here on bioremediation models, but ramifications to other disciplines have been also explored. This softer approach allowed us to explore the potential a discipline can offer for integrated modeling, and to underline the need for more explicit interdisciplinary integration of research.

3. Adequacy of the models to represent the phenomena

3.1. Overview of the models

3.1.1. Hierarchical classification

Table 1 presents the classes of models identified in the literature. The 'raw material' used for delineating these

Table 1. Classes of models identified in the literature (see Appendix 1–3).

Class	Sub-class	Appendix 1 – metals	Appendix 2 – organic pollutants	Appendix 3 – other relevant
Mixed	Organism level	x		x
	TDM level	x	X	x
Biotic	Organism level	x	X	x
	Population level	x	X	x
	TDM level	x	X	x
	Food web level	x	X	x
	Many levels	x		
Abiotic	(Modeling the influence of organic matter)	(x)		
	Infra-ecosystem level	x		
	Ecosystem level	x	X	
	Landscape level	x	X	x
Theoretical		x		x
Methodological		x	X	

'x' indicates that models of that class can be found in the corresponding group of articles. In bold are classes of integrated models.

classes can be found in Appendix 1–3. We take into discussion each class and describe it according to the criteria used for classification. The most interesting models from integration point of view are the mixed models and the biotic ones dealing in the same model with several hierarchical levels. The overview of the other classes and subclasses can provide hints about opportunities for developing other integrated models.

The characteristics of each class are presented below in the following order: problems approached, eco-level of application (for mixed and biotic models), type of relation between parameters, space distribution (acronyms: M – models for metals, OP – models for organic pollutants, G – other relevant 'general' models). The types of solutions and the modeling principle are not synthesized at this point, and will be touched shortly in Section 5:

- *Mixed models, at organism level*: (M) The problems tackled are linked to biogeochemical processes involving plant roots and soil, the models are relevant at infra-ecosystem and ecosystem level, are deterministic, space distributed or not; (G) bioturbation effect on redox potential and on reactive transport, relevant at infra-ecosystem and ecosystem level, deterministic, space distributed or not.
- *Mixed, at TDM level*: (M) Metal contamination of crops and ground water, reduction of metal oxides by bacteria, prediction of bacterial community structure from geochemical data, relevant at ecosystem and landscape scale, deterministic, space distributed or not; (OP) the effects of microorganisms (growth) on degradation of OP and clogging of pores (with implication on transport by groundwater), relevant at ecosystem and landscape scale, deterministic, space distributed or not; (G) influence of root growth on soil water flow, water uptake in crops, coupled water and sediment quality, transport, and (plankton) primary production, effects of microbial activity on redox potential dynamic, methods for efficient application of biogeochemical models at landscape scale, relevant at ecosystem and landscape scale, deterministic (eventually with stochastic components – Monte Carlo simulations), space distributed or not.
- *Biotic, organism level*: (M) Uptake and bioaccumulation by plants or soil invertebrates, relevant at infra-ecosystem and ecosystem level, deterministic or stochastic, with or without distribution in space; (OP) uptake and bioaccumulation by plants, relevant at infra-ecosystem level, deterministic, space distributed or not; (G) rhizosphere processes, uptake by root, general model of bioaccumulation of pollutants, root penetration as dependent on soil resistance to penetration, relevant at infra-ecosystem level, deterministic, space distributed or not.
- *Biotic, population level*: (M) Estimation of concentrations in plants, soil invertebrates, and animals with large mobility, relevant at ecosystem and landscape scale, stochastic models (including cellular automata simulations), with or without space distribution; (OP) the effects of OP on population parameters, landscape scale, deterministic and stochastic, space distributed or not; (G) forest growth for restoration purposes, soil water flow as influenced by root

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growth, deterministic, ecosystem scale, space distributed.

- *Biotic, TDM level*: (M) Relation between microbial community (structure, activity) and metals, metal removal in wetlands by macrophytes, relevant at ecosystem scale, deterministic or stochastic, space distributed; (OP) microbial biomass, activity, chemotactic transport, implications for clogging, relevant at infra-ecosystem, ecosystem and landscape scale, deterministic, space distributed or not; (G) comparison of stochastic methods and neural networks for predicting the distribution of community structure in function of abiotic parameters.
- *Biotic, food web level*: (M) Effects of metals on detritivorous food webs, and on litter consumption by invertebrates, relevant at ecosystem scale, stochastic or deterministic, not distributed in space; (OP) bioaccumulation in aquatic food webs, relevant at ecosystem scale, deterministic or stochastic, space distributed; (G) not space distributed: stochastic characterization of the variability in soil food web structure, deterministic modeling of contaminants dilution by growth, reciprocal relation between biodiversity and ecosystem disturbance, weak interaction in food webs and their role in the stability of community structure (highly relevant for the evaluation of the impact of metals on the biodiversity maintenance ecosystem service), and space distributed: modular ecosystem modeling (developing collections of models simulating various ecosystem components).
- *Biotic, many levels*: (M) Exposure of populations to metals (in case of mobile populations models are space distributed and include stochastic and deterministic components, a mixture of regressions, empirical equations, deterministic assumptions and Monte Carlo simulation).
- *Abiotic, influence of organic matter*: Influence of organic matter on metals speciation (binding of metals, complexation), relevant at infra-ecosystem, ecosystem and landscape level, stochastic, not space distributed. We delineated this rather narrow class because the organic carbon is a key parameter for modeling the bioavailability of metals, and there is a potential of coupling the ideas developed in OP models with M models taking into consideration that OP is part of the general 'organic matter' in soil and water.
- *Abiotic, infra-ecosystem level*: (M) Speciation and mobilization of metals in soil, removal of metals from acid mine drainage by precipitation, mostly stochastic, not space distributed (OP models not retained in this class, already existing, because they do not provide relevant information for our objective here).
- *Abiotic, ecosystem level*: (M) Metal transport in soil, speciation of metals in water, stochastic or deterministic, distributed in space or not, (OP) oxidation of organic matter in groundwater, deterministic, space distributed.
- *Abiotic, landscape level*: (M) Transport of organometallic colloids or metals by groundwater, and attenuation by physical and chemical processes, deterministic, distributed in space; (OP) reactive transport models with no parts for the bacterial role: transport by and attenuation in groundwater, deterministic (eventually with stochastic components), mostly space distributed; (G) groundwater transport of pollutants, problems of preferential flow, models based on geographic information systems (GIS) for surface waters and aquifers, influence of climate on energy fluxes from watersheds (these general models can be used for setting the major external driving forces of the contaminated areas).

If we further synthesize the information concerning model involving biological systems we obtain the pattern from Table 2. One can remark that the organism level models can be relevant at both infra-ecosystem and ecosystem, depending on the scale of the organism, and TDM level models can be relevant at all ecological scales, depending also on the scale of the organisms grouped into the TDM (bacterial TDMs can be modeled

Table 2. Ecological levels of relevance and the types of relations between parameters in the analyzed models.

Class	Subclass	Ecological level			Relation type between parameters	
		Infra	Ecosystem	Landscape	Deterministic	Stochastic
Mixed	Organism level	x	x		x	
	TDM level		x	x	x	
Biotic	Organism level	x	x		x	x
	Population level		x	x	x	x
	TDM level	x	x	x	x	x
	Food web level		x	x	x	x
	Many levels		x	x	x	x

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at infra-ecosystem scale). Thus, the hierarchy of biological systems cannot be simplistically linked to the hierarchy of ecological systems. At organism level most of the models are deterministic, with few exceptions, while when going up in the biological hierarchy modeling increasingly requires stochastic tools. While the abiotic–biotic integrated models at organism and TDM level developed by now are, to our knowledge, deterministic, the models integrated across several biological levels involved a complex portfolio of deterministic and stochastic tools. The solution for constructing the most advanced model we found (integrated model across several biological levels, Cormont et al., 2005) was to assume, not in agreement with reality, that the scales of action of the organisms of the food web are similar to that of the final consumer (and this became the scale of the cell used for running the cellular automata model). Another minus of this model is that it lacks the coupling by abiotic variables with models of metals transport. This is not insurmountable, because the model is space distributed. Biological models which are not space distributed cannot be related, in their current form, to the two (or three)-dimensional (2D or 3D) transport models.

We can add to the above ones two more classes. They could be expanded in terms of the number of analyzed articles, but we discuss them here in order to illustrate their potential importance:

- *Theoretical*: (M) Investigations of the mathematical properties of formalisms potentially useful for modeling bioremediation; (G) analyses of the available statistical instruments for describing the uncertainty and variability, and for the identification of relevant scales in ecosystem study, theoretical arguments against the excessive use of deterministic models, distributed control in food web networks.
- *Methodological*: (M) Determination of metals distribution in the soil profile by physical methods, mapping of the mine tailings at landscape scale (both models are deterministic and space distributed, thus potentially highly increasing the efficiency of data acquisition stage at ecosystem and landscape scale); (OP) physical method for detecting organic contaminants in soil, mathematical methods for solving coupled equations for reactive transport models.

At the end of this section, we mention that a detailed analyses of the mathematical formalisms of the models from Appendix 1–3 is ongoing, covering the entire set of articles extracted from libraries, and including the construction of an on-line available information system with the equations and parameters used. The results will be communicated in future publications.

3.1.2. Disciplinary approach

3.1.2.1. Delineation of the class of bioremediation models. We focused on this class of models because of their practical importance in the context of the implementation of the future Soil Directive and of the Water Framework directive. From an applied science perspective, there are two strategies for controlling the undesired export of contaminants from the landscape units: to control the emission from the source, and to control the fluxes after they have been emitted from the source. The first strategy has two branches (1a) is based on technologies for reducing the emissions from point sources, and (1b) involves technologies for reducing the emissions from contaminated lands. Some technologies for reducing the emissions from the point sources are in fact biotechnologies: they involve organisms (in particular microorganisms). As for the second branch of the first strategy, the main export pathways from the contaminated ecological systems are: (1a) from soil profile to the local groundwater – by leaching, (1b) from the local groundwater to the regional groundwater and/or surface water ecosystems, (2) from the top soil to surface water ecosystems – by runoff, (3a) from the soil-profile to local vegetation by bioaccumulation, and (3b) from the local vegetation to human population by use of the vegetation in the human food chain. The remediation of the contaminated ecological systems involves action at the level of the pools of contaminants in soil and/or water and action, directly or indirectly, at the level of the above-mentioned fluxes. This can be done *ex situ* or *in situ* by various technologies, including or not biological organisms. When it is done using organisms one speaks about bioremediation.

The second strategy supposes the use of buffer ecosystems, in particular wetlands for the removal of metals from water. This can be done (1) in the immediate vicinity of the point source of metals (treatment wetland, natural or man made), (2) at the base of the up-land diffuse source of metals (transversal riparian buffer zones), or (3) at large distances in order to control the river pollution resulted from many point sources (longitudinal riparian buffer zones – floodplains performing the pollutants retention service). Variants 2 and 3 are controllable by landscape planning techniques and *in situ* measures. In all variants mathematical modeling can be used for understanding the processes supporting the pollutants retention, and eventually optimizing this retention (in man-made wetlands case also for designing the wetlands).

To sum up, from the point of view of their purpose, there are three types of mathematical models in this area:

- Models serving the design of biotechnologies for reducing the outputs of contaminants from point sources.

- Models for *in situ* and *ex situ* bioremediation of contaminated sites.
- Models of contaminants fate in treatment or buffer ecosystems.

From a basic science perspective all these models describe biological and biogeochemical processes at various hierarchical levels of biological and ecological organization: from individuals to population and communities, and from microcosms, to ecosystems, and to local landscapes. They can be further subdivided using the controlling criteria. The first type of models and the models for *ex situ* bioremediation describe well-controlled processes, which do not involve conceptual difficulties comparable to those occurring with respect to natural systems. The other types of models describe natural processes intended to be controlled only to some extent by management measures. Their reference class is more or less the same, whether the ‘‘bioremediation’’ key word is present or not in their description. So we can delineate the class of biogeochemical models of quasi natural systems to be the subject of our analyses here. Their potential and limitations can be easily extrapolated to the bioremediation models *sensu stricto*.

Modeling the biogeochemistry of contaminant is a matter of modeling the abiotic processes, the biotic processes, and the coupling in between. Consequently, relevant for our analyses will be not only comprehensive large-scale biogeochemical models (which actually are missing), but also models dedicated to the abiotic processes (such as hydrological models, to the extent that they point out different approaches than the current self named bioremediation models, but relevant for them), or to biological systems (to the extent that they have the potential to couple with geochemical models).

3.1.2.2. Explicit bioremediation models. The widest subtype of such models is reactive transport models (in Table 1 these models are grouped in the mixed-TDM type and in the abiotic-landscape level type). We concentrate here on their ‘‘bio’’ character.

Steefel and MacQuarrie (1996) overview some of the methods currently used to model the dynamics of reactive transport in porous media. Fundamental to tractable modeling is that the biological mass is conceptualized as a chemical species, composed of various elements such as carbon, hydrogen, oxygen, nitrogen, potassium, phosphorus, etc. The biomass reacts as a chemical species and is subject to chemical thermodynamic principles. Jaffe et al. (2001) develop a reactive transport model, consisting of a set of coupled, steady-state mass balance equations, accounting for advection, diffusion, bioturbation and reaction of an organic substrate, electron acceptors, corresponding reduced species, and contaminant metals of interest. The model also accounts for release of oxygen and uptake of nitrogen by plant roots, as well as flow induced by evapotranspiration. Yeh et al. (2001) states that the developing field of bioremediation, combined with a greater awareness of the importance of subsurface bacteria in mediating key geochemical processes, has stimulated interest in the coupling of chemical and microbiologic models. Jaffe and Rabitz (2003) present a numerical model for simulating the biogeochemical dynamics of trace metals, metalloids, and radionuclides, in saturated porous media under biostimulation via the injection of a carbon source. The model consists of a set of coupled, steady-state mass balance equations, accounting for advection, diffusion, dispersion, and a kinetic formulation of the transformations affecting an organic substrate, electron acceptors, corresponding reduced species, and uranium. Generally, the modelers in this field would accept that ‘‘additional research may be needed – both experimental and numerical – to elucidate mechanisms associated with the complex interactions that take place between microbial processes and flow and transport processes in soils’’.

Lovley (2003) comes with a different philosophy. According to him, in contrast to the relatively simple mathematical expressions that can describe the geochemical equilibration of a given element in waters of various compositions, or the flow of water in different subsurface matrices, mathematical descriptions of the metabolism of microorganisms under various environmental conditions will be very complex. At present, models that include microbially catalyzed reactions rely on kinetic constants to describe the rates of microbial metabolism. These rate constants are typically fixed numbers that are derived from laboratory studies or are estimated for the environment under study by varying the constants until the model output fits the available geochemical data. This type of modeling of microbial processes has little predictive value over a diversity of contaminated sites (Lovley, 2003). On this base he proposed the development of models of bacteria and their coupling with geochemical reactive transport models.

But reactive transport modelers continued their efforts to internalize biological phenomena in the structure of the models. Islam et al. (2004) propose a multi-component reactive solute transport model coupled to kinetic biodegradation and precipitation/dissolution model, and geochemical equilibrium model to assess the impact of contaminants leaking from landfills on groundwater quality. The fluid flow model can also be coupled to the transport model to simulate the clogging of soils using a relationship between permeability and change in soil porosity. Olson et al. (2006) simulate how chemo-taxis affect bacterial migration to the contaminated region under various flow and initial conditions. Results show that this phenomenon may be important in some permeability circumstances. Wood et al. (2006) modify a reactive solute transport code with a user-defined subroutine that represented the important biological processes affecting the fate and transport of the pollutant.

Beck et al. (2006) study an idealized bioremediation model involving a substrate (contaminant to be removed), electron acceptor (added nutrient), and microorganisms in a one-dimensional soil column. Using geometric singular perturbation theory they construct traveling waves corresponding to the motion of a biologically active zone, in which the microorganisms consume both substrate and acceptor.

Assuming that a biological model should including some formalism specific to the functioning of biological systems, and taking into consideration that many reactive transport models introduce the contribution of bacteria as a constant term in the equations, we can conclude with respect to many reactive transport models that they are not true biogeochemical models. Their main limitation is that they adopt wrong ontological premises – biolevels cannot be fully reduced to physics and chemistry. The scientific accuracy is frequently sacrificed for the tractability of the modeling. Reactive transport models are valuable for various applied issues, but lack in our opinion the evolution potential from a basic science perspective, in what concerns their biological part. The interesting direction for them might to be coupled with models describing the biological processes at the relevant scales.

Another interesting potential which could be underlined is adopting the right ontological assumption, namely that there are irreducible mathematical laws for each level of the matter organization and, based on this assumption, developing (under a provincialist paradigm, *sensu* Rosenberg, 1985) portfolios of coupled models in the direction suggested by Lovley (2003). While still in its infancy, systems biology is rapidly developing, and the potential use for bioremediation (Bansal, 2005) was explicitly reiterated. It is also underlined in particular its role in understanding the effects of the deficiency or excess of elements and in assessing the exposure risk associated with elements (Iordache and Kothe, 2004). Not the least, the idea of organism modeling is closer also in the case of plants relevant for bioremediation (Weber et al., 2004; Kramer, 2005), to such extent that modifying the genetic structure of the plants in order to facilitate valuable interspecific interactions such as those with fungi has been advanced (Gohre and Paszkowski, 2006).

Another group of bioremediation models refers to processes involving plants. In some cases they are built on the platform of reactive transport models (e.g. Seuntjens et al., 2004).

An old model on the effects of plants on the bioremediation of contaminated soil and water is reported by Davis et al. (1993). Simulation results are presented for a hypothetical vegetative buffer zone over a shallow aquifer. Thoma et al. (2003) present a mathematical model for phytoremediation that accounts for the growth and senescence of roots. Given observations of growth patterns under different management conditions (fertilizer, species selection) model simulations can provide guidance for selection of appropriate strategies. According to Whiting et al. (2003) the concentration of a metal in the rhizosphere can be estimated using solute transfer models that incorporate: the metal concentration in the bulk soil solution, the buffer power of the soil, diffusion coefficient for the metal, water movement, root size and morphology, and the rate of entry of metal into the roots. In general, such models can be used to identify constraints to efficient phytoextraction (whether plant or soil) and to determine whether commercial phytoextraction is feasible. Mathur (2004) develop a numerical model that determines the uptake of cadmium by plants grown to remediate contaminated soils. Mezzari et al. (2004) present a model built in order to simplify and represent existing and possible metabolic activities for the transformation of some organic pollutants in plant cells. Mugunthan and Shoemaker (2004) model the hydrological-mediated fluxes of contaminants in order to optimize the long-term monitoring costs of the bioremediation efficiency. Bushey et al. (2006a, b) develop a plant uptake model for cyanide. A physiologically based model describing plant uptake, transport, and metabolism of cyanide species was developed to reflect the processes that influence the movement of cyanide into and throughout the plant. Plant compartmentalization (root, stem, and leaf) corresponded to the level of detail in the data collected via hydroponic experiments. Inclusion of more detailed intra- and intercellular processes would create a model inconsistent with the macroscale nature of the data. Mass balances around each compartment were developed via kinetic representations for the mass transfer processes and were combined to form a model describing the fate of cyanide species within plant–water systems (Bushey et al., 2006a, b).

Robinson et al. (2006) consider that field demonstrations at each site are not practical; therefore validated mechanistic models are required to calculate the effect of phytoremediation on metal fluxes. Although various aspects of vegetation–trace element interactions have been investigated in detail, he says, there is, as yet, no quantitative model that integrates the afore mentioned interactions thus calculating the environmental "fate" of trace elements in plant–soil systems. This is illustrated by the current body of literature on the role of vegetation for the immobilization of trace elements on contaminated sites. A wealth of information exists on plant metal tolerance and plant metal-accumulation, whereas the effects of phytostabilization on the mobility

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of the trace elements have received only minor attention. Central to such models is an understanding of root–metal interactions in these typically heterogeneous media. Existing "whole system" models provide a frame work of water and solute-transport equations into which chemical and biological interactions could be incorporated (Robinson et al., 2006).

In Verma et al. (2006) a model for simulating heavy-metal dynamics in soil, water and plant root system is developed and discussed in the context of rhizofiltration. Once the water movement is simulated, governing equations for heavy-metal transport in unsaturated zone taking into account sorption/desorption, metal uptake by plant species is solved to obtain temporal and spatial variation of heavy metals. Various linear and non-linear isotherms are available in literature for sorption and desorption process, which can be used for heavy metals and soil. Heavy-metal ions are transported to plant roots by mass flow and diffusion (Verma et al., 2006).

According to Seuntjens et al. (2004), generally, two types of process-based models are available to describe root uptake of nutrients. The first type of models is mechanistic models that predict the transport of plant nutrients such as phosphorus, manganese, or multiple ions through the rhizosphere. In a second type of models, water flow and chemical transport in the macroscopic soil–plant–atmosphere continuum is modeled using the Richards'and the convection–dispersion equation with sink terms for water and nutrient uptake. They appreciate that these models suffer from a poor representation of micro-scale processes occurring in the rhizosphere and present a mechanistic model which describes root uptake and leaching of heavy metals in the plant root zone, accounting for solution- and surface-complexation (kinetic), mineral dissolution, heavy-metal diffusion towards the root, root uptake, root exudation, ligand degradation and convective–dispersive transport of the soluble species.

To sum up, the bioremediation models referring to plants are currently mechanistic in nature and either refer to some plant parameters coupled or not with a hydrogeochemical model, or refer to the compartmentalization of some contaminant in the plant. They seem not to deal with the phenomena at contaminated site scale, i.e. they do not model plant communities, but only individual plant processes. However, we have seen from the analytical chapter that there are cases of models dealing with the influence of metals on population level parameters, so by cross-disciplinary fertilization this type of remediation models can evolve.

3.1.2.3. Other models potentially relevant for bioremediation modeling. This heterogeneous group includes models for various types of ecosystems, and models of processes directly relevant for bioremediation.

Fried (1991) reviews the characteristics of biogeochemical models of contaminants in aquatic systems. Aquatic systems are often present in contaminated landscapes. The mathematical models are categorized in two families according to scale: global and local. Global models are further subdivided into black box and gray box. Black box models represent the water body as a system with no assumed physical structure, considering only inputs and outputs which are mathematically related usually by a convolution equation or by an ordinary differential equation (e.g. a mass balance dilution equation). These oversimplified models generally provide a first approach to the phenomenon. Gray box models represent the water body as a system with a few structural properties. The local models are structural, accounting for the various features of contaminant transport and physico-chemical transformations and interactions: (1) convection (or advection) of contaminants (i.e. its movement with the mean flow); (2) dilution of contaminants with inflowing water; (3) removal of pollutants in particulate form by sedimentation; (4) dissolution of gases or of soluble parts of contaminants; (5) biochemical or physico-chemical reactions of contaminants with their environment (biodegradation by microorganisms, adsorption/desorption on sediments, chemical transformation, precipitation when the solubility threshold is exceeded, co-precipitation of secondary components with the primary precipitate when the newly formed precipitate provides a large reactive surface for simultaneous adsorption of these components); and (6) radioactive decay. Local models are usually based on a set of partial differential equations; sometimes they consist of a mixture of structural and gray box models. The basis of global models is the mass conservation principle relating inputs and outputs of the system, taking into account the reactions within the system that either increase or decrease contaminant concentrations or masses. The local or structural models, accounting for the various mechanical and physico-chemical phenomena, are based on a set of equations describing water flow and contaminant transport. They usually consist of three equations: conservation of total mass, conservation of momentum, and dispersion–convection (Fried, 1991).

We presented this extended summary from Fried (1991) for its clarity and because it points out that there is not more biology in this class of biogeochemical models than in reactive transport models. On the other hand, a complementary research direction is that of food-chain models in aquatic ecosystems, not coupled with abiotic mass transfer phenomena (e.g. Jorgensen, 1995).

An important research direction is that of bioaccumulation models in terrestrial systems. Results of pot trials and *in situ* analyses of plant–soil interactions were integrated by Robinson et al. (2002) to produce a

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generalized model that predicts plant metal-uptake. For some metals, plant uptake was found to be a function of transpiration, metal concentration in soil solution and a root absorption factor. It was concluded that a consistent method of measuring the soluble fraction of metal in the soil solution is essential before an index of root absorption factors can be obtained for different plant species and metals. In Robinson et al. (2003) changes in soil metal concentration are mechanistically predicted on the basis of plant water use, metal concentration in soil solution, soil density, plant root distribution and the so-called root-absorption factor.

The need for risk assessment methodologies lead to modeling efforts referring to both bioaccumulation and toxic effects on the organisms. Sauve et al. (2000) consider that environmental risk assessment of metals depends to a great extent on modeling the fate and the mobility of metals based on soil–liquid partitioning coefficients. A large variability is observed among the reported values that could be used to predict metal mobility and bioavailability. They propose a semi-mechanistic model based on the competitive adsorption of metal and H^+ [dependent on solution pH, total metal content, and log(soil organic matter)] as a tool to predict dissolved metal concentrations. A comprehensive analysis of the bioaccumulation models coupled with ecotoxicological models was done in the frame of a European Science Foundation (ESF) project (Wensem, 2003). They state that ecosystem modeling and, more specifically, modeling of food-web processes provides a proper vehicle to study the ecotoxicological impacts and to make the risk assessment. They conclude that an important obstacle to the use of food-web models in ecotoxicological risk assessment is the lack of hard data, or more precisely a database containing these data. This includes ecophysiological and life history parameters (data on consumption, mortality and the like, as well as data on concentration–effect relationships for those parameters) for the various functional groups in an ecosystem. Supplementary research in order to use food-web models for ecotoxicological risk assessment involves the further development of food-web models (modifying and extending their structure), especially models describing natural, complete terrestrial ecosystems. It also involves collecting the required input data and parameter values either in the laboratory or in the field. Furthermore, a comprehensive set of field data is required for validation purposes (Wensem, 2003).

Landner and Reuther (2005) review the biotic ligand model (BLM). The BLM concept, now developed for Cu, Ni, Ag and Zn, is considered as the currently most practical technique to assess the ecotoxicity of metals on a site-specific basis. A basic assumption of the BLM is that metal toxicity occurs as the result of metal ions reacting with binding sites at the organism–water interface, represented as a metal–biotic ligand (metal–BL) complex. The concentration of this metal–BL complex directly determines the magnitude of the toxic effect, independent of the physical–chemical characteristics of the test medium. Hence, the acute toxicity of a trace metal to an organism can be calculated when metal speciation, the activity of each cation in solution, and the stability constant for each cation to the BL(s) for the organism are known (Landner and Reuther, 2005). Direct measurements of the occurring metal species give the picture at a single moment. Because this is a very dynamic compartment it may be more correct to assess the mobility and toxicity risk of metals on mathematical models, such as the BLM. On the other hand, for a convincing critique of the BLM assumptions see Hassler et al. (2004).

Andretta et al. (2006) discuss the most important theoretical aspects of polluted soil risk assessment methodologies, which have been developed in order to evaluate the risk, for the exposed people, connected with the residual contaminant concentration in polluted soil, and make a short presentation of the major different kinds of risk assessment methodologies. They also underline the relevant role played, in this kind of analysis, by the pollutant transport models and describe a new and innovative model, based on the general framework of the so-called cellular automata (CA), initially developed in the European Esprit Project COLOMBO for the simulation of bioremediation processes. The authors describe the future research activities they are going to develop in the area of a strict integration between pollutant fate and transport models and risk analysis methodologies.

The retention time of metals in constructed wetlands was sometimes assessed by mathematical modeling (e.g. Wood and Shelley, 1999).

Soil science and plant science provide also interesting ideas to the bioremediation modelers. For instance, Devranche and Bollinger (2001) provide a model for the release of metals from soil under reducing conditions. Nowack et al. (2006) show that several mathematical models have been developed to simulate processes and interactions in the plant rhizosphere. Most of these models are based on a rather simplified description of the soil chemistry and interactions of plant roots in the rhizosphere. In particular the feedback loops between exudation, water and solute uptake are mostly not considered, although their importance in the bioavailability of mineral elements for plants has been demonstrated. The aim of their work was to evaluate three existing tools to model rhizosphere processes. A simple modeling approach to quantify the microbial biomass in the rhizosphere was developed by Sung et al. (2006). The results indicate that plants increase microbial concentrations in the soil by providing root exudates as growth substrates for microorganisms. Since plant roots are initially small and do not produce large quantities of exudates when first seeded, the addition of exogenous substrates may be needed to increase initial microbial concentrations at the start of phytoremediation projects (Sung et al., 2006).

IAEA (2006) provides a synthetic image on the possibility to model biological effects in radioactively contaminated sites:

Biological factors are difficult to incorporate satisfactorily into coupled models, owing to the dependence of reaction kinetics upon an enormous variety of site specific environmental conditions. Therefore, establishing a database that is applicable generally to biologically mediated processes is problematic. However, some recent studies have sought, with some degree of success, to couple microbial metabolism to redox changes and contaminant transport processes. Biological reactions have been simulated in a variety of ways that may be grouped into the following categories:

(a) *Instantaneous reactions*: Where the rate of reaction is fast relative to groundwater velocity, local equilibrium may be assumed and very simple relationships can be employed to describe the fate of the contaminant plume. Such models are unlikely to hold true in most natural systems, since even though attachment to surfaces may be reversible, the desorption step is normally slow in comparison.
(b) *First-order decay*: Biological reactions are treated in a manner analogous to radioactive decay. The main advantage of this method is its simplicity; the main disadvantage, the absence of any mechanistic basis.
(c) *Monod kinetics*: This describes the growth of bacterial cultures as a function of a limiting nutrient. The basic equation has been modified by a number of workers over the years to incorporate additional controls. The method is the most widely used at present but, in any case, the approach is purely empirical.
(d) *Michaelis–Menton kinetics*: This differs from the above in its derivation from a mechanistic analysis of enzymatic reactions. It is employed when the substrate is not regarded as a critical control on reaction progress. Michaelis–Menton-based analysis is the most complex of those listed here and has the most demanding data requirements.
(e) *Modeling food chain transfer*. Contrary to the models used for aqueous and airborne transport, which are largely mechanistic in nature, food chain and soil-to-plant transfer models are typically empirical or semi-empirical in nature. Extensive use is made of default parameter values for various models. The underlying reason for this seems to be that the most extensive use of them is being made in emergency situations, when there is no time to undertake a comprehensive site assessment.

To conclude this Section 3.1.2.3, there are many opportunities for interdisciplinary transfer of ideas profitable for the field of mathematical modeling in bioremediation.

To conclude the Section 3.1.2, an important limitation of the bioremediation models seems to be the current state of knowledge concerning the modeling of biosystems. In short (details in Section 3.2), the major problem with organisms is that they are influenced by the "objective" environment in a way depending on their scale-specific capacities to "perceive" and react to the environment in order to fulfill their goal function, so measuring the parameters relevant for modeling them should take into consideration this aspect. The correlated potential is linked to the integration of the future results from systems biology, cognitive sciences, and many other fields such as biogeochemistry, ecotoxicology, soil science or plant science.

3.2. Research directions for improving the models adequacy to phenomena

In the first part of this section we advance several ideas within the framework of hierarchical theory of biological and ecological systems (adopted at the start of the review), and in the second part we propose an alternative theoretical framework.

As long as food web models are still in the development phase (Allesina et al., 2008), one cannot hope to meaningfully model the biogeochemical cycles taking into consideration the full complexity of the ecosystem, because modeling the transfer of certain elements between the compartments of the ecosystem requires knowledge about patterns of biomass transfer. Reasonable more modest attempts can address biogeochemical processes in shorter food web chains, or the biogeochemical role of particular populations. On this direction there is a need for exploring the literature about the processes involving different types of organisms in the biogeochemistry of metals. This can be done easier when there are appropriate reviews available on this topic. For instance the processes involving microorganisms (in need for mathematical modeling) are (Haferburg and Kothe, 2007):

- metal solubilization by heterotrophic leaching, metabolite excretion including organic acids and H^+, redox reactions,
- effects of soluble metal compounds on microbes and metal immobilization by biosorption, transport, intracellular sequestration, and precipitations,
- effects of insoluble metal species on microbes, particulate adsorption, entrapment by polysaccharide and/or mycelial network,
- metal immobilization by precipitation or reduction,

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- influence of environmental factors e.g. pH, O_2, CO_2, nutrients, salinity (ionic strength) and metal toxicity on microbial growth and metabolism,
- influence of microbial activities on the environment, e.g. alterations in pH, O_2, CO_2, and redox potential, depletion of nutrients, mineralization of polymers by exoenzymes, and metabolite excretion, and
- environmental factors which direct the equilibrium between soluble and insoluble metal species towards metal immobilization or mobilization.

At another level of analyses, there is a tension between the complexity of the phenomena in the field and the inherent simplicity of the manageable models. One idea for surpassing this situation is to build portfolios of models.

For instance, there is need for both short-term (e.g. a few years) and very long-term (e.g. decades) models (Jaffe and Rabitz, 2003). Long-term models need to account for processes such as weathering, intra-particle diffusion, and co-precipitation. They recommend that the preliminary modeling effort should be based on first principles rather than empirical data so that it will be more robust. The Systems Integration element will not work as a "modeling service". It might eventually link certain models from individual projects in some hierarchical framework, but individual projects should identify modeling resources to meet their own specific needs (Jaffe and Rabitz, 2003). The idea of a portfolio of models is present also at Voinov et al. (2004). They used a modular ecosystem modeling approach to create a flexible landscape model structure that is easy to modify and extend for particular case studies and applications. The Library of Hydro Ecological Modules (LHEM; http://iee.umces.edu/LHEM) includes modules that describe hydrologic processes, nutrient cycling, vegetation growth, decomposition, etc., both locally and spatially. LHEM is implemented within the framework of the Spatial Modeling Environment (SME; http://iee.umces.edu/SME3) that integrates modules and places local simulation models into a spatial context (Voinov et al., 2004).

The main challenge of this view seems to be how to meaningfully link these project-based models. There are some suggestions in this respect in the literature.

Young (2002) discusses the problems associated with environmental modeling and the need to develop simple, 'top-down', stochastic models that match the information content of the data. It introduces the concept of data-based mechanistic (DBM) modeling and contrasts its inductive approach with the hypothetical deductive (deterministic and reductionistic) approaches that dominate most environmental modeling research at the present time. A similar view is expressed by Romanowicz and MacDonald (2005). Their paper attempts to relate different modeling approaches dealing with uncertainty in environmental processes. The literature review is based on hydrological, geophysical and environmental risk modeling, but the conclusions are relevant to all scientists working on environmental problems, which are almost invariably poorly defined. They argue that modeling of environmental processes should be stochastic rather than deterministic. One of the advantages of using both mechanistic and stochastic model is that the last type can show that metals may not be the main factor with adverse effects in contaminated areas. For instance, Anand et al. (2003) reports that soil nutrients and moisture strongly influence soil microbial variation, not soil pH and heavy-metal contamination (the two main influences from the smelter pollution that they anticipated). This suggests that the impact of smelter on soil microbial community is disappearing and that soil erosion is probably one of the main negative impacts of mining activity at present. It seems that soil erosion is the main factor limiting the growth and development of soil microorganisms. The erosion leads to dramatic decrease of thickness of soil organic horizon, as well as to losses of macro-nutrients necessary for many groups of soil microorganisms.

Wu and David (2002) argue that there is a need for more than a coupling of bottom-up and top-down approaches in the case of large complex system. Hierarchy theory, as well as empirical evidence, suggests that complexity often takes the form of modularity in structure and functionality. Therefore, a hierarchical perspective can be essential to understand complex ecological systems. Several hierarchical levels could be identified in the structure of the system, and modeled top-down and bottom-up. In their paper they present a spatially explicit hierarchical modeling approach to studying the patterns and processes of heterogeneous landscapes. Neither extremely reductionist nor metaphysically holistic approaches seem to be productive when dealing with such phenomena as self-organization and emergent properties (Wu and David, 2002).

The above view contrasts with an important point related to the economy of the modeling activities and advanced by Grayson and Bloschl (2000): the "Dominant Processes Concept". They convincingly argue that in moving beyond the notion of "trying to model everything" we should be developing methods to identify dominant processes that control processes response in different environments (landscapes and climates) and at different scales, and then develop models to focus on these dominant processes. There is an increasing awareness that the development of a spatial model is not it itself useful, unless it can be properly tested so that it can provide more credible predictions, or more insight into process understanding (Grayson and Bloschl, 2000).

So it may be that even the hierarchical approach is only one of the possible approaches in a portfolio of models. Or that the various types of models in the portfolio can be organized in a hierarchical manner, even if we are not able to produce a hierarchical model.

Overlapping in space the models is still another idea. For example Bragg et al. (2004) present three models and discuss the boundaries in time and space between them, concluding that they are not discrete, but overlap due to the multiscale expression of ecological and physiological processes. This idea is supported by factual overlap of the space–time scale of the driving forces causally determining the processes in the contaminated area (Thompson et al., 2001), and by existing theory of modeling overlapping systems (e.g. Stankovic and Siljak, 2001).

Thus, it seems that various possibilities of organizing the portfolio of models can be in a hierarchical style, by coupling top-down and bottom-up models, and by overlapping models in space at a certain hierarchical level of the system's structure, under the usual constraints of modeling (financial, technical, time and data availability and accuracy – Fried (1991) and Bauch and Anand (2004)).

One idea may be to develop (bottom-up) mechanistic models of metals' behavior under the (top-down) constraint of the results of the holistic modeling (Fig. 1).

Another idea may be to couple models developed based on experimental, small-scale data, with models developed based on field, large-scale data, but dealing with the same processes. The data set produced as a result of the experiments will be characterized by a higher number of parameters, but a lower variability of parameters values, while the data set produced from the field study will consist in a lower number of parameters but with much higher variability of values due to the natural space–time heterogeneity. These data sets with different characteristics could be used for the production of mathematical models following the scheme pictured in Fig. 2. The models developed based on the experimental data can be extrapolated at field scale by software programmed in GIS and using maps of the basic control parameters distribution and eventually modular submodels of derived control parameters. The results obtained after the extrapolation can allow one to check the (non-linear) correlations obtained from field data, and, to the extent that the fit between the two approaches will be good, to point out some of the mechanisms underlying the field correlations. A variety of other inter-comparisons between the models could be performed, as described in Fig. 2. The overall result might be a coherentized portfolio of models used finally for the simulation of metals mobility in different ecosystems types and degrees of metals contamination and under different scenarios of climatic changes.

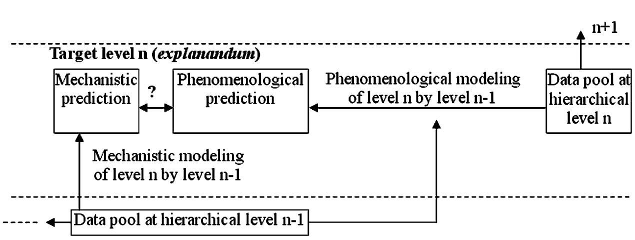

Fig. 1. Overall structure of a modeling approach in the hierarchical paradigm. Each level is characterized by specific, emergent properties, which when measured lead to specific data sets. Phenomenological models are (1) those describing patterns of variation and correlation (laws) of the properties characterizing a certain level (2) those correlating statistically (or by other methods without explanatory power, such as neural networks) the properties at lower levels and higher levels. Mechanistic models are those linking deterministically (assuming causal effect) the properties specific to lower levels with those specific to the integrating level.

3.2.1. Alternative concept framework

As we have already underlined, the above ideas are based on the assumption that there is a hierarchy of ecological systems, with space–time-specific scales. However, by following the last consequences of the most advanced identification methodology developed for ecosystem (Pahl-Wostl, 1995), we arrive to different conclusions. The next paragraph and Fig. 3 are common with a text fragment included in a review dealing with systems identification of ectomycorrhiza communities (Iordache et al., submitted).

The basic unit at which to consider diversity (a development from the elementary community notion) is provided by Pahl-Wostl (1995) under the name of trophic–dynamic module. We have already used this concept in the classification of models. A TDM is defined as the groups of biological populations having (1) rates of biomass cycling (inversely correlated with lifetime of the individuals) of the same order of magnitude, (2) the same location in space and time, and (3) the same role in the food web. Application of criteria 1 leads to dynamic classes, further application of criteria 2 leads to dynamic modules, which by criteria 3 are split in TDMs. The above definition can be amended (Iordache and Bodescu, 2005) with the remark that some populations can be included in more TDMs at the same time, because of their internal structural diversity (for instance deciduous tree populations have parts with very different rates of biomass cycling, leaves and wood – criteria 1, or parts with different location in space – below vs. above grounds – criteria 2; so they will belong to at least 3 TDMs – 2 aboveground and one below ground; frog populations have parts – tadpoles and adults – differing both in space location and role in food web). The notions of "same order of magnitude", "same location in space and time", and "same role in

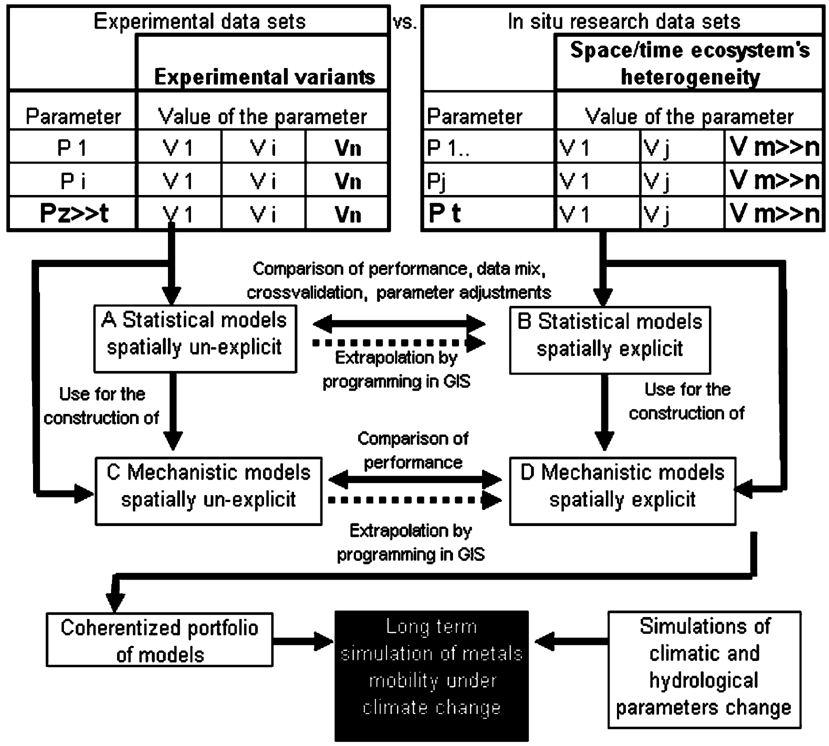

Fig. 2. Diagram showing the detailed structure of the modeling approach for developing a coherent portfolio of models.

food web'' are at the latitude of the researcher, and can be set more constraining, or more relaxed. If constrained at maximum, they will lead to a model identical with the ''reality'' (isomorphic model). If relaxed too much they will lead to a model too aggregated and having lost the key characteristics of the real system (simplistic model). If set at an appropriate intermediate level they will lead to a model simple enough, but keeping the basic characteristic of the system (homomorphic model). The scale of the TDMs varies hugely from one to another, so it does not make sense to speak about one specific scale of the ecosystem processes. In particular it makes no sense to speak about a simple nested hierarchy of ecosystems (Fig. 3A). The alternative, in the hierarchical paradigm, is to identify the exact scale of emergence of new structural (e.g. new TDMs) and functional (e.g. increase in overall biological productivity, or changes in the rates of biogeochemical processes) properties, and to model the real mathematical function linking scale and emergence of new properties in different areas and in different periods of time.

If the afore given argument is still not convincing because it is based on the (not generally accepted) concept of TDM, one can go down to the biological entities universally accepted, individuals and populations (the existence of the communities as real entities is disputable under the Gleasonian, individualistic, paradigm). Fig. 3B presents how the hierarchy of ecosystems can be obtained starting from a point of observation in space and applying a set of arbitrary scales of observation.

Now one can remark that there is a problem with assuming that new TDMs or increasing rates of ecosystems processes are the *emergent* properties at each hierarchical level, namely that these emergent properties are of *the same type* for each level. This is completely different from what is meant by emergent properties in the hierarchies of physical systems, where different types of properties are expected to be characteristics to the new level, beside the additive ones which are common to all levels (think for instance to temperature as characteristic to aggregates of molecules, and conceptually reducible to the kinetic energy of the molecules). We suggest that actually there is no such *objective* thing as hierarchy of ecological systems, and that the productive systems made of organisms and their environments (let us call these systems developmental systems – in short *devos*, in tune with the evolutionary literature) simply overlap and interact. These *devos*, and aggregates of them, are appropriate as the units for understanding and modeling the organisms, the population and the communities, without need for supposing, for basic research purposes, a hierarchy of systems. The function from Fig. 3 can be kept for describing the relationships between scale and different types of devos in a given study area. For instance herbaceous vegetation is characterized by a space scale of about 1 m^2, earthworms by 5–10 m^2, moles by 400 m^2, shrew by 200–800 m^2, and so on. The key element is under this framework not to identify the scale of the ecosystems, but to adequately conceptualize the relations between devos and with the abiotic systems.

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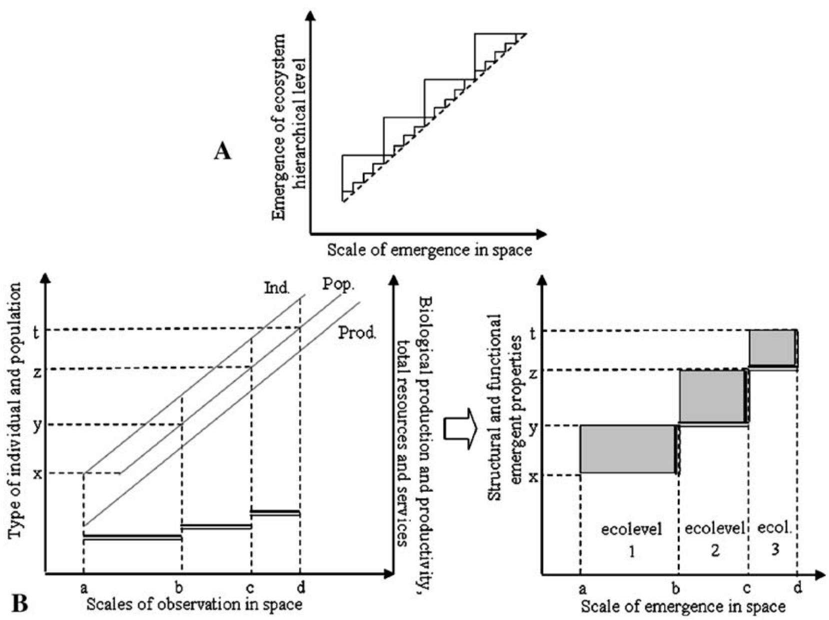

Fig. 3. (A) Simplistic models of the relationship between space–time scale of analyses and the emergence of ecosystem hierarchical levels. The linear model (dotted line) assumes that there is linear appearance of new emergent properties when increasing the scale of analyses, without need to privilege a certain scale (this model is preferred by those considering the ecosystems are methodological concepts applicable at any scale). The nested hierarchy models (continuous line in smaller or larger steps) assumes that at certain scales there are jumps of emergent properties allowing the identification of an ecosystem level, then these ecosystem interact over a range of intermediary scales and at other points there is another jump, and so on (such models are preferred by those considering the ecosystems are "real" entities). Note that their can be different nested hierarchy models depending on the privileged scale at which emergent properties are identified. (B) The relationship between the scale of biological structural elements and processes (individuals, populations, left graph-right axes, production and productivity, right graph-left axes) and the hierarchical structure of ecosystems (right graph). At scales of observation from a to b (corresponding to ecological level 1) one can perceive all types of individuals (and their populations) from x to y, but only some of the individual types from y to z (and not their populations). Then MTDs including populations of type y to z are said to "emerge" at higher hierarchical ecological level 2. Gray areas on the right graph suggest the multidimensional spaces characterizing each ecological level, in which the processes supporting the productivity of each level can be conceptualized. Note that the linear models from the left graph can be cut in a different way leading to alternative hierarchies.

The influence of space and time scales on the biological processes in food webs is of maximal importance (Koppel et al., 2005), and an acceptable concept framework is lacking. There are a number of interesting questions which can be put in the presented framework:

1. What is the real form of the functions presented in Fig. 3B (left graph, assumed linear for the sake of simplicity here) when the observer starts to increase the observation window from a certain point of observation?
2. How does this function vary as one move the starting point of observation in space? If one has the form of the function established for several points (on a continent, let us say) can one infer something about its form specific to other starting points?
3. How does this function change as we start the investigation from the same point, but at different moments in time?
4. Are their scales of ecological level perception more appropriate than others? (i.e. scales ensuring the maximal integration of the ecological system, and thus maximal manageability)
5. If the answer to question 4 would be affirmative, do these appropriate scales of perception remain enough time stable in order to use this scientific knowledge for operational changes in the structure and mission of the institutions dealing with the natural capital?

In our opinion the hierarchical view of ecosystem has been adopted (1) by analogy with the physical, objective, hierarchy of systems and (2) because the socio-economic systems are hierarchically organized and characterized by specific time–space scale. Because of the managerial needs in socio-economic systems we have cut the function from Fig. 3 (whatever its actual form is – monotonous increasing, and defined on real numbers set with values in natural numbers set, anyway) into appropriate intervals in function of our space 'window' of interest, and then conceptualized this as a hierarchy of systems. That this is the case is suggested also by

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the fact that a key element in eco-ontologies is their telonomic organization (Fonseca and Martin, 2004), leading to a search for goal functions characterizing the ecosystems as a typical research direction, similar to what happens socio-economic sciences.

As we humans are interested in natural resources and services (produced by the network of *devos*), the theory of hierarchical ecological systems should describe natural resources and services as emergent at different hierarchical levels. However, this should be an interpretation of the knowledge about the functioning of human developmental systems (*devos*). Thus, the knowledge concerning the overlapped human systems is *basic*, when descriptive and intending to discover the evolutionary mechanisms of society's dynamics, but can be translated into *applied* knowledge, when the purpose is to optimize the functioning of the current societal systems, which are hierarchical. The rest of biological knowledge, referring to the functioning of the *devos* of other species (and implicitly to natural resources and services for other species), is only basic knowledge.

The knowledge of objective (physical) type is absolutely needed in order to provide the reference framework allowing the conceptualization of the connections between *devos* (Fig. 4). The relation between autonomist biological knowledge (based on the acceptance of epistemicly irreducible teleonomic behavior of biological entities) and reductionist biological knowledge (based on the interpretation of biological entities as purely physical ones, with acceptable explanations only in terms of – efficient – causes, see Rosenberg (1985) for an analysis) consists in the interpretation of the resources and services needed for the functioning of a certain devos in terms of structural elements and processes of an objective reality. This interpretation is actually a representation about the perception of (the knowledge about) the objective reality manifested by the teleonomic entity (TE). It is an act of knowledge about another act of knowledge, and it is neither subjective (performed from the perspective of a human in terms of resources and services), but nor objective (in the physical sense) knowledge. It is autonomist biological knowledge. Following this line of research one can build a representation of the differences between the knowledge capacities of the teleonomic entities, and eventually explain this change in evolutionary, autonomist, terms.

Conceptualizing the connections between devos by the interplay of objective reality allow us the representation of life on Earth as overlapping devos. But we

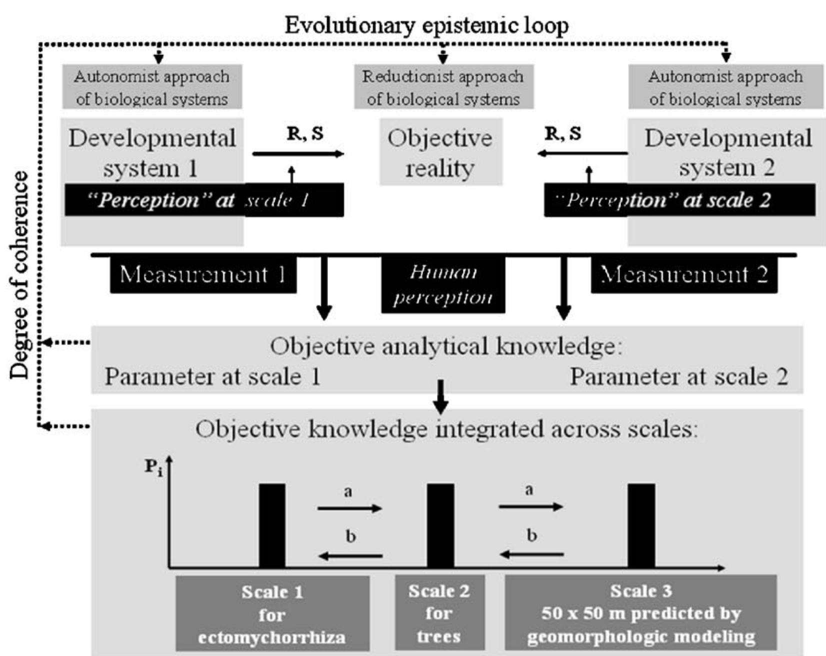

Fig. 4. The developmental systems of different types (devos) perceive objective entities (which provide resources R and services S) at different scales. In order to model the behavior of devos we need to measure the relevant parameters at space–time scales specific to the teleonomic entities from the structure of the devos. If the same parameter (or a set of parameters) is measured at different scales and one obtains the same value (suggested by equal stick of the inseted graph), one can not simply extrapolate across scales. This is because of the formally irreducible heterogeneity of the objective environment. One needs a specific empirical research to establish the conditions for up-scaling (or bottom-up modeling of other parameters, (a) on the inseted graph) and downscaling (or top-down modeling of other parameters, (b) on the inseted graph). These conditions will be investigated in a reductionist, physical, objectivist paradigm, and the degree of coherence of the integrated knowledge, and its coherence with the starting concept model, can lead to adjustment of the initial concept model (evolutionary epistemic loop).

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should not forget the representation of the objective reality is an act of knowledge of humans. Thus, the appearance of the ''objective module'' in the knowledge system of humans, as a trait fully separating humans from other species, may be interpreted as offering a selective advantage. However, this module has a key, but limited role in the knowledge process. It cannot be applied alone when the object of research are teleonomic entities, i.e. entities identified by analogy with the teleologic behavior of humans.

The unique character of every teleonomic entity precludes any attempt to model the long-term dynamic of the systems including TE in their structure. Eventually models of the principles of change can be developed (models of the evolution, in the sense of the theories of evolution). However, short-run models (at time scales smaller than the evolutionary time specific to the TE kind in question) can be developed and can be relevant for human decisions if their time window is comparable with the time window of interest for humans. Models at lower and larger time scales have only basic science interest. A criterion for the practical interest in models is the compatibility of their time window with the time window of decision makers. The same holds for the space window of the models.

We can reserve the term ecosystem to the management units of humans, and approach them by the hierarchical theory. The upscale mechanism is in this case the fluxes connecting the units, based on emergent TDMs or on abiotic fluxes (hydrological or atmospheric). However, this will not ensure us the in depth understanding of the objective reality behind ecosystems. One needs and evolutionist phase in the development of ecology, including the so called systems ecology as a special case describing the functioning of human devos. The next great syntheses will be between developmental science, cognitive science, ecology, and the synthetic theory of evolution (more on this can be found in Iordache, 2009).

There is nothing predictable or reducible to lower systems in the emergent properties of the ecological systems at any hierarchical level, because they depend on how we managerially cut the space function of emergence. The peculiar configuration of the emergent properties should be known empirically (phenomenological). Their prediction from lower hierarchical levels should be mediated by understanding the influence of smaller devos on the objective systems which is perceived within larger devos. A reverse connection can also be conceptualized (larger devos influencing smaller ones); in this sense one can speak of top-down causation, which makes no sense in the case of hierarchies of physical systems. But this top-down causation is an artifact of imposing the human social hierarchical structure on a complex system with no hierarchical organization. Thus, the bottom-up and top-down causation in ecological hierarchies are biologically speaking usual horizontal (within the same level), effective (in Aristotelian sense) causations.

The emergent properties of ecological hierarchies can be predicted eventually in the following sense: after describing the form of the space function of emergence one can predict how the cutting of this function into intervals will generate ''emergent'' properties at the end of the intervals. This may be of applied importance in the design of the administrative units in a country.

Modularity is frequent in the conceptualization of the organization of biological (Winther, 2001; Mitchell, 2005) and ecological systems (Pahl-Wostl, 1995). We interpret the so-called hierarchy of ecological systems as a modular representation of the relationship between the space–time scale and the observation of the new types of biological systems and their associated processes. As such, one cannot expect them to refer to well integrated objects, but to rather fuzzy systems. The fuzziness of the environment is resolved by decision. One should note that this kind of objectification, or labeling, is explicitly goal dependent (Khanna, 1990). In this case the environment is dependent on the goals associated to the management of the natural capital

So the modular approach for modeling the ecosystems as ''wholes'' (Voinov et al., 2004) is not only appropriate, it is also the only one in agreement to the instrumental status of the ecosystems. There is no particular cognitive need to produce true holistic models of ecosystems unless they are characterized by a very large integration due to steep surrounding abiotic gradients. But there could be an institutional need related to the control of resources and services. In particular, the integration of water, air, soil, and ''biodiversity'' management and monitoring in a target zone is a matter of integrating action and information between the specific scales of the processes, and not necessarily of producing a holistic model of the area. Because most frequently the target zone is a module, and not a real object in nature (in which the biological systems would have evolved to such an extent that the degree of integration is very high). However, inside the target zone there could be instances of community subsystems with high degree of integration, or the target module might be part of a larger system with high degree of integration. This should be analyzed case by case and points out that when one want to effectively manage a target system (for instance eco level 2 in Fig. 3) one has to screen also the lower and higher ecological levels in order to be aware of the mechanisms supporting the resources and services at target level, and of the role of the target level in the production of resources and services at higher level. As the financial (public) resources for modeling are limited, the best and most ethical strategy is to focus rather on processes than on ecosystems approached holistically (and for sure not on whole socio-ecological systems), and especially on those processes highly relevant for the production of natural resources and services valued by the financing people. Consequently, the lack of large-scale holistic (socio-ecological) biogeochemical models noticed in the previous sections appears, in the light of the perspective presented in this section, to be not only reasonable, but desirable.

Which are the consequences of this alternative concept model for the integrated modeling in biogeochemistry?

The concept of heterogeneity of the parameters relevant to organism is relative to the time scale and the knowledge capacities of the organisms. For instance soil pH, or concentration of Zn, as control parameter for ectomycorhiza, for annual plant, for trees and for moles should be measured at different scales, and a key element in an integrated modeling (food web for instance) is the scale relation between these parameters (Fig. 4).

Consequently a fundamental biogeochemical problem is how to average the values measured at smaller scale for up-scaling, and how to characterize the distribution of the values at small scales when the evaluation of the parameter was performed at larger scale. What form has the small-scale distribution function for parameters measured bulky at larger scales? We suspect that the forms of these distribution functions are not independent on the characteristics of the devos with different space–time scale for which the measured parameters functions as control parameter at a certain scale. A criticism to current statistical approaches might be that they are biologically neutral, i.e. do not take explicitly into account the potential influence of bio-systems in the conceptualization of statistical tools. The empirical characterization of the distribution functions needed for different up-scaling or downscaling situations can be, a major research direction for developing integrated biogeochemical models.

Thus, while for management we need modeling based on the theory of hierarchical systems, for basic research of biological systems we might be more interested in modeling based on a theory of overlapped systems.

It is interesting to note that under this framework one can not expect that a budget of microelements assessed in large catchments will be simply the addition of the budgets of their sub-catchments, because (1) the boundary conditions of the sub-catchments have their own dynamics, specific to the functioning of the system of larger scale (for instance the change in the landscape structure can be unpredictable at small scale, but predictable at larger scale) and (2) buffering and remobilization areas can occur on the flow path of underground and surface waters (so called hot spots and hot moments). We launch the hypotheses that the errors in the prediction of budgets of elements in catchments based on the smallest catchments with permanent streams will increase as go from catchments of low-order streams to catchments of high-order streams. The *testing method* could be coupling models for the budgets in small catchments and comparing the results with the results of models developed for the integrating catchments. Math modeling of the microelements budget performed as integrated modeling (separate sub-models for the involved mechanisms coupled in between). One can also not expect that the bioaccumulation in mobile organisms can be predicted based on concentrations in organisms which are their trophic base, on their local abundances, and on the trophic preferences of the top consumers, because the biotic and abiotic structural elements perceivable only at large scale would interfere with the simple accumulation in trophic chains by the way it controls the availability of food resources at large scale and indirectly the feeding behavior of mobile organisms. A second interesting hypothesis to test would be that the error of predicting the bioaccumulation of heavy metals in organisms from terrestrial food chains increases as we go up in the food chain. The *testing method* could be comparing the performances of deterministic models of bioaccumulation (cellular automata type) with neural networks-based models to predict the accumulation in plants, carabids, rodents and birds. We expect that the differences in predictions will become larger as the mobility (scale of observation of the population) of the organisms increase, and that the neural networks-based models will be more accurate in the validation phase. Testing in the same research program both hypotheses is in tune with the integration of hydrological, biogeochemical and ecological research in catchments, a research direction proposed also by other authors (Tenhunen and Kabat 1999, Vink and Peters 2003).

4. The difficulties of allocating values to the parameters

Beside the unsurpassable practical limits at ecosystem level (e.g. Jorgensen's principle of incertitude), there are also more manageable limits in allocating values to the parameters such as the heterogeneity/homogenization problem and the up-scaling problem. Depending on them there are various formal theories utilizing these concepts.

A more explicit treatment of spatial patterns and scaling can often enrich field research, permitting us to form better hypotheses (Thomson et al., 1996). MacDonald et al. (1999) point out that models at macro-scale do not resolve pore-scale variability; substrate and biomass concentrations are bulk averages; these models give unrealistic predictions. Jaffe and Rabitz (2003) argue that heterogeneities play a role in transport as well as directly influencing micro-environmental-scale

Please cite this article as: Iordache, V., et al., Integrated modeling of metals biogeochemistry: Potential and limits. Chemie Erde-Geochemistry (2009), doi:10.1016/j.chemer.2008.12.001

chemical and biological processes. All aspects of biogeochemical processes need to consider multi-scale heterogeneities. The full consequences of such heterogeneities are not completely understood at this time. Detailed modeling, laboratory, and field studies are needed to assess the regimes where heterogeneities play a significant role. The dispersion of data on different length scales and for different sites needs to be documented (Jaffe and Rabitz, 2003). The substantial microbial and geochemical heterogeneity at a contaminated site demonstrates that closely spaced sampling intervals, horizontally and vertically, in both sediment and groundwater are necessary in order to obtain a more in-depth understanding of microbial processes and the relative contribution of attached and planktonic populations to *in situ* uranium bioremediation (Vrionis et al., 2005). Becker et al. (2006) point out that studies relating the issues of microbial activity and community structure to the spatial organization within the soil matrix are lacking. A patchy distribution of metabolic activity and metal contamination was demonstrated. The authors suggest that the soil matrix consists of a set of spatially isolated islands populated by microbes, particularly during the bulk of the year when the soils are not saturated with a continuous water layer. Joynt et al. (2006) show that soils contaminated with both heavy metals and hydrocarbons for several decades have undergone changes in community composition, but still contain a phylogenetically diverse group of bacteria (including novel phylotypes) that warrant further investigation. Samples with similar fingerprints also had similar contaminant concentrations. They had previously demonstrated that metal-resistant and metal-sensitive bacteria can be readily cultivated from both metal contaminated and uncontaminated soils; this probably reflects the small-scale spatial heterogeneity in metal content in these environments (Joynt et al., 2006). To conclude, at laboratory scales, complete mixing and homogeneity conditions can be (and usually are) enforced and resulting theories are conditioned on those assumptions. However, at field scales physical, chemical and biological heterogeneity and incomplete mixing are the rule rather than the exception (Scheibe, 2006).

Dungan et al. (2002) distinguish among three different categories to which spatial scale-related terms may be applied: (1) the phenomenon being studied, for example the spatial structure of vegetation and the processes that affect it; (2) the spatial units or sampling units used to acquire information about the phenomenon, for example quadrates on the ground or pixels in an image; and (3) the analysis of the data, used to summarize them or make inferences. They then review how changing scales within two of these categories (sampling and analysis) can make a substantial difference to the inferences about the third category (phenomena). The observation scales can influence the inference, and no structure can be detected which is smaller than the size of the sampling unit or larger than the extent of a study (Dungan et al., 2002).

Thus, based on the screening of the literature one can say that the heterogeneity of the real systems at a certain hierarchical level cannot be predicted based on principles. This is in tune with what we expected in the frame of the conceptual model presented in the last subsection. What can be done in the framework of the hierarchical theory is to empirically describe the systems heterogeneity by phenomenological and stochastic models. Partly because the study of spatial structure has arisen more or less independently in various branches of science (e.g. geology, geography, ecology, hydrology, engineering) and with somewhat different motivations and for different applications, a great variety of methods have been proposed in the past decades (Dale et al., 2002). Authoritative methods for the analyses of relevant spatial scales in an ecosystem, using spatially regular or irregular data, are proposed, e.g. by Legendre and Borcard (2003). However, all of these methods are independent on biologically relevant assumptions, for the sake of objectivity, which might be a bad strategy when the interest is to develop integrating models describing biological systems.

An interesting point concerning the up-scaling problem comes from hydrology, where the relative simplicity of the studied phenomena made possible to frequently reach this level of modeling. In many small catchments, the hydrograph is dominated by the displacement of pre-event water. The difference can be illustrated simply within a simplified kinematic wave description of the flow processes but is in reality much more complex because of the effects of heterogeneities, immobile storage, fingering and preferential flows (Beven, 2006). Because of the non-linearities involved, simple averaging of local scale flux relationships are unlikely to produce an adequate description of the closure problem at the elementary watershed scale (Beven, 2006). The author states that the search for appropriate closure schemes is the second most important problem in hydrology of the 21st Century (the most important is providing the techniques to measure integrated fluxes and storages at useful scales). It is absolutely essential that these problems will be addressed in a coherent way, rather than simply assuming that looking across scales will eventually allow "bottom-up" physics-based theorizing to be successful (Beven, 2006). He stresses that these arguments apply to a much wider class of environmental models. This is one of the reasons, from his perspective, why we now have so many different lumped and distributed model formulations to represent catchment responses and why we have mostly been satisfied to find parameterizations acceptable if they work after calibration.

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Kennedy et al. (2006) comes with a methodological contribution. Computational complexity of many models means that modeling all grid cells on a large landscape is computationally burdensome. One approach is to reduce the computational burden of the model by constructing a simplified metamodel that reproduces the bulk properties of a detailed model over a range of input (driver) variables. The structure of the metamodel is developed through hypothesis building and expert understanding of the detailed model and then parameterized by running the detailed model across the full range of input variables (Kennedy et al., 2006). Because of its lower computational burden, this simplified model can be applied to larger landscapes more readily than its more detailed counterpart. Although an elegant and powerful approach, development of the structure for the meta-model can be challenging, especially when multiple feedbacks in the detailed model prevent easy hypothesis building. Most biogeochemical models ignore adjacency effects between cells however a more efficient approach is possible (for any combination of input variables, the model output will be the same regardless where on the landscape it falls; thus, the models are not truly spatial (Kennedy et al., 2006). The authors developed a method to sample the model outputs in input variable space rather than geographic space, and to then use simple interpolation in input variable space to estimate values for the remainder of the landscape.

In conclusion, the up-scaling–downscaling may fail or not depending on the research question, the process that the model attempts to simulate. In the case of abiotic (e.g. hydrological) models, the problem may be satisfactorily tackled, and current research advanced a lot in this directions. However, when coming to biogeochemical models involving the description of the behavior of the biological system involved, the hierarchical approach requests empirical investigations of the heterogeneities in each level, without providing criteria for defining these heterogeneities, let at the decision of the researcher.

The potential linked to the heterogeneity and up-scaling limits, in a hierarchical theoretical framework, refers to the development of a portfolio of top-down and bottom-up models for each kind of ecosystems in the contaminated landscape, after the empirical research for delineating *in situ* the elementary units of models application (e.g. in the way suggested in Fig. 2). The potential in the frame of overlapping systems framework has been already mentioned in the previous subsection.

5. The computational resources to solve the mathematical model

It is not the purpose of this review to enter into the details of this subject. However, we can point out its structure. On the one hand one can expect intra-paradigmatic improvements such as new numerical methods or analytical solutions for special cases. More interesting would be extra-paradigmatic research directions for the improvement of the mathematical modeling of complex systems.

The bioremediations processes are very complex phenomena that imply chemical reactions, diffusion and dispersion of contaminant, chemotaxism of bacteria, water flow through porous soil etc. All that processes have different time and space scale, different production rate that need many parameters to be quantified. The most appropriate mathematical models consist into set of coupled partial differential equations and ordinary differential equation that involve non-linearities, singularities and parameters (Jaffe and Rabitz, 2003; Olson et al., 2006; Wood et al., 2006).

The non-linear character of the equations rise questions of the existence, uniqueness and long time behavior of the solution (Alt and Luckhaus, 1983-the existence results for a class of diffusion equations). Also, the presence of the parameters in the model demands a study of the dependence of the solution on the parameter, the stability of the equilibrium points, the existences of the bifurcation points etc (Alt and Luckhaus, 1983).

Each of the mathematical facts give a deep insight to the physical phenomena and, more than that, can answer if the mathematical model is adequate to describe the physical process. Unfortunately there exists a gap between the complexity of the model and the mathematical answers to the questions since only very simple models can be used for studies based on analytical solutions.

Up to now the extensive use of the mathematical models consists in the numerical simulation of the bioremediation processes. The most used methods for discretizing the space derivatives in partial differential equations are finite element method, finite differences method (Verma et al., 2006; Seuntjens et al., 2004)) and recently, finite volume control (Eymard et al., 2000; Ion et al., 2002; Ion, 2005). For the discretization of the time derivatives, the Euler scheme (explicit or implicit) and Crank-Nicholson scheme (Olson et al., 2006) are most used.

To obtain credible results one needs to know some basic facts about the numerical algorithm, especially the stability of the time-dependent scheme and the convergences of the space and time approximations.

In the numerical resolving process some algorithms need to solve very large dimension non-linear algebraic equation (Verma et al., 2006; Seuntjens et al., 2004) that require very fast computers.

One way to cope with this is the use of parallel computers, which allows the prediction of the effects of bioremediation interventions safely and cheaply in a realistic time-scale. Nevertheless, the data amount resulting from a real field simulation is so large that the only way to analyze it, in an effective way, is to work with its graphical interpretation, converting the huge numerical data volumes into 3D animation (Baracca et al., 2001).

It may be that the development of new mathematical tools, more adapted to biological phenomena, would contribute to changing the landscape of models in this area. For instance, Schryver et al. (2006) use non-linear analyses with artificial neural networks with good results to describe the relationships between groundwater contamination with metals and the structure of bacterial communities as measured by molecular markers. Other examples of neural networks use are Fang and Liang (2003), or Winter et al. (2005). Beside neural networks, another new tool is the Multivariate Adaptative Regression Splines (MARS). It has been used for instance for predicting the denitrification rate based on data sets at European scale (Pinay et al., 2007). However, new mathematical tools as a remedy (ANN) need to be adapted to necessities.

6. Discussions

6.1. Basic science aspects

There is a strong trend towards developing integrated models in environmental sciences. This holds also for the area of metals biogeochemistry. It may be that a change in paradigm is approaching, and, if it is to catalyze it, one needs to have a picture of both the technical aspects of the modeling, and of the theoretical and institutional constraints eventually limiting the integrated approach.

A family of paradigms and theories exists without any in principle priority or right to dominate the market of models development. It's somehow like "anyone's invited", but the principle "first come, first served", holds as well. The cultural differences between various disciplines might had an influence on the evolution of modeling efforts, but proving this is a matter of socio-historical research. Our intention was only to describe the relative strength of the involved actors in the modeling market, and eventually to speculate on the potential future institutional developments. We don't have illusions about the relative strength of the internal (normative, epistemic) driving forces of the scientific endeavor, compared to the external (socio-economic) ones. The first ones are just technological constraints in the production of scientific knowledge, subsumed strategically to the missions of the productive organizations. There is however a logically independent evolution of the scientific aspects compared to the institutional aspects. They can be described independently, but projection of future developments can be done only based on both of them. This review focused on the scientific issues.

Populations, communities, assemblages of communities, etc are entities resulted from the evolutionary processes, and emergent at scales larger than developmental systems. Different parameters should be modeled if we are interested in the management of individuals, or in the management of populations.

There are as many overlapping systems as developmental systems are. Discretizing the system of overlapping basic systems is the delineation of ecosystems problem (related to a certain extent to the fuzzy objects identification problem). This way of thinking is difficult to understand and accept if we work with a Newtonian representation of space, as a reference frame in which the bodies are located. However, if we are familiar with relational, Einsteinian concept of space, the things become simpler. The unpleasant feeling of overlapping things disappears, and we see that what we are stating is only that some structural elements are common to various objects. The simplest way to delineate productive hierarchical levels is to look for structural emergent properties: (populations of) teleonomic entities dependent on resources distributed over large areas, or abiotic emergent features (river systems). However, in the modeling activity the term space in its classic sense can be used, since this is the custom in the development of models for Earth processes.

We have provided arguments that not every system large in (Newtonian) space is necessarily at a higher hierarchical levels than the systems smaller in space. It may be that there is simply a parallel functioning of the systems at different time scales. The eventual disappearing of the human-dominated systems as a result of climate change, for instance, might have no effect on the functioning of bacterial systems, excepting for those living in our bodies and artefacts. So not any small-scale process occurring in an area is relevant for modeling a large-scale process specific to that area, and not any large-scale process provides boundary conditions for relevant for the modeling of small-scale processes.

The unique character of every organism precludes any attempt to model the long-term dynamic of the systems including organisms in their structure. Eventually models of the principles of change can be developed (models of the evolution, in the sense of the theories of evolution). However, short-run models (at time scales smaller than the evolutionary time specific to the organisms in question) can be developed and can be relevant for human decisions if their time window is comparable with the time window of interest for humans. Models at lower and larger time scales have only basic science interest. So a key criterion for the practical interest in models is the compatibility of their time window with time window of decision makers. The same holds for the space window of the models.

6.2. Applied science aspects

The public expects from managers to take rational decisions about the design of management plans of the natural capital, especially in costly context such as those involved by restoration or remediation measures. Mathematical models able to simulate the behavior of the system under different managerial scenarios (e.g. Bauch and Anand, 2004) are thought to be the best tools supporting such rational decisions. These two ideas generated the concept of decision support systems (DSSs) for the management of the natural capital and in particular for the management of the contaminated systems.

A decision support system to assess the potential of phytoremediation in the management of heavy metals polluted soils and sediments (Phyto-DSS) was developed in the frame of an EUsupported project, PhytoDec (Bardos, 2002). The accent of this DSS has been put mainly of phytoextraction, and less on phytoremediation. Robinson et al. (2003) propose a DSS to predict the effect of phytoextraction on soil metal concentration and distribution, as well as the economic feasibility of the process in comparison to either inaction or the best alternative technology. Sometimes the DSS is not the focus of the research, but the consequences for decision makers are explicitly extracted. Wethasinghe et al. (2006) focus on understanding the uncertainty in biokinetic parameters in describing biodegradation under natural and enhanced remediation conditions, and discuss the implication of uncertainty of key parameters on decision-relevant information. They extend the results of their analysis to health risk assessment and risk-based economic analysis. Also, Linacre et al. (2005) use a deterministic actuarial model to show that the uncertainty in project success may significantly increase the perceived costs of remediation works for decision-makers.

At this very general, non-specific level one can ask: *is the goal of taking fully rational decisions reasonable*? To answer this question it is sufficient to be aware that contaminated ecosystems are complex natural systems.

Complex systems prediction is very often not possible not only because the parameters defining the relationships between variables may change (phenotypic evolution), but also because the functional relation itself may also change (genotypic evolution) since they are involved in the process of becoming of the system, generating therefore more novelty (Ramos-Martin, 2003). The complex systems would be characterized by and intrinsic principle of incertitude (Jorgensen and Svirezhev, 2004; Stanciulescu, 2005). Because there are no precise solutions for complexly organized systems, there is no one method for their study. It isn't quite "anything goes", but we cannot tell what might work without trying it (Collier, 2003). In this context it is stated that what can be predicted is not the individual trajectory of the system, but rather some general structural patterns of the whole system (Pahl-Wostl, 1994).

The external control by management requires an anthropogenic controller and goal function, both of which are lacking in a natural system (Fath, 2004). Local, short-term thresholds, which are what we most commonly manage, are constantly shifting due to changes in the spatially extensive and/or slow variables (Groffman et al., 2006). Taking into consideration the non-linearity of the complex systems and there real, non-stochastic, indeterminacy (due to biological evolution, for instance), one can say that there cannot be a final mathematical model of such systems: models assisting the decision making will evolve (in an evolutionary epistemology sense). Consequently, the managers of contaminated lands, as any other managers of ecosystems, should practice a management in agreement with the internal possibilities and trends of the system (Haken and Knyazeva, 2000) and adopt an adaptive rather than a standard rationality. No final decision is possible in principle, hence the emerging paradigm of the "adaptive management". From these considerations arise a first limitation of the mathematical models: models are useful only at tactical decision level, not at strategic level; models cannot uplift the responsibility from the decision maker, and should not be presented as doing this. But here is also the first potential: once correctly evaluated, models are the most useful tools for rational decision making about contaminated lands, if we keep a grain of relativity.

As we have seen, the number of models dedicated to the biogeochemical cycles of metals in terrestrial and wetland systems is low. The commercial software and the published models developed by the study of contaminated areas are relatively simplistic. But the accumulated knowledge is consistent (Hazen and Tabak, 2005; Tabak et al., 2005), which provides a base for developing more elaborated models, whether in the context of bioremediation, or of the risk assessment for environmental management (Chapman and Wang, 2000; Apitz and Power, 2002; Andretta et al., 2006).

There are many mechanisms involved in the mobilization of metals by (Kabata-Pendias, 2001; Antoniadis and Alloway, 2002; Hafner et al., 2005). Beside the knowledge of the simple existence of these mechanisms there is also quantitative information about how they work. What is missed in this field is a general, not contingent, quantitative knowledge concerning the relationships between control parameters and metals mobility in real terrestrial systems. Such knowledge can be provided only by mathematical models integrating the large numbers of involved variables. The difficulty which blocked the refinement of this kind of models is related to the large heterogeneity of the control parameters, the distribution in space, as well as to the large number of relationships between the control parameters for each metal. In these conditions, to set up mathematical relations between the control parameters of metals mobility and their mobility proved to be not yet feasible *in situ*.

The new mathematical tools mentioned in the previous subsections could be applied in order to describe relationships between the control parameters of metals mobility in the uppers soil horizons, on the one side, and the contamination degree of the groundwater and of plants. Extensive data sets needed for the analyses are often already available. Once the analyses are performed, one would have a holistic phenomenological description of the relationships in mathematical forms at site scale.

One limitation of this approach is to uncover mathematical laws with 1 member of the reference class (the studied site). This limitation can be surpassed only by studying a population of sites across large gradients. There is a large opportunity here: long-term research network for the study of contaminated sites as basic science experimental areas.

Another limitation of the holistic approach is that the discovered mathematical laws will give no indication about the mechanisms supporting them. This indication can be provided only by a reductionist (bottom-up) approach. By now reductionism has created unwarranted biases in certain mathematical models and experimental designs. Reductionist models may incorporate unnecessary lower level details that compromise verisimilitude and predictive success. However, without this approach one cannot have an image on the involved mechanisms, and thus on the possibilities of controlling the metals' mobility. Therefore one can proceed this way, having in mind that the reductionist frame has to be re-verified after each step of upgrading and prediction.

Also, one could investigate the possibility of developing (bottom-up) mechanistic models of metals' behavior under the (top-down) constraint the results of the holistic modeling (as suggested in Fig. 1). The main focus from the reductionistic perspective will be on the difficulty of allocating values to the parameters under high field heterogeneity. The heterogeneity problem can be dealt with, as we have seen, by empirical research for delineating *in situ* the elementary units of models application (systems identification) and using a portfolio of models covering the diversity of the elementary units. Different processes require different space–time scale of the elementary units and models' development. Programming in GIS can then be used for up-scaling the models' results from the elementary units of application to the site and for linking the results of the models with different space–time scale (Iordache and Bodescu, 2005).

7. Conclusions

We performed an analysis of a family of models relevant for the integrated modeling in metals biogeochemistry, by two approaches: a hierarchical one, and a disciplinary one. The hierarchical approach was done in the theoretical framework accepting the existence of a hierarchy of ecological systems, and split the population of analyzed models into classes based on their relevance for various biological and ecological hierarchical levels. We identified two types of integrated models: between abiotic and biotic components at the same levels, and between biotic components across hierarchical levels. The complementary, disciplinary approach, focused on bioremediation models. The delineation of the class of bioremediation models proved that practically all biogeochemical models are relevant for this class, while only some of the analyzed model have been explicitly declared as 'bioremediation models'. Based on these analyses we identified a set of research directions, and proposed an alternative, complementary theoretical framework for basic research problems.

With regard to bioremediation models, we could identify three levels of potential for development. The strategic potential: if correctly evaluated, models in bioremediation are the most useful tools for rational decision making. The tactical potential, of reactive type: internalizing the future knowledge arising from systems biology, and many other fields such as cognitive sciences biogeochemistry, ecotoxicology, soil science or plant science. The tactical potential of proactive type: (a) Combing physico-chemical mechanistic "in principle" approach with uncovering the mathematical laws directly at the bio-geo level by empirical research and use of the existing new mathematical tools and (b) Empirical research for delineating *in situ* the elementary units of models application and the use of programming in GIS and new generation GIS software for up-scaling the models' results from the elementary units of application to the site. And, finally, the operational potential: long-term research network for the study of contaminated sites as basic science experimental areas for implementing the proactive operational potential.

Acknowledgements

We wish to thank to the organizers of the Symposium on Remediation in Jena, October 2006, "Bio-Geo-Interactions and reactive transport", and especially Prof. Georg Büchel and Prof. Erika Kothe, for the challenging opportunity to start the preparation of this article, and two anonymous reviewers and Dr. Dirk Merten for valuable criticism of a previous version of the article. The analyses of the models were prepared in the frame of research projects funded by the Romanian programs CNCSIS, PNCDI2 (Partnerships CNMP and Ideas UEFISCSU), and by the German program DAAD.

Appendix 1

See Table A1 for details.

Appendix 2

See Table A2 for details.

Appendix 3

See Table A3 for details.

Table A1. Articles dealing with models directly relevant for the biogeochemistry of metals.

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Choi et al. (2006)	Vertical concentration profiles of the model species and estimates of fluxes of the solute substances across the sediment–water interface	1	1	1	Numerical (finite difference). Transport part and reaction part separated in order to surpass the non-linearity due to Monod kinetic	No	D	One-dimensional mass-balance, effects of plants accounted by source–sink terms, root density function	Deductive (reactive transport model)
Seuntjens et al. (2004)	Root-zone modeling of heavy-metal uptake and leaching in the presence of organic ligands	1	1	2	Numerical (finite difference, Newton–Raphson algorithm, Courant criterion for advective transport, the von Neumann criterion for dispersive transport)	Yes	D	Model describes leaching and uptake of heavy metals in the plant root zone. The model couples rhizosphere processes with convective–dispersive transport of the components into deeper soil layers	Deductive model
Jorgensen (1976)	An ecological model for heavy-metal contamination of crops and ground water	1	3	2	Analytical	No	D	The model is based upon the hypothesis that, at least for the most toxic metals – Cd, Pb and Hg – uptake by crops will take place as a first-order reaction. The distribution of heavy metals between soil and soil water is, for a given type of soil, described by means of a distribution coefficient	Inductive
Yeh et al. (2001)	Modeling and measuring biogeochemical reactions: system consistency, data needs, and rate formulations	1	3	2	Numerical. Gauss–Jordan elimination. QR decomposition. Numerical integration for ODE	No	D	Bioreduction of ferric oxide by dissimilatory iron reducing bacteria (DIRB)	Ad-hoc and reaction based formulations deductive parts and empirical functions
Schryver et al. (2006)	Application of non-linear analysis methods for identifying relationships between microbial community structure and groundwater geochemistry	1	3	3	NA	Yes	D	Models are constructed using feedforward artificial neural networks (NN) to predict PLFA classes from geochemistry. Non-linear principal components (NPC) are extracted from the PLFA data using a variant of the feedforward NN	Inductive
Mino et al. (2006)	Modeling lead bioavailability and bioaccumulation by *Lumbriculus variegatus* using artificial particles. Potential use in chemical remediation processes	2	1	1	NA	No	S	Artificial particles, specifically a diverse selection of chromatographical resins, have been used as a useful experimental model to predict the bioavailability and bioaccumulation	Inductive (experimental-based model)

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Table A1. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Verma et al. (2006)	Simulation of heavy-metal dynamics in soil and uptake by plant roots	2	1	1	Numerical (finite difference method)	No	D	Models rhizofiltration. The governing non-linear partial differential equation is solved numerically using Picard's iterative technique	Inductive parts (Van Genuchten and Nielsen equations) + deductive parts (Darcy 's law + Richards equation)
Whiting et al. (2003)	Applying a solute transfer model to phytoextraction: zinc acquisition by *Thlaspi caerulescens*	2	1	1	Analytical	No	S	Model based on data collected for a few soil parameters. Solute transfer model is developed to predict the concentration of Zn in the rhizosphere solution	Inductive
Rainbow (2007)	Trace metal bioaccumulation. Models metabolic availability and toxicity	2	1	2	Analytical	No	D	Accumulated metal concentrations are interpreted in terms of different trace metal accumulation patterns, dividing accumulated metals into two components – metabolically available metal and stored detoxified metal	Inductive
Robinson et al. (2002)	Phytoaccumulation, metal uptake from contaminated soils	2	1	2	Analytical. Formulas of metal amount taken by the plants are given	Yes	D	Pot trials and *in situ* analyses of plant–soil interactions are integrated to produce a generalized model that predicts plant–metal uptake	Inductive. Empiric formulas are given
Robinson et al. (2006)	Phytoremediation for the management of metal flux in contaminated sites – review	2	1	2	Analytical	Yes	D	An outlook of the phytoremediation models, divided in phytoextraction and phytostabilization. Advantages and the implementation difficulties for each method are presented	Inductive
Luoma and Rainbow (2005)	Biodynamics as a unifying concept	2	1	2	Analytical (ODE systems for biodynamic model)	Yes	D	Biodynamic metal bioaccumulation model combines targeted, high-quality geochemical analyses from a site of interest with parametrization of key physiological constants for a species from that site	Inductive (compiled results from publications that forecast species-specific bioaccumulation)
Robinson et al. (2003)	Phytoextraction and economic viability of the models	2	1	4	Analytical. Formulas of metal amount taken by the plants are given. Formulas of the costs and profitability	Yes	D	Model of metal accumulation as a function of transpiration and bioavailable metal. Economical side of the model. Costs and benefits	Inductive parts – empiric formulas are given. Deductive parts – costs and economic viability formulas

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Dimopoulos et al. (1999)	Estimation of metal concentration in grasses	2	2	2	NA	No	S	Neural networks. The proposed model is a multilayer perceptron (MLP) trained by backpropagation	Inductive
Klok et al. (2007)	Field effects of pollutants in dynamic environments. A case study on earthworm populations in river floodplains contaminated with heavy metals	2	2	2	NA	No	S	The average flooding was used to classify each site. A non-linear exponential curve of the form exp(a + bx) was used to relate the average weight to heavy metals. The presence/absence of the species *L. rubellus* was modeled by means of logistic regression	Inductive
Chow et al. (2005)	Exposure of mobile animals to metals	2	2	3	NA	Yes	S	Empirical function of exposure followed by Monte Carlo simulation of habitat use	Deductive + individual based landscape (GIS) inductive model
Becker et al. (2006)	The spatial relationship between microbial community dynamics and local heavy-metal contamination from a chronically contaminated site	2	3	2	Numerical	Yes	S	Examines the microscale environment in soils where contaminant distribution is heterogeneous, to determine local effects on microbial activity and diversity, using geostatistical tools	Deductive
Lung and Light (1996)	Modeling copper removal in wetland ecosystems. The quantification of the assimilative capacity of heavy metals by wetland ecosystems	2	3	2	Analytical (Nielsen's copper kinetics equation)	No	D	Model has been developed to simulate the fate and transport of copper introduced to a wetland ecosystem. Modeled water quality variables include phytoplankton biomass and productivity, macrophyte biomass, total phosphorus in the water column, dissolved copper in the water column and sediments, particulate copper in the water column and sediments, and suspended solids	Deductive parts (kinetics equation) + inductive parts (model calibration)
Hobbelen et al. (2006)	Effects of heavy metals on the structure and functioning of detritivore communities in a contaminated floodplain area	2	4	2	NA	No	S	Multivariate correlations between the distribution of metals and other control parameters and the structure of the community	Inductive
Hobbelen and Gestel (2007)	Using dynamic energy budget modeling to predict the influence of temperature and food density on the effect of Cu on earthworm-mediated litter consumption	2	4	2	Analytical	No	D	The model can describe mass fluxes, but this study focused on energy fluxes. It uses two state variables: the volume of the structural body mass, *V*, and the energy density, *E*	Inductive

Table A1. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Péry et al. (2006)	Mechanistic models to perform population risk assessment	2	1, 2	2	Analytical (tools to identify compounds physiological mode of action, to estimate toxicity parameters from mechanistic models at individual level and to change scale from individual to population)	No	S	Four models: a kinetics model; an energy-based effects model, linking effects on the life cycle and compound body residues, a matrix approach to derive population growth rate, and an energy-based population model to derive carrying capacity. The whole system is applied to cadmium and copper	Inductive (coupling of four models)
Marinussen and Zee (1997)	Exposure of mobile animals to metals	2	1, 2	2, 3	Toxicokinetic equation solved analytically	Yes	D/S	One-compartment toxicokinetic model, geostatistical interpolation, Monte Carlo simulation of habitat use	Deductive parts + geostatistical inductive model + individual based landscape model
Cormont et al. (2005)	Exposure of mobile animals to metals	2	1, 2, 4	2	NA	Yes	D/S	Models on bioaccumulation based on a combination of empirical regressions, empirical equations, and deterministic assumptions	Inductive parts + deductive parts + individual based landscape model – cellular automata (dedicated code)
Weber et al. (2006)	Iron speciation in interaction with organic matter: modeling and experimental approach	3a	NA	1	NA	No	S	NICA-Donnan model used here assumes a bimodal continuous distribution for binding constants. Two different types of sites are distinguished on the basis of the average proton affinity constant values	Inductive (model calibration)
Benedetti et al. (1996)	Metal ion binding by natural organic matter	3a	NA	2	NA	No	S	Model evaluates Cu and Cd binding from three field systems, a mountain lake and two sandy soils, using model parameters calibrated for natural organic matter analogues with laboratory measurements. NICCA Donnan model takes into account both competitive and electrostatic effects	Inductive (model calibration), empirical

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Christensen et al. (1999)	Complexation of Cu and Pb by DOC in polluted groundwater: a comparison of experimental data and predictions by computer speciation models	3a	NA	3	NA	No	S	WHAM and MINTEQA2 models. The WHAM model overestimated the complexation of Cu and Pb in the groundwater samples, particularly at high degrees of complexation. MINTEQA2 includes a submodel for estimations of the complexation of metals with dissolved organic matter	Inductive (model calibration)
Dijkstra et al. (2004)	Leaching of heavy metals from contaminated soils	3	NA	1	NA	No	S	Mineral saturation indices, solution speciation, and sorption processes were calculated with a speciation and transport model set up in the ORCHESTRA modeling framework	Inductive
Ernstberger et al. (2002)	Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS	3	NA	1	Numerical	No	S	Dynamic numerical model of DGT induced fluxes in soils (DIFS). It assumes first-order exchange between solid phase and solution and diffusion transport in both the soil solution and the hydrogel. The DIFS model fitted changes in accumulated mass with time very well	Inductive
Ge et al. (2005)	Modeling of Cd and Pb speciation in soil solutions by WinHumicV and NICA-Donnan model	3	NA	1	NA	No	S	Tested the effectiveness of two models, WinHumicV and the Non-Ideal Competitive Adsorption (NICA)-Donnan model. WHAM Model V accounts for a wide range of metal binding strength by considering metal complexation at single HC binding sites. NICA-Donnan model considers that the distribution of site strengths is composed of two parts, which are most likely due to the carboxylic- and phenolic-type groups	Inductive, presentation of a software dealing with two models summarily presented
Tonkin et al. (2002)	Modeling metal removal onto natural particles formed during mixing of acid rock drainage with ambient surface water	3	NA	1	NA	No	S	Small- and large-scale mixed experiments. Linear regression analyses were used in all subsequent error analyses	Inductive, PHREEQC dedicated software based on empirical model

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Table A1. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Tusseau-Vuillemin et al. (2003)	Dynamic numerical model to characterize labile metal complexes collected with diffusion gradient in thin films devices	3	NA	1	Numerical (system of differential equations solved numerical, iteratively integration using an explicit Eulerian scheme, conservation equations, diffusion equation, chemical mass balance)	No	D	Model describes the diffusion of free metal, ligand, and a metal complex from the bulk solution to the chelating resin via the hydrogel and the dynamics of association and dissociation of these species	Deductive
Michel et al. (2007)	Comparison of different approaches for heavy-metal transport in acidic soils	3	NA	2	Analytical models + calibration + statistical evaluation	Yes	D/S	Empirical and mechanistic models were tested: Sorption isotherms considering concentrations (Freundlich-1, Langmuir-1) or ion activities (Freundlich-2, Langmuir-2), cation exchange (CE) and competitive sorption (CSM)	Deductive (calibration + testing of empirical models)
Unsworth et al. (2006)	Model predictions of metal speciation in freshwaters compared to measurements by *in situ* techniques	3	NA	2	NA	No	S	Measurements of trace metal species *in situ* in a softwater river, a hardwater lake, and a hardwater stream were compared to the equilibrium distribution of species calculated using two models, WHAM 6, incorporating humic ion binding model VI and visual MINTEQ incorporating NICADonnan. Diffusive gradients in thin films (DGT) and voltammetry at a gel integrated microelectrode (GIME) were used to estimate dynamic species that are both labile and mobile. The Donnan membrane technique (DMT)	Inductive
Sekhar et al. (2008)	Hydrogeochemical modeling of organo-metallic colloids in the Nsimi experimental watershed, South Cameroon	3	NA	3	Numerical (the transport part is solved using an operator split approach wherein a finite volume method is used for solving the advective equations while a classical finite difference method is employed for solving the dispersive equations)	Yes	D	The processes of adsorption, aqueous speciation and mineral precipitation/dissolution are represented in the model	Deductive

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Zhu (2003)	A case against K_d-based transport models: natural attenuation at a mill tailings site	3	NA	3	Analytical + numerical results (dedicated code)	Yes	D	Contaminant transport model using a multi-component coupled with reactive mass transport model compared to a distribution coefficient (K_d)-based transport model	Deductive. Dedicated code
Beck et al. (2006)	Geometric construction of traveling waves in a bioremediation model	4	3	1	Hybrid. Geometrical construction of the solution and the numerical experiment to compare the results.	No	D	Non-dimensional form of the Oya–Valocchi bioremediation model. Geometrical construction of the traveling waves	Deductive model Geometrical construction of the traveling waves
Shultis et al. (1999)	Determining soil contamination profiles (Cr) from intensities of capture-gamma rays using above-surface neutron sources	5	NA	1	Analytical (PGNAA model, integral equations) + numerical (discretization of the PGNAA model, piece-wise linear approximation, piece-wise quadratic approximation)	Yes	D	Method of linear regularization with and without an iterative positivity constraint, the Backus–Gilbert method, and the maximum entropy method are applied to the soil contamination problem	Deductive, well funded from mathematical point of view
Farrand and Harsanyi (1997)	Mapping the distribution of mine tailings the Coeur d'Alene River Valley, Idaho, through the use of a constrained energy minimization technique	5	NA	3	Analytical (constrained vectorial minimization problem)	Yes	D	Constrained energy minimization (CEM) technique, which on a pixel-by-pixel base maximizes the response of the target signature and suppresses the response of undesired background signatures. Solves constrained minimization problem	Deductive, vectorial analyses

T = type of model (2 – biotic, 3 – abiotic, 3a – involving interaction with organic matter, 1 – mixed (abiotic and biotic), 4 – theoretical, 5 – methodological), B = biological hierarchical level (1 – organism, 2 – population, 3 – trophic-dynamic module, 4 – food web), E = ecological hierarchical level (1 – subsystem of an ecosystem, 2 – ecosystem, 3 – landscape), D/S = deterministic/stochastic.

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Table A2. Articles dealing with models relevant for biogeochemistry of organic pollutants.

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Brun and Engesgaard (2002)	Modeling of transport and biogeochemical processes in pollution plumes	1	3	3	Analytical (+ literature survey)	Yes	D	Two-step process models which rely on partial equilibrium approach (PEA), that assumes the organic degradation step and not the electron donor–acceptor consumption step, is rate limited. A three-dimensional, two-step PEA model is developed	Deductive (literature survey, mainly chemistry)
Ulbrich et al. (1997)	Estimation of microbial growth under conditions of contaminated sediment input	1	3	2	Numerical	Yes	D	Submodel of sediment transport and submodel of microbial growth	Deductive (simplified advection–diffusion equation, logistic equation and a Michaelis–Menten-like approach)
Clement et al. (1996)	Macroscopic models for predicting changes in saturated porous media properties caused by microbial growth	1	3	3	Analytical (equations that modes changes in porosity specific surface area)	No	D	Macroscopic estimations of average biomass concentration. Model based on a set of analytical expressions that models changes in porosity, specific surface area, and permeability caused by biomass accumulation in porous media	Deductive
Clement et al. (1997)	Microbial growth and transport in porous media under denitrification conditions	1	3	3	Hybrid (analytical equations and numerical determination of the detachment coefficients)	No	D	One-dimensional porous media columns under anoxic conditions. Advection and dispersion equations and microbial and accumulation phenomena are described	Deductive parts (deduced analytical equations) + inductive parts (least squares method for determining coefficients)
van Breukelen et al. (2004)	Reactive transport modeling of biogeochemical processes and carbon isotope geochemistry inside a landfill leachate plume	1	3	3	Analytical + numerical (PHREEQC-2 code)	No	D	Biodegradation of dissolved organic carbon (DOC) was simulated assuming first-order oxidation of two DOC fractions with different reactivity, and was coupled to reductive dissolution of iron oxide	Deductive
Clement et al. (2000)	Natural attenuation of chlorinated ethene compounds: model development and field-scale application at the Dover site	1	3	3	Numerical (MODFLOW and RT3D codes)	Yes	D	Multi-dimensional and multi-species reactive transport model was developed. The model can simulate several simultaneously occurring attenuation processes including aerobic and anaerobic biological degradation processes. The model has 3 components: groundwater flow contaminant transport, and biogeochemical reactions	Deductive

Bushey et al. (2006a)	Developing of a model for cyanide species uptake by willow	2	1	1	Analytical	No	D	A physiologically based model describing plant uptake, transport, and metabolism of cyanide species. Introduction of an empirical equation	Inductive parts + deductive parts + individual-based model
Bushey et al. (2006b)	Parameter estimations of the plant uptake model (see Bushey et al., 2006a)	2	1	1	NA	No	D	Parameter estimation based on experimental data, using the least-squares optimization	Deductive
Mezzari et al. (2004)	Mathematical modeling of RDX and HMX in poplar tissue culture	2	1	1	Analytical. ODE systems are given for three different model parameters estimated with linear regression	Yes	D	Three different models to represent the transformation pathways of RDX and HMX within plant cells; ‘‘green liver’’ model. Models composed by ODE systems	Three inductive models are presented
Newman and Jagoe (1996)	Bioaccumulation models with time lags: dynamics and stability criteria	2	1	1	Analytical (stability criteria for ODE)	No	D	The addition of realistic time lags to the simple bioaccumulation models. The implications in ecotoxicology of the deterministic oscillations in concentrations	Inductive parts (empirical assumptions) + deductive parts
Sibly et al. (2005)	Population-level assessment of risks of pesticides to birds and mammals in the UK	2	2	3	NA	Yes/No	S/D	Two types of model: simple life-history models distinguishing two life-history stages, juveniles and adults; and spatially explicit individual-based landscape models	Deductive
Sung et al. (2006)	Estimation of microbial biomass	2	3	1	Numerical (fully implicit finite-difference method)	No	D	One-dimensional mass-balance of organic carbon coupled with Monod equation rate of microbial growth, diffusive supply of substrate from the root.	Deductive (organic carbon mass-balance and microbial growth model)
Thoma et al. (2003)	Mathematical model of phytoremediation for petroleum-contaminated soil	2	3	1	Analytic model + numerical testing (fourth-order adaptive solvers (Runge–Kutta) + backward differentiation formulas and the modified Rosenbrock method)	Yes	D	Model for root length density that combines the generally accepted spatial (exponential decrease with depth) and temporal (sinusoidal) variability of root length. The model is based on variable volume compartments that have individual first-order degradation rate constants	Deductive parts + inductive parts (length density empirically described)
Johnson et al. (2003)	Contribution of anaerobic microbial activity to natural attenuation of benzene in groundwater	2	3	2	NA	No	D	Anaerobic biodegradation of hydrocarbons, using a variety of terminal electron acceptors (TEAs). Models redox-dependent, differential degradation rates. Equations for degradation rate, mass-balance of the bacterial group	Deductive parts (modifications of the equations that model the microbial growth rate)

Table A2. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Olson et al. (2006)	Mathematical modeling of chemotactic bacterial transport through a two-dimensional heterogeneous porous medium	2	3	2	Analytical (Knudsen diffusion, transport equation, Darcy equation, bacterial conservation equation) + Numerical (Krank Nicholson finite difference)	Yes	D	The two-dimensional domain subsurface environment containing a region of low permeability with trapped contaminant surrounded by regions of higher permeability. Influence of Knudsen diffusion upon bacterial motility and chemotactic sensitivity	Deductive
Simpson et al. (2003)	Improving the worthiness of the Henry problem as a benchmark for density-dependent groundwater flow models	2	3	2, 3	Analytical	No	D	Anaerobic biodegradation of hydrocarbons, using a variety of terminal electron acceptors (TEAs). Models redox-dependent, differential degradation rates. Equations for degradation rate, mass-balance of the bacterial group	Deductive parts (modifications of the equations that models the microbial growth rate)
MacDonald et al. (1999)	Mass transfer limitations for macroscale bioremediation modeling and implication on aquifer clogging	2	3	3	Analytical	Yes	D	Two different methods were used: (a) effectiveness factor approach based on the traditional biofilm model (b) effectiveness factor approach based on the up scaling approach.	Deductive
Luna et al. (2005)	Spatial bioaccumulation modeling in a network of bayous	2	4	2	Numerical (fourth-order Runge–Kutta, SNBM dedicated software)	Yes	D	Model of the bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in aquatic food webs with SNBM software. The bioaccumulation model is a time-dependent, set of first-order ordinary differential equations that are solved numerically	Deductive (dedicated software on a given model)
von Stackelberg et al. (2002)	The use of spatial modeling in an aquatic food web to estimate exposure and risk	2	4	2	analytical (general decomposition of the probabilities)	Yes	S	Models implemented in this study include a spatial submodel to account for spatial and temporal characteristics of fish exposure and a probabilistic adaptation of the Gobas bioaccumulation model to account for temporal variation in concentrations of polychlorinated biphenyls (PCBs) in sediment and water	Deductive (extension of a method)

Barry et al. (2002)	Modeling the fate of oxidizable organic contaminants in groundwater. Subsurface contamination by organic chemicals	3	NA	2	Hybrid. analytical parts (conservation equations, flow and transport, interphase mass transfer, biogeochemical reaction modeling) + numerical (split-operator (SO) algorithms)	Yes	D	Comprehensive modeling framework, including geochemical reactions and interphase mass transfer processes such as sorption/desorption, non-aqueous phase liquid dissolution and mineral precipitation/dissolution, all of which can be in equilibrium or kinetically controlled	Deductive parts + inductive parts
Clement et al. (2004)	Analytical model for computing residence times near a pumping well	3	NA	3	Numerical (dedicated code RT3D)	Yes	D	Quantification of the dissolution characteristics of a trichloroethene dense non-aqueous phase liquid (DNAPL) source entrapped in a three-dimensional saturated sand tank model	Deductive parts (modified version of a dissolution model) + inductive parts (empiric factor)
Hammond et al. (2002)	Modeling multicomponent reactive transport on parallel computers using jacobian-free Newton–Krylov with operator-split preconditioning	3	NA	3	Numerical (parallel algorithms, finite volume method, Newton–Raphson method, iterative solver, FGMRES, Newton–Krylov method)	Yes	D	Sequential degradation of PCE in 3D heterogeneous flow. Introduces technique for solving the non-linear system of equations involved with multicomponent geochemical transport. The Jacobian-free, Newton–Krylov method implemented with PARTRAN code	Deductive
Li et al. (2007)	An integrated fuzzy-stochastic modeling approach for risk assessment of groundwater contamination	3	NA	3	Numerical (Monte Carlo method)	No	S	(a) Monte Carlo simulation for the fate of contaminants in the subsurface through a 3-D multiphase multi-component numerical model to account for stochastic uncertainties, (b) examination of simulation results that were expressed as cumulative distribution functions,(c) quantification of environmental guidelines and health impacts using fuzzy membership functions acquired from a questionnaire survey, (d) quantification of environmental and health risks based on fuzzy and stochastic inputs, and (e) assessment of general risk levels based on a fuzzy logic approach	Deductive, reactive transport model, assessment of general risk levels based on a fuzzy logic approach
Mugunthan and Shoemaker (2004)	Time-varying optimization for monitoring multiple contaminants under uncertain hydrogeology	3	NA	3	Numerical. Optimization algorithms	Yes	S	A new algorithm (MS-ER) is presented. A simulated annealing algorithm (SA-ER) and a genetic algorithm (GA) are presented, together with the implementing costs	Deductive

Table A2. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Prechtel et al. (2006)	The evaluation of contaminated sites with respect to their potential for natural attenuation to relevant orders of magnitude in concentration and reasonable time scales requires estimating future plume behavior	3	NA	3	Numerical (non-standard locally mass conservative finite element discretizations)	Yes	D	Universal software tool capable of reflecting the relevant processes of contaminant propagation and transformation, including, for example carrier facilitation or general temperature dependent decay reactions	Deductive (numerical simulations, not detailed)
Rolle et al. (2005)	Contaminant transport scenario modeling as a tool for a critical evaluation of natural attenuation	3	NA	3	Numerical (spatial and temporal discretization)	Yes	D	The influence of different parameters (e.g. transversal dispersivity, groundwater velocity, recharge, biodegradation rates, availability of electron acceptors, etc.) on steady state plume length	Inductive
Mercer et al. (2007)	A non-intrusive neutron device for *in situ* detection of petroleum contamination in soil	5	NA	2	NA	Yes	D	The method extends the capability of common soil moisture gauges, by using two neutron detectors, one located near the source and the other far from it	Inductive
Quezada et al. (2004)	General method for solving coupled multi-dimensional, multi-species reactive transport equations	5	NA	3	Hybrid (three stages, first two are analytical, Laplace transformation applied, and finding the analytical solution of the transformed system, and the last stage is numerical by finding the numerical-inverse Laplace transform)	Yes	D	A three-step transformation process, where Laplace and linear transformation procedures are applied sequentially to uncouple the governing set of coupled partial differential equations. The problem is solved using an elementary solution in the uncoupled domain. The computed concentration values are then inverted using inverse linear and inverse-Laplace transform steps to compute the final results	Deductive

Legend as in Table A1.

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Table A3. Other articles indirectly relevant for the modeling of biogeochemical processes.

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Meile et al. (2003)	Explicit representation of spatial heterogeneity in reactive transport models: application to bioirrigated sediments	1	1	1	Analytic model (flow equation for an incompressible fluid) + numerical testing. Galerkin finite element, conjugate gradient and preconditioned techniques and direct solvers	Yes	D	A model that explicitly calculates the effect of flushing of macrofaunal burrows on dissolved chemical species distributions	Deductive
Park and Jaffe (1996)	Vertical distribution of redox potential in sediments, with bioturbation included as facilitating dispersion	1	1	1	Numerical (finite difference). To eliminate the non-linearity, the concentration in the denominator of the Monod kinetic term (*C*) is replaced by the concentration obtained during the previous iteration	No	D	Six sequential microbial reactions, subsequent chemical reactions, and one-dimensional (vertical) advective/dispersive mass transport	Deductive (reactive transport model) + simplifying assumptions about redox potential at non-equilibrium
Meysman et al. (2007)	Quantifying biologically and physically induced flow and tracer dynamics in permeable sediments	1	1	2	Analytic model (flow equations, reactive transport model) + numerical results	Yes	D	A quantitative description of pore water flow and the associated transport of various solutes and particles, in presence of bioturbation. Widely different problems modeled by the same flow and tracer equations	Deductive (simplification of the momentum equation). No details about the numerical implementation
Berg and Driessen (2001)	Water uptake in crop growth models for land use systems analysis	1	3	3	Analytic	Yes	D	Examines simple approaches that could be used in crop growth simulation models for application in land use systems analysis	Deductive (review of few methods)
Cabelguenne and Debaeke (1998)	Experimental determination and modeling of the soil water extraction capacities of crops of maize, sunflower, soya bean, sorghum and wheat	1	3	2	NA (experimental)	No	D	Calculated available moisture, to describe the water extraction capacities of the five crops, and formalize these descriptions	Inductive
Clausnitzer and Hopmans (1994)	Simultaneous modeling of transient three-dimensional root growth and soil water flow	1	3	2	Numerical (3D finite-element)	Yes	D	Root apices are translocated in individual growth events as a function of current local soil conditions. A three-dimensional finite-element grid over the considered soil domain serves to define the spatial distribution of soil physical properties and as framework for the transient water flow model	Deductive

Table A3. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Lindenschmidt et al. (2007)	Structural uncertainty in a river water quality modeling system	1	3	2	Analytical (Monte Carlo uncertainty analysis)	Yes	S	Three models coupled from the WASP5 package (Water quality Analysis Simulation Program): DYNHYD (hydrodynamics), EUTRO (dissolved oxygen, nutrient and phytoplankton dynamics) and TOXI (transport and transformation of sediments and micro-pollutants)	Inductive (empirical relationships using regression curves derived from field data)
Thullner et al. (2005)	Modeling the impact of microbial activity on redox dynamics in porous media	1	3	3	NA	No	S	Expressions for microbial growth are incorporated into a geochemical reaction network linking redox reaction rates to the activity of the microorganisms. A flexible simulation environment, the Biogeochemical Reaction Network Simulator (BRNS) is used for this purpose	Deductive, not involving too much mathematics.
Kennedy et al. (2006)	A method to efficiently apply a biogeochemical model to a landscape	1	3	3	Numerical (3D interpolation)	Yes	D	A method to sample the model outputs in input variable space then use simple interpolation in input variable space to estimate values for the remainder of the landscape	Inductive
Bengough (1997)	Modeling rooting depth and soil strength in a drying soil profile. Combined root growth and water extraction	2	1	1	Analytical	No	D	Root elongation rate is calculated as a function of the penetrometer resistance which is determined by the soil water contents	Inductive
Darrah et al. (2006)	Modeling the rhizosphere: a review of methods for ‘upscaling’ to the whole-plant scale	2	1	1	Analytical (initial-value, parabolic, second-order partial differential equation (PDE) with two boundary conditions)	No	D	Minimal mechanistic model assumes that the outer boundary of the rhizosphere is of infinite extent or imposes a zero-flux boundary at some radial position calculated as a function of root density at harvest	Deductive
Galassi et al. (1989)	Parameter estimation and the simulation of a simple bioconcentration model	2	1	1	Numerical (results of the BIOCON software)	No	D	Two compartments model (environment and organism) and the uptake and release rate are assumed to be simply proportional to the toxicant concentrations respectively in the medium and in the organism	Deductive, results for software, description of the system of equations, nothing about the numerical solution from behind

Nowack et al. (2006)	Verification and intercomparison of reactive transport codes to describe root-uptake	2	1	1	Hybrid. Analytical solution. Numerical solutions. (Runge–Kutta method,linear interpolation)	Yes	D	Implementing and testing a rhizosphere model with three geochemical computational tools (ORCHESTRA, MIN3P, and PHREEQC).	Inductive parts + deductive parts
Bauch and Anand (2004)	Mathematical analysis of a simplified forest growth model, for restoration	2	2	2	Hybrid, analytical deduced ODE + numerical solutions for exemplification	Yes	D	Population dynamic model (ordinary differential equation model)	Deductive modeling. Simplified assumptions on a given model
Manel et al. (1999)	Comparing discriminant analysis, neural networks and logistic regression for predicting species distributions: a case study with a Himalayan river bird	2	3	3	Analytical	No	S	Multiple discrimant analysis (MDA), logistic regression (LR) and artificial neural networks (ANN) in predicting this species' presence or absence from 32 variables describing stream altitude, slope, habitat structure, chemistry and invertebrate abundance	Inductive
Berg and Bengtsson (2007)	Temporal and spatial variability in soil food web structure	2	4	2	Hybrid. Analytical + numerical simulation on dedicated codes ANCOVA, StatView 5 and SuperANOVA	No	S	(1) the temporal and spatial variability of a detrital food web and its components, (2) the effect of taxonomic resolution on the perception of variability over time and across space, and (3) the importance of organic matter quality as an explanatory factor for variability in food web composition	Inductive, codes without too much explanations
Herendeen and Hill (2004)	Growth dilution in multilevel food chains	2	4	2	Analytical + numerical	No	D	The propagation of growth dilution in all trophic levels of a food chain. Study of concentration as well as overall mass of contaminant in each level, for different functional relationships between levels.	Inductive parts + deductive parts
Voinov et al. (2004)	Modular Ecosystem Modeling	2	4	2	Analytical	Yes	D	Modular approach. Developing collections of modules simulating various components of ecosystems or entire ecosystems under various assumptions and resolutions	Inductive parts (choosing the best model for each module) + deductive parts (the already given models)
Hughes et al. (2007)	Reciprocal relationships and potential feedbacks between biodiversity and disturbance	2	4	2	NA	No	S	Conceptual model that decomposes the relationships into component parts, considering sequentially the effect of diversity on disturbance severity, and the effect of realized disturbance on diversity loss, subsequent recruitment, and competitive exclusion.	Inductive

Table A3. (*continued*)

Source article	Problem tackled by the model	T	B	E	Analytical/numerical/hybrid (numerical + analytical)	Sp	D/S	Short description of the model	Modeling principle
Maser et al. (2007)	Weak trophic interactions and the balance of enriched metacommunities	2	4	2, 3	Analytical	No	S	Incorporates the continuous, well-mixed, modeling approach into spatially explicit map lattice. The equations governing food-web interactions incorporate empirical estimates of interaction strength with non-linear food-web dynamics	Inductive, empirical assumptions
MacQuarrie and Mayer (2005)	Review of reactive transport modeling in fractured rocks	3	NA	3	Analytical (transport equations, equilibrium reactions equations, kinetic reactions)	Yes	D	Modeling of hydrodynamic processes leading to migration and dispersion of chemical species transport and geochemical processes reactivity.	Deductive, review, several equations
Saaltink et al. (2003)	Analysis of a deep well recharge experiment by calibrating a reactive transport model with field data	3	NA	3	Analytical + numerical (1 D finite element discretizations)	Yes	D	Modeling of the hydrogeochemical effects of deep well recharge of oxic water into an anoxic pyrite-bearing aquifer. Kinetic expressions have been used for mineral dissolution–precipitation rates and organic matter oxidation. Hydrological and chemical parameters of the model were calibrated to field measurements	Inductive (calibration of an existing model)
Simpson et al. (2003)	Analytical model for computing residence times near a pumping well	3	NA	3	Analytical solution of the equation + numerical exemplification	Yes	D	Analytical solution for calculating the residence time of fluid flowing toward a pumping well in an unconfined aquifer has been developed. The analytical solution was derived based on a radial, steady-state, Dupuit–Forchheimer flow model	Deductive
Simunek et al. (2003)	Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone	3	NA	3	Analytical (Richards equation, double-hump-type equations)	Yes	D	Review various approaches for modeling preferential and non-equilibrium flow and transport in the vadose zone. They range from relatively simplistic models to more complex physically based dual-porosity, dual-permeability, and multi-region-type models	Deductive (Richards equation is combined with composite (double-hump-type) equations)

Please cite this article as: Iordache, V., et al., Integrated modeling of metals biogeochemistry: Potential and limits. Chemie Erde-Geochemistry (2009), doi:10.1016/j.chemer.2008.12.001

Spiteri et al. (2007)	Modeling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems	3	NA	3	Analytical	Yes	D	1D reactive transport model (RTM) is used to obtain a mechanistic understanding of the fate of phosphorus (P) in the saturated zone of two contrasting aquifer systems	Deductive. Little mathematics, application to two basins
Lee and Windt (2001)	Present state and future directions of modeling of geochemistry in hydrogeological systems	3	NA	3	Analytical	Yes	D	Two classes of geochemical models are commonly used, i.e., static and hydrodynamic models; included processes, thermodynamic databases, missing phenomena, numerical behavior and performance	Deductive
Fried (1991)	Geographically based models for surface and estuarine waters and river/aquifer interfaces	3	NA	3	Analytical	Yes	D	A review of a variety of local models as water flow and contaminant transport and global models as biochemical oxygen demand (BOD), dissolved oxygen (DO)	Inductive parts (global models, transfer functions) + deductive parts (local models)
Hipsey et al. (2004)	Numerical and field investigation of surface heat fluxes from small wind-sheltered water bodies in semi-arid western Australia	3	NA	3	Numerical (finite difference method, fully implicit scheme with Picard linearization, fully implicit scheme with Picard linearization, successive over-relaxation method)	Yes	D	Numerical model of the disturbed momentum and turbulence fields in the region modified by the wind-shelter accounted for the presence of a water body downwind (modified Wang and Takle model).	Deductive parts (modified form of previous model)
Romanowicz and MacDonald (2005)	Uncertainty and variability in environmental systems	4	NA	2, 3	Analytical	No	S/D	A review of top-down approaches to the modeling of environmental processes	Deductive
Legendre and Borcard (2003)	Important space scales in an ecosystem	4	NA	2	Analytical	Yes	S	Using the tables of abundance of species (sites × species) which represents the best (multi)variable-answer for studying the feedback of the ecosystems to the natural variables or to those induced by human action	Deductive
Young (2002)	Using of the inductive statistical approaches against the large deterministic models	4	NA	2	Analytical. Developing of the ‘top-down’ stochastic models. Introducing of the concept of data-based mechanistic (DBM)	No	S	The DBM water quality and rainfall-flow models	Inductive modeling. Time dependent models
Fath (2004)	Distributed control in ecological networks	4	NA	3	Analytical	No	S	A review of top-down approaches to the modeling of environmental processes	Deductive
Dale et al. (2002)	Reviews of spatial statistical methods and describes the relationships among them	4	NA	3	Analytical	Yes	S	Review of mathematical models used in spatial statistic analysis: SADIE, LISAs, cluster detection, circumcircle method, cross product, etc.	Inductive correlations between given models

Legend as in Table A1.

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Please cite this article as: Iordache, V., et al., Integrated modeling of metals biogeochemistry: Potential and limits. Chemie Erde-Geochemistry (2009), doi:10.1016/j.chemer.2008.12.001