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Elimination of Kinetic Modeling: Importation of Experimental Results into Environmental Simulations

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Abstract:

Simulations for environmental impact assessments (EIAs) usually depict reactive conversion with closed kinetic models for pollutant decay, byproduct formation, or bacteria decay. But complex reactions with organic matter frequently neither fit known rigorous mechanistic models nor do they correlate with models that rely on limited empiric assumptions. Spline models are better suited to integrate information from experiments into an environmental model. Direct importation of experimental results may also be recommended for Lagrangian models. For example, bioassay results for zooplankton can directly determine particle fate in Lagrangian simulations. This article presents several examples for improving model accuracy with model designs which permit direct importation of experimental results. In many cases, this approach allows for the elimination of the task of kinetic modeling for both continuum and Lagrangian models in environmental impact assessments. In addition, the accuracy of the simulation can be increased when kinetic model fitting is replaced with direct importation of experimental results.

Keywords: biocide, decay kinetics, EIA, Lagrangian model, spline.

1. Introduction

Environmental impact assessments of biocide or pollutant discharges usually include discharge simulations to assess dilution and dynamic pollutant distributions. Many introductory approaches have been published for water quality related EIAs [1] and the predominantly used Finite Volume Method [2]. More detailed papers on the involved physics have been published as well [3]. Various models for such simulations have been reviewed [4]. New, mainly unstructured mesh type models [5, 6] continue to be developed. EIAs are a ubiquitous factor present in the launching of plant operations. In fact, such simulations are conducted even in emerging economies that rely on mining and natural resources, presenting an important research topic in most countries with environmental regulations [7, 8]. Suitable algorithms for species transport models have been reported [9]. Fig. 1 shows the typical work flow process for embedding chemical reactions in water quality simulations.

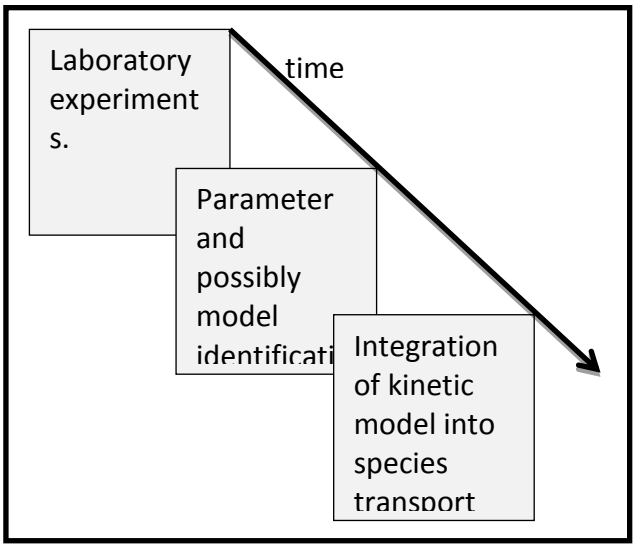

Figure 1. Normal workflow for embedding kinetics in CFD.

Approximating conversion and decay of organisms based on the available data structure, directly importing experimental esults, can significantly reduce fitting errors and increase the accuracy of simulations. Furthermore,

this eliminates kinetic modeling and model parameter identification.

2. Methodology

The following categories classify various possible constituents in water quality modeling:

- Planctonic bacteria, that are a sensitive receptor, or pathogenic constituent of discharge from urban areas, such as fecal coliforms.
- Planktonic eukarya (multi-cell organisms transported by water currents and dispersion), fish, or benthic (residing on sea floor) organisms.
- Pollutants, such as biocides, which undergo reactions with organic matter.

The type of conducted experiments depends on the water quality concern. Bioassays are conducted if impact on marine organisms is suspected or anticipated. The type of bioassay used depends on whether eukaryotes or bacteria are investigated. Monitoring the lethality of most eukaryotes is a trivial record of the number of used zooplanctonic organisms. Measuring the lethality for bacteria is accomplished using bioreactor measurement techniques. Monitoring the reaction rates of organic matter with pollutants such as biocides is a task of instrumental analyses.

The technique to directly import experimental results depends on the modeling, that is, whether e.g. Lagrangian or continuum modeling has been chosen. It is a part of the modeling and programming process to define arrays in the simulation so that, that experimental results can be imported. First example, it may be assumed that complex animals, such as zooplankton, fish and benthic eukarya, are preferably depicted and approximated with Lagrangian models. This is because the experimental setup for bioassays corresponds well to a set of particles with defined properties. For example, if ten shrimp are exposed to a biocide, e.g. residual chlorine, then ten particles can be defined with corresponding properties in terms of lethal concentration and response times. It is, of course, best to have data on varying concentrations in order to approximate a lethal concentration versus the response time relationship. The toxicological metabolism of planktonic bacteria may sometimes be more complex than e.g. biocide conversion with organic matter; but planktonic bacteria have kinetics governing properties (such as that organisms of one species show a similar reactive pattern) that allow us to calculate proportionality relationships which correspond well to ordinary differential equations. This explains why pollutant reactions with organic matter rarely fit into common kinetic models, whereas planktonic bacteria growth or decay might fit well into closed form kinetic models. Fig. 2 illustrates the workflow of suggested approaches for the following categories: 1.) eukarya, such as zooplankton, fish, and benthic animals, 2.) pollutant reactions with organic matter, 3.) planktonic bacteria or panthogens, such as fecal coliforms.

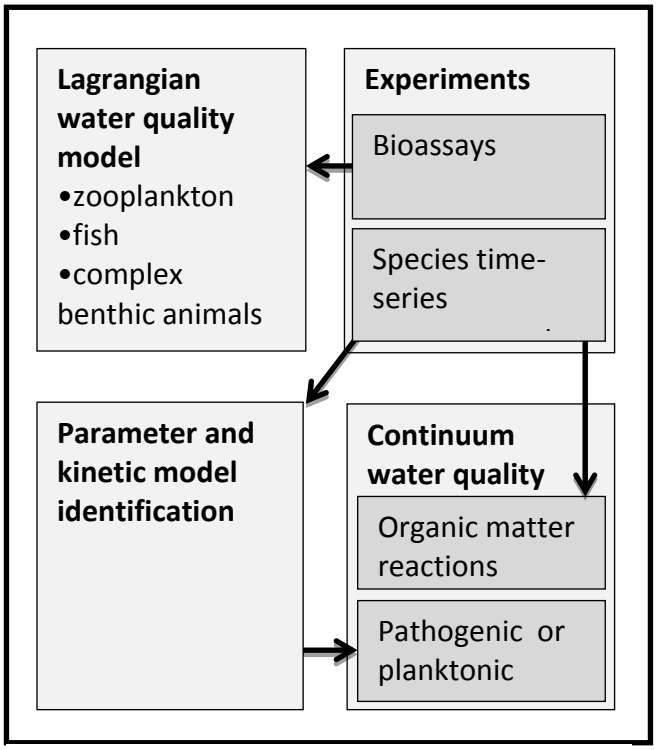

Figure 2. Suggested approaches for different categories.

2.1. Importing experimental results for Eukaryotes

For each organism, a matrix containing two vectors, one for pollutant concentrations and one with the corresponding response time, may be noted as $m_{i,j}$ with the size *2,n* for n organisms used in bioassays. Because organisms may pass temporarily through regions with acceptably low pollutant concentrations, a recovery mechanism could be introduced into simulations. Otherwise, the response time for non-critical concentrations may be noted with the time corresponding to the normal life span of an organism. If no reproduction is modeled, all non-critical concentrations should be set to zero in order to avoid progressing intoxication in areas of non-critical concentrations. Omitting recovery times can be considered as accurate if discharge plume dynamics and response times for lethality are assumed to be small compared to recovery times. This obviously holds for discharges and plumes emanating from industrial or urban effluents. However, omitting recovery times may be justified as part of a more conservative, careful approach, whereas EIA clients might be eager to include recovery times in order to minimize the forecasted impact.

If an organism passes through lethal concentrations, which will depend on the pollutant distribution, then the time wise integrated concentration may be recorded as a

fraction of the time wise integrated lethal concentration (= lethal concentration *i* times response time *i*). This permits to model accumulation and progressing intoxication of organisms passing through varying concentrations. If no lethality is linked to a particular (comparatively low) concentration, then the intoxication stops until the organism passes again through critical concentrations. The model requires to identify at each time step the concentration *i* in the matrix $m_{i,j}$ which is closest to the calculated concentration (in a control volume) in order to know the corresponding response time *i*. For particles (which represent organisms) that travel through lethal concentrations of a pollutant, the percent intoxication is calculated relative to their response times. This allows to simulate the progressing intoxication, as the particle travel through varying concentrations.

2.2. Modeling of bacteria in bodies of water for EIAs

Modeling bacteria in environmental impact assessments is done for two different purposes, 1.) modeling pathogenic bacteria, such as fecal coliforms, or 2.) modeling the decay of planktonic bacteria under pollutant exposure. The first situation is much more common considering the typical problem of sewage effluent from urban areas. For example, fecal coliform decay rates, which vary substantially depending on solar radiation, can be measured in laboratory experiments. In order to accurately model this phenomenon, the kinetics must change throughout the simulated day and consider the absorption of solar radiation along the water column.

Bioassays are conducted to determine the impact on planktonic bacteria. Growth may be assumed to be proportional to bacterial plankton concentration $c(t)$ and nutrient availability $s(t)$; lethality for bacteria is assumed to be proportional to the pollutant concentration c_p with proportionality constants k_i:

$dc/dt|_{growth}=k_0\, s(t)\ c(t)$ (1)

$dc/dt|_{lethality}=-k_1\, c_p(t)c(t)$ (2)

I.e. $dc/dt|_{growth}= k_0\,(s_0-k_2c(t))c(t)$

and $dc/dt|_{lethality} =-k_1\, c_p(t)c(t)$ where k_2 is the nutrient availability per bacterial plankton concentration ratio.

Which means that

$dc/dt = k_0\,(s_0-k_2c(t))c(t)- k_1\, c_p(t)c(t)$, which can be noted as $dc/dt = k_0\,(s_0-k_2c(t)- k_1\, c_p(t))\, c(t)$.

Obviously, a steady state occurs when

$0= s_0-k_2c_\infty- k_1\, c_p(t)$ (3)

This indicates a steady state bacterial plankton concentration of $c_\infty= (s_0 - k_1\, c_p(t))/k_2$.

c_∞, k_1 and k_2 are usually unknown prior to conducting of the experiments. If the initial nutrient availability s_0 is not documented or unknown, then noting $c_\infty= k_3 - k_4\, c_p(t)$ with $k_3=s_0/k_2$ and $k_4=k_1/k_2$ produces three unknowns. However, in this case the nutrient availability in the bioassay must be equal to the one in the modeled environmental system. In reality, due to the varying intensity of solar radiation on photosynthetic organisms, this can hardly be realized. Therefore, nutrient conditions, including solar radiation intensity I_{SR} should always be identified and documented.

The resulting three unknowns show that bioassays for the measurement of bacterial plankton should record at least three measurement values. Note that the nutrient availability has been intentionally formulated in abstract fashion, considering that the kinetics of algae growth involves multiple components, such as solar radiation and carbon dioxide concentration $c_{CO2,}$ where $k\ \ s(t)$ would correspond to $k_5\, c_{CO2}\, I_{SR}$.

2.3. Spline models: Importing experimental results for reactions with organic matter

Pollutants such as biocides might undergo various reactions with organic matter. In this section, the spline approximation is shown for a biocide: chlorine. Within the bromide rich seawater of the Arabian Gulf, free residual chlorine will form hypochlorous acid, which will form chloride and hypobromous acid [10]. The development of hypochlorous and hypobromous acid, as well as halogenated matter plumes depend on reactive consumption or accumulation and oxidants mass-exchange with the atmosphere.

The nonlinear Hypobromous acid reaction with organic matter (to products such as TBM) can be simulated using spline approximations, which fits itself to laboratory measurements.

Table 2. Example of laboratory measurements of kinetic data to which the simulation creates a spline approximation.

Time [minutes]	Residual Chlorine [g/m³]	TBM [Mol/m³]
0	3.345	6.750E-06
0.5	2.352	5.395E-04
1	1.53	6.780E-04
6	1.13	7.317E-04
18	0.868	7.396E-04
24	0.753	7.714E-04
48	0.474	7.921E-04
72	0.211	8.009E-04
96	0.103	7.999E-04
120	0	8.013E-04
168	0	8.019E-04

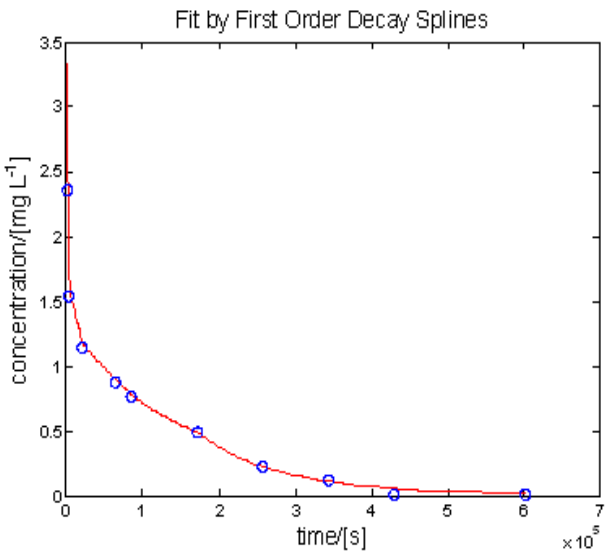

Figure 7. Decay of residual chlorine according to laboratory measurements (blue points) and simulation (red line).

An individual first order decay constant which corresponds to a particular concentration interval is selected for each cell for each time step. The spline fitting (Fig. 7) can be made to depend on a variety of factors including temperature – otherwise it is run with data which have been taken at a temperature range which corresponds to the simulated case.

3. Conclusion

Approximating conversion and decay of organisms according to the available data structure, allowing for direct importation of experimental results can significantly reduce fitting errors and increase the accuracy of simulations. Furthermore, it eliminates kinetic modeling and model parameter identification. Reactions with organic matter and eukaryote models benefit most from directly coupling experiments with modeling. Bacteria fate can be depicted via closed form models or spline models.

REFERENCES

[1]. Johannes Lawen, Yu Huaming, Patrick Linke, Ahmed Abdel-Wahab editor. Industrial Water Discharge and Biocide Fate Simulations with Nonlinear Conversion 2nd Annual Gas Processing Symposium; 2010 January 10-14, 2010; Doha, Qatar: Elsevier; 2010.

[2]. Johannes Lawen, Huaming Yu, Georg Fieg, Ahmed Abdel-Wahab New unstructured mesh water quality model for coastal discharges Environmental Modelling & Software. 2013;40(2):330-5. Epub 23rd October 2012.

[3]. Johannes Lawen, Huaming Yu, Georg Fieg, Ahmed Abdel-Wahab, Tejas Bhatelia. New Unstructured Mesh Water Quality Model for Cooling Water Biocide Discharges Environmental Modeling Assessment. 2014;19(1):1-17. Epub 23rd october 2013.

[4]. Johannes Lawen, Georg Fieg, Huaming Yu, Ahmed Abdel-Wahab editor. Review of Cooling Water Discharge Simulation Models. 3rd Gas Processing Symposium; 2012 12th May 2012; Doha, Qatar: Elsevier; 2012.

[5]. Johannes Lawen, Ahmed Abdel-Wahab, Georg Fieg, Mohamed Abdel-Moati, editor. The First Water Quality Model from the Arabian Gulf and a New Endogenous Model Development Capacity in the Region. International Conference on Water, Energy and Environment; 2011 14th - 17th November 2011; Sharjah, UAE. Sharjah, UAE: American University of Sharjah; 2011.

[6]. Johannes Lawen, Ahmed Abdel-Wahab, Georg Fieg, editor. Anoxic Water Simulations and Vertical Sub-Meshing to Depict Strong Vertical Gradients. International Conference on Water, Energy and Environment; 2011 14th - 17th November 2011; American University of Sharjah, UAE. American University of Sharjah, UAE: American University of Sharjah; 2011.

[7]. Johannes Lawen, Ahmed Abdel-Wahab, Patrick Linke, Mohsin Al-Ansi, Mohamed Abdel-Moati, editor. An Advanced Simulation Tool for Environmental Assessment of Cooling Water and Wastewater Discharge. Qatar University Life Science Symposium 2010; 2010 15th December 2010; Qatar University, Doha, Qatar: Qatar University; 2010.

[8]. Ahmed Abdel-Wahab, Ahmed Khodary, Johannes Lawen, editor. Environmental Impact Assessment of Cooling Water Discharge into Seawater. Research and Industry: Fostering Synergy; 2012 21st May 2012; Qatar National Convocation Center, Doha, Qatar. Texas A&M University at Qatar, Doha, Qatar: Texas A&M University at Qatar; 2012.

[9]. Johannes Lawen, Ahmed Abdel-Wahab, Tejas Bhatelia, Georg Fieg. Fluid Flow Direction Guided Solution of an Implicit Adaptive Upwind Approximation for Advection Simulations. Unpublished 2015.

[10]. Abdel-Wahab, A., Khodary, A., Bensaleh, N., Formation of Trihalomethanes (THMs) during Seawater chlorination, Journal of Environmental Protection, 2010.