USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: A prediction system for transport and fate of toxic substances in surface waters

Focus Categories: TS, MOD, WQL

Keywords: 274-Water Quality Modeling, 251-Toxic Substances, 48-Contaminant Transport, 206-Rivers, 197-Reservoirs, 272-Water Quality Control

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Non-federal (matching) Funds Pledged: $15,882

Direct cost $8,712; Indirect cost $7,170

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Statement of Critical Regional or State Water Problems

Toxic substances from chemical spills and non-point source runoff into rivers, reservoirs or lakes pose a potential risk to human health and aquatic lives. Accidental spills can be caused by train derails and truck collisions during ground transportation, leaking from factories and storage tanks, and obsolete navigation (barges in the Midwest waterways and tankers in other regions). More than a thousand toxic spills related to rail alone have been recorded every year in the United States (Elmer-Dewitt 1991). The sites of recent spills were Marshalltown, Iowa, in 1995 and Duluth, Minnesota in 1993. The National Environmental Law Center reported an average of forty-five chemical accidents per month in the Great Lakes States alone. Toxic substances spilled into surface waters are primarily pesticides, herbicides, fungicides, and organic compounds, e.g. sodium methyl dithiocarbamate, methyl isothiocyanate, polychlorinated biphenyls, and polycyclic aromatic hydrocarbns (Gu et al. 1996; Rosario et al. 1994). Toxic contamination in streams and reservoirs may also result from storm events at landfills and superfund (toxic disposal) sites and agricultural runoff as non-point sources (Schnoor et al. 1992; Hayes 1988), especially in the agricultural states such as Iowa and the North Central region. Toxic contaminants from spills and runoff have a significant impact on the environment and continue to be a serious threat to the Nation's and regional watersheds and water resources. The inevitability of toxic spills and runoff points to the need for a full understanding of the behavior (transport and fate) of toxic chemicals in surface waters and an effective tool for prediction to assist contamination control, remediation management and watershed protection.

Statement of Results or Benefits

Expected results include (1) an integrated 2-D river and reservoir toxic contaminant simulation model that will be tested and validated with field data for selected watersheds and past spills and (2) a real-time computer prediction and analysis program to provide information on locations and concentrations of spilled or runoff-carried toxic chemicals in a receiving waterbody. The proposed research will advance the understanding of transport and fate of toxic contaminants in surface waters and provide effective prediction techniques for contamination control. Simulations can be performed before, during, and after a spill or a storm event for short-term or long-term predictions and cleanup and postaudit assessment. The real-time prediction and analysis system serves as a tool for quick assessment, emergency response, contamination remediation, and river or reservoir management within the short period after an actual incident. Predicting the location and concentration of toxic chemicals can guide data collection during a spill or runoff event. The integrated real-time computer program can be used by an emergency response and remediation team to make predictions, to warn water plants about closing intake structures, and to notify fisheries and reservoir management personnel. The program can be integrated into a regional or state contingency plan for emergency response and remediation management to minimize the consequences of a toxic runoff or spill, which will benefit the public and the environment.

Nature, Scope, and Objectives of the Research

Concern has been growing over accidental chemical spills into streams, reservoirs, or lakes because of the potential risk to human and aquatic lives, threat to downstream drinking and industrial waters, and damage to the ecosystem and the environment. Toxic substances into surface waters resulting from instream shipping, railroad, ground transport, and distributed sources, e.g., agricultural runoff, are primarily pesticides, herbicides, fungicides, organic compounds, and other chemical contaminants (Hayes 1988; Jasen 1988; Schnoor et al. 1992; Rosario et al. 1994). More than 1,000 toxic spill incidents related to rail alone are recorded every year in the United States (Elmer-Dewitt 1991). The inevitability of toxic spills points to the need for a full understanding of spill behavior in surface waters, including physical processes, chemical reactions, and biodegradation. An effective tool for fate and transport prediction of spilled chemicals and contamination levels is needed to assist contamination remediation and to minimize the consequences of a toxic spill and runoff. On the other hand, lack of understanding of toxic substance behavior in a reservoir can hamper effective implementation of spill control measures.

An integrated two-dimensional (2-D) mathematical model is needed to simulate the variations of flow, sediments, and contaminants with time and in the vertical and longitudinal directions in a stream and reservoir system. A real-time computer prediction and analysis program, which has been lacking, is necessary for serving as a tool for quick assessment, emergency response, contamination control, and river or reservoir management within the short period after a spill and runoff. The model is expected to easily and quickly predict the fate and transport of spilled toxicants and pollutants in a river or reservoir system before a spill and runoff or during an actual emergency response. The model may also be used for post-audit simulations. The computer program is expected to be user friendly and, as a part of the toxic spill response program, assist (1) contingency planning before a possible spill and runoff, (2) data collection and contamination control during the emergency response to a reported accident, and (3) cleanup and post-audit assessment of the environmental impact of a past event. The program should be operational on a microcomputer or personal computer. In the event of an toxic spill or runoff, the model can be used on a real-time basis to forecast the location and distribution of the spilled materials.

Numerical models were first developed in 1970s for the fate and transport of toxic chemicals in surface waters (Thomann 1978; Smith et al. 1977). The screening-level EXAMS model for the premanufacture testing of toxic chemicals in site-specific water quality problems (Burns and Cline 1985) does not include a simultaneous mass balance equation for suspended sediment. The existing analytical models by Richardson et al. (1983) and by van Gils (1988), which does not capture kinetics of physio-chemical reactions, are simple and descriptive or conceptual and suitable only for first approximation. Gu et al. (1996) developed and applied a longitudinal 1-D simulation model for contaminated density currents in the Shasta Reservoir during and following the 1991 Sacramento River toxic spill. The model was intended to describe the gross flow behavior and to analyze the dilution mechanism of the contaminant plume in different flow regimes and under stratified reservoir conditions. However, the model treated the spilled chemicals as a conservative tracer, excluding the kinetics of physical and chemical processes. Other existing 1-D models (Schnoor et al. 1992), including WASP5/TOXIC5 (Ambrose et al. 1987, 1993), are not capable of providing insight into mixing processes and depicting the fate and transport of toxic substances under various flow regimes in a river/reservoir system. Therefore, a 2-D model capable of simulating toxicant concentration levels at various times and locations in a river and reservoir system has been lacking, in addition to the needed real-time prediction and analysis program for emergency response and remediation management.

The ***objectives*** of the proposed research are (1) to develop and validate an integrated 2-D mathematical model that simulates and predicts the fate and transport of toxic chemical spills and runoff in rivers and reservoirs or lakes, (2) to develop a real-time prediction and analysis computer program for emergency responses and remediation management, and (3) to incorporate the prediction system into an existing regional contingency plan or a toxic contamination control program at the state level. Real-time modeling must be fast or by the time that analysis and results are received the priorities for contamination control may have changed. To meet the requirements, the following special features of the model will be considered: (a) interactive, (b) operable on a personal computer or microcomputer, (c) directly accessible to input data, (d) automatically linked to the hydrologic and hydrodynamic database, and (e) short prediction time compared to actual spill travel time. The menu-driven computer simulation and analysis program to be developed will include a data entry module, an integrated spill model, and a visualization/output data presentation module. The program can yield travel times and concentration curves versus time at various locations and provide timely information by forecasting the location and distribution of toxicants in the event of a toxic spill or runoff.

Research Plan and Approach

The proposed research will develop and validate an integrated 2-D mathematical model and a real-time computer program that predicts the fate and transport of toxic substances in rivers and reservoirs or lakes, investigates the flow behavior and mixing processes in various flow regimes, and evaluates their effects on the dilution of spilled or runoff-carried chemicals and water quality conditions in a stratified reservoir or lake. To achieve the objectives of the proposed research, the tasks to be performed are as follows.

> *Task 1. Formulate the 2-D toxic substance model, develop the computer code (FORTRAN), and obtain numerical solutions.*

The three components and interactions of toxic substances in a stream and reservoir system (flow of water, transport of sediments, and fate and transport of toxic chemicals) will beformulated and integrated. The physical and biochemical processes will be internally linked by coupling the unsteady equations for flows, sediments, and toxic contaminants. The model will incorporate the kinetics of physical processes (sediment adsorption and desorption, and volatilization or vaporization, i.e., gas transfer through air-water interfaces), chemical reactions (hydrolysis, photolysis, and oxidation), and biological transformations (biodegradation or reduction, biological oxidation, and cometabolism). Complete lateral mixing of inflow, small lateral variations, steady-state bed sediment, and instantaneous local equilibrium for sorption are assumed in model development. The equations governing two-dimensional multiphase flow and multiprocess mass transport and reactions in Cartesian coordinates are continuity, momentum, temperature, total chemical in water column, adsorbed chemical in bed sediment, suspended sediment, and density. The toxic substances to be simulated may be from (impulse, pulse, and continuous) point sources or (distributed runoff) nonpoint sources. In the equations, nonpoint sources dependent of watershed geophysical conditions and physiochemical characteristics are included as forcing functions of the mass balance equations. Point source chemical spills are handled as boundary conditions at the upstream end of the water body, defined by a point source input varying with time. A finite-volume method will be used for simultaneous numerical solutions of the model.

> *Task 2. Develop the real-time prediction and analysis program incorporating the 2-D model and establish a data base module and a graphics visualization module for the program.*

The model simulating the fate and transport of spilled or non-point source toxic chemicals will be incorporated into a computer prediction and analysis program consisting of the following three modules for ease and quickness: (1) a menu-based preprocessor for interactive data preparation and execution of other modules, (2) the spill model for prediction, simulation, and analysis, and (3) a post-processor that provides a graphic interface for visualizing the results of the spill model to keep track of a spill in a waterbody.

The real-time model uses site-specific environmental, meteorological, hydrological, and hydraulic data to predict the fate and transport of a particular type of spilled chemical released at a known location on the order of hours or days. Spatial and temporal scales are therefore much smaller than those used in long-term models. By reducing time steps (e.g., from day to hour), diurnal weather processes and factors not significant in long-term modeling (e.g., evaporation) are considered in the real-time modeling. The model requires such input data as river and reservoir geometry, flow-rate (velocity), spill volume, location, duration, type and characteristics of spilled toxic substances, wind speed and direction, and air and water temperatures.

A general consideration in the development of the integrated real-time computer prediction and analysis program is that the model be quick and easy; straightforward to install, run, and manipulate; and user friendly for prospective users, experts, or laymen. Real-time modeling must be fast or by the time that analysis and results are received the priorities for spill control may have changed. To meet the requirements, the model must have the following special features: interactive, operable on a personal computer or microcomputer, directly accessible to input data, automatically linked to the hydrologic and hydrodynamic database, and shorter prediction time than actual spill travel time.

The data entry module serves as the user-friendly interface for interactive processing of input data and directs the action to other modules. The module is a tool that can be used to input the necessary data to make a quick, crude run in an emergency or a more detailed run for long-term modeling. In a menu-driven and integrated model like the one discussed, users are guided through all aspects of data entry, simulation, and interpolation by helpful screen displays and prompts. The model will generate well-organized tables and easily visualized graphics to trace a spill plume in a waterbody on screen promptly. This will be achieved by using a Visual Graphics package. It is also necessary to design this model so that a future stochastic model for uncertainty analysis and confidence limits can be easily added later.

Throughout the time span of an actual spill, from first notification to final deposition, information must be obtained to evaluate the impact. With the computer program, assessment and evaluation can be made by collecting sufficient data about the spill situation and behavior so that a decision about the most effective or feasible physical response method can be made. The preliminary phase of evaluation is based on initially available data or the first rapid collection of data needed to determine if a physical response measure is necessary. The second phase is more methodical, i.e., it enhances, refines, and enlarges the initial database to get comprehensive information for decision making about the response operation.

Task 3. Test and validate the model against field data and observations.

The model to be developed will be tested and validated against the field data of past spills into the Sacramento River and Shasta Reservoir (Rosario et al. 1994; Gu et al. 1996) and the observations of contaminated density currents (carrying toxic chemicals) in Des Moines River and Saylorville Reservoir, Iowa. Other candidate sites are Wild Rice River, Minnesota and Sheyenne River, North Dakota.

On July 15, 1991, between 49,000 to 72,000 liters of VAPAM liquid formulation were estimated to have spilled into the Sacramento River, California about 48 km upstream from the Shasta Reservoir (Rosario et al. 1994). VAPAM, sodium methyl dithiocarbamate (Na-MDTC), is a fumigant with a fungicidal, nematicidal and herbicidal action. Water sampling activities (at 20 locations) were conducted by the California Regional Water Quality Control Board in order to keep track of the spill in the Sacramento River after it entered the Shasta Reservoir. The field measurements also served to determine the contamination level of the waterbody and the speed at which the spilled chemical plume was moving in the river and reservoir towards the Shasta Dam. The measured methyl isothiocyanate (MITC) concentrations, a much more toxic daughter product of Na-MDTC, will be used to test the model.

The model will also be tested against the field data collected by the Rock Island District of the Army Corps of Engineers, Illinois, from Saylorville Reservoir and Des Monies River, Iowa. This test will focus on the fate and transport of pesticides, including atrazine, alachlor, and dieldrin. The measured chemical concentrations in water, fish, and sediments will be used to validate the model.

Task 4. Report and information transfer.

A final report will be written to describes the theory and the model and incorporate the results of testing and validation. A manual and user's guide for will be provided. Major findings, conclusions, and recommendations for further study will also be summarized in the report. Proposals will be written to seek further funding from other agencies. A schedule for the proposed tasks are listed in Table 1.

Table 1. Proposed schedule for completion of the research tasks

Task	Year 1				Year 2			
	1-3	4-6	7-9	10-12	1-3	4-6	7-9	10-12
1	xxx							
2		xxx	xxx	xxx				
3					xxx	xxx	xxx	
4								xxx

Related Research

Preliminary work (Task 1) has been conducted with the fund ($9000) requested from the Iowa State University Research Grants (July 1997-June 1998). Formulation of the model and development of the numerical solutions and computer program have been performed. Preliminary numerical simulation results have been obtained (Fig. 1), which will help the principal investigator (PI) to achieve the objectives of the proposed research. The experience gained by the PI through the first phase (Task 1) of the research will provide a basis for extending this work with a focus on test and validation of the model and development and application of the real-time prediction system. Other related work by the PI in the area of surface water quality modeling include reservoir contaminated currents (Gu et al. 1996, Gu and Chung 1998, and Chung and Gu 1998) and development of a watershed–based approach and integrated model for water quality management and non-point source pollution control in Iowa (Austin et al. 1997). The PI is currently a control member of a national spill committee organized by ASCE's Water Resources Planning and Management Division, working on spill modeling and remediation.

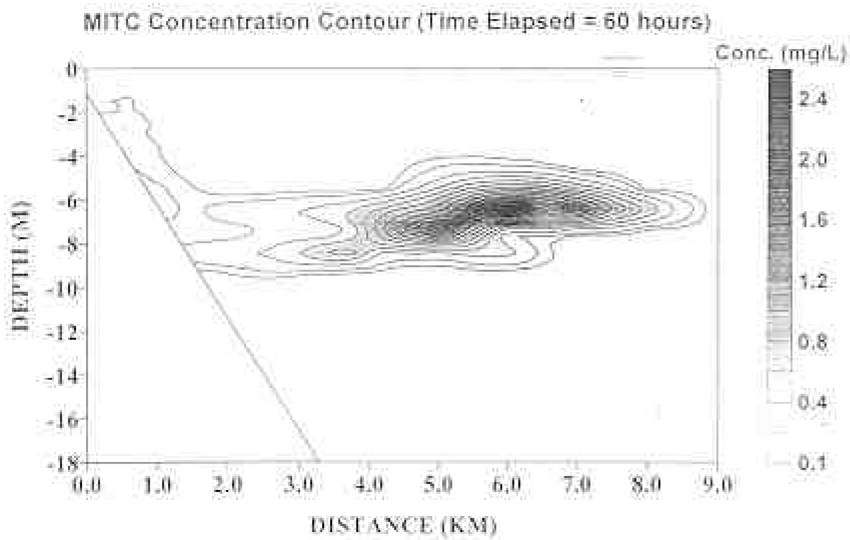

Fig. 1 Simulated concentrations of a toxic substance (MITC) in the Shasta Reservoir, California.

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