



MODELING THE FATE AND TRANSPORT OF ATRAZINE IN THE UPPER CHESAPEAKE BAY

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ABSTRACT

The fate and transport of atrazine, including effects of photodegradation and a potential reaction with polysulfides, in the Upper Chesapeake Bay is investigated. A hydrodynamic model that includes all relevant physical and chemical processes is used to show that atrazine is transported vertically down the water column to the sediment water interface where it may react with naturally occurring polysulfides. Limited field data supports these results. Based on reaction rates reported in the literature, model results show that neither photolysis nor the reaction with polysulfides decrease the concentration of atrazine in the Upper Bay in any significant amount. Our modeling study shows that the minimum reaction rate required to decrease the concentration of atrazine in the bottom layer is $10^{12} \text{ M}^{-1} \text{ s}^{-1}$. The wide range of reaction rates used to obtain these preliminary results suggests that a potential reaction between an herbicide or pesticide and polysulfides is not a significant removal mechanism for agrochemicals in the Upper Chesapeake Bay.

Keywords: Chesapeake Bay, hydrodynamic model, atrazine, photolysis, polysulfides

INTRODUCTION

The decline of the general health of the Chesapeake Bay and surrounding ecosystems has been a thriving research topic for over twenty-five years. A sub-topic of this research concerns the fate and transport of pesticides and herbicides that are applied in the Chesapeake Bay watershed and play a major role in the deterioration of the state of the Bay. This study focuses on the fate of atrazine, the most widely used herbicide in the United States, in the Upper Chesapeake Bay.

Atrazine is a member of the *chloro-s-triazine* family of herbicides and is used extensively in the Chesapeake Bay watershed to control weed growth in corn and sorghum crops. In 1991, atrazine was one of fourteen compounds placed on the "Chesapeake Bay Toxics of Concern List" by the United States Environmental Protection Agency (USEPA) Chesapeake Bay Program. Studies conducted over the past twenty-five years consistently report detectable concentrations of atrazine in the top 1-m layer of the main stem of the Bay as well as in its major tributaries and sub-estuaries (Foster and Lippa, 1996; Johnson *et al.*, 1994; Hall *et al.*, 1999). Concurrently, other studies reported that atrazine has detrimental effects on aquatic flora and fauna. For instance, Jones and Winchell (1994) reported that significant concentrations of atrazine or persistent

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exposure to lower levels may result in changes in species composition and diversity, with species susceptible to atrazine being replaced by more resistant ones, and Solomon *et al.* (1996) showed that atrazine inhibits growth of various species of submerged aquatic vegetation (SAV) in localized areas susceptible to agricultural runoff. In addition, atrazine appears to be a potent environmental endocrine disrupter (Moore and Waring, 1998). The persistence of atrazine and its possible toxic effects have recently drawn considerable attention and concern to the degree at which this herbicide is used in the Chesapeake Bay watershed.

This paper discusses preliminary results from an integral approach combining field data analysis and a comprehensive modeling methodology used to investigate the behavior and distribution of atrazine in the Upper Chesapeake Bay where the Susquehanna River is the largest input of atrazine to the entire Bay. Available data have been compiled to identify the current concentrations of atrazine in the Bay as well as in the major inputs to the Bay (Salmun and Goetchius, 2002). These data are then combined with a three dimensional, numerical model that includes all relevant physical and chemical processes that are believed to govern the fate of atrazine in the Bay. The model captures horizontal advection and horizontal and vertical diffusion of atrazine as well as transformation of atrazine via photolysis and the potential reaction between atrazine and polysulfides located in the sediment porewaters. The main objectives of the study are to determine the distribution of atrazine in the Upper Bay and to investigate the effects of two transformation processes, photolysis and a potential reaction with polysulfides present in anoxic sediment porewaters, on the fate of this herbicide.

THE MODEL

The model used for this study, GEMSS, was developed by J.E. Edinger Associates, Inc. GEMSS is a comprehensive software package used for three-dimensional, time-varying simulations of rivers, lakes, estuaries, and coastal water bodies. This finite element model is designed in a modular fashion to allow coupling of existing modules (hydrodynamic module, water quality module, etc.) with user defined modules (Edinger, 2001). In the present study, the hydrodynamic module is coupled with two user-defined modules, which are described below, that simulate photolysis and the reaction with polysulfides in the Upper Bay. The hydrodynamic and transport calculations (not shown) are based on the horizontal momentum balance, continuity and constituent transport equations, and the equation of state, all of which are semi-implicit in time.

The rate of change of atrazine concentration, C , is governed by the advection-diffusion equation,

$$\frac{\partial C}{\partial t} = -\frac{\partial UC}{\partial x} - \frac{\partial VC}{\partial y} - \frac{\partial WC}{\partial z} + \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) + J - k_p C - \gamma k_{sw} C, \quad (1)$$

where (U,V,W) are the flow components in the spatial directions (obtained from the hydrodynamic module), (D_x , D_y , D_z) are the coefficients of turbulent diffusion, J represents sources and sinks (river input, hydraulic flushing, etc.), k_p is the first-order rate constant for photolysis, k_{sw} is the pseudo-first order rate constant for the reaction between atrazine and polysulfides, and γ is 0 except in the bottom layer within the anoxic zone where it is unity.

The first-order reaction rate for photolysis, k_p , is computed according to

$$k_p = k_{p0} S_R \frac{(1 - e^{-\alpha H})}{H \alpha}, \quad (2)$$

where k_{p0} is the direct near-surface rate reported by Torrents *et al.* (1997) as 0.033 h^{-1} , S_R is an empirical parameter derived from solar radiation parameters relevant to the measured k_{p0} , H is depth of the mid-point of the grid element, and α is the extinction coefficient. The extinction coefficient is estimated from Zafiriou (1977) as $1.8/\text{m}$, which corresponds to an electromagnetic wavelength of 312 nm in coastal waters.

The pseudo-first order rate constant for the reaction with polysulfides is derived from an equation describing the flux of atrazine from the overlying water column into the sediment porewaters and can be expressed as

$$k_{sw} = \frac{\sqrt{k_2 [S_n^{2-}] D_{eff}}}{d}, \quad (3)$$

where k_2 is the second-order rate constant for the reaction between atrazine and polysulfides, D_{eff} is the effective diffusion, $[S_n^{2-}]$ represents the concentration of polysulfides, and d is the depth of the anoxic layer. The pseudo-first order rate constant is only applied at the bottom grid elements within the anoxic zone, which for this study is defined as the region of water below 15 m . We use a value of $5.6 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ for k_2 , as reported by Lipka and Roberts (in press), and an average depth of the anoxic layer, d , of 4 m . Currently, measurements of polysulfides in the porewaters of the Chesapeake Bay are not available, however measurements taken from a surrounding salt marsh, the Great Marsh in Delaware, are reported as 0.33 mM (Boulégué *et al.*, 1982). This value is used in the present study as $[S_n^{2-}]$ during June, July, and August. $[S_n^{2-}]$ is zero for April, May, and September. D_{eff} is estimated as $2 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ (Vanderborght and Billen, 1975).

In the following subsections we describe the set-up of the Upper Chesapeake Bay model grid, forcing, and initial and boundary conditions. Typical model calibration results are also discussed.

(a) The Upper Chesapeake Bay Model Grid

The physical region described in the Upper Chesapeake Bay model includes approximately the northern 135 km of main stem of the Bay, the Baltimore Harbor, and the Susquehanna, Chester, and Choptank Rivers (see Figure 1). A horizontal grid of approximately $1 \text{ km} \times 1 \text{ km}$ is used. There are 24 vertical layers of non-uniform thickness; 1-m resolution for the first fifteen layers, 2-m resolution for the next six layers, and 3-m resolution for the last three. A total of 2,718 grid elements are used in the domain. The bathymetry was digitized using ArcView and a series of nautical maps obtained from National Oceanic and Atmospheric Administration (NOAA).

(b) Initial Conditions

The initial state for the simulations is obtained from vertical profiles of salinity and temperature that correspond to four different regions in the geometrical domain. We used data from thirty-seven stations located in the Upper Bay that are available through the Chesapeake Bay Program (Figure 1). The four regions are shown in Figure 1 and are characterized by

measurements taken from stations CB2.2, CB3.3C, CB4.2C, and CB4.4.

Preliminary results from the Roberts research group at Johns Hopkins University are used to initialize the atrazine concentration in the Upper Bay. The initial concentration of atrazine is 375 ng/L from the surface layer to 8 m, 325 ng/L for depths of 9 m to 16 m, and 275 ng/L from 17 m to the bottom layer. Although these results are from field samples taken at only one point at one time, they are the best approximation of atrazine concentration in the Upper Bay available to date.

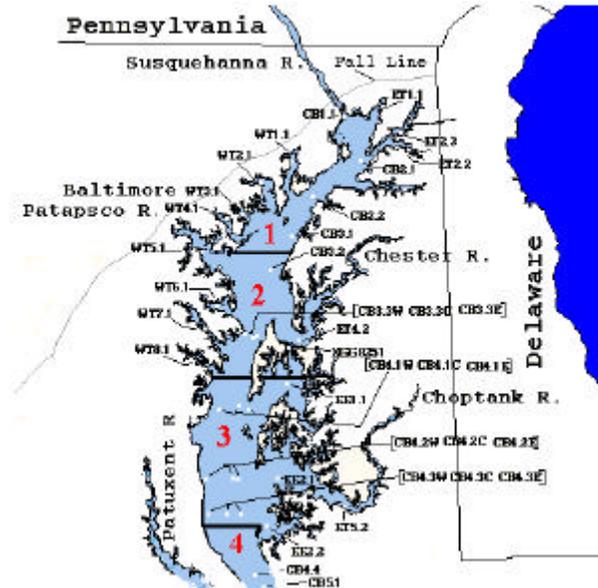


Figure 1. Four regions used for initialization of the Upper Chesapeake Bay model.

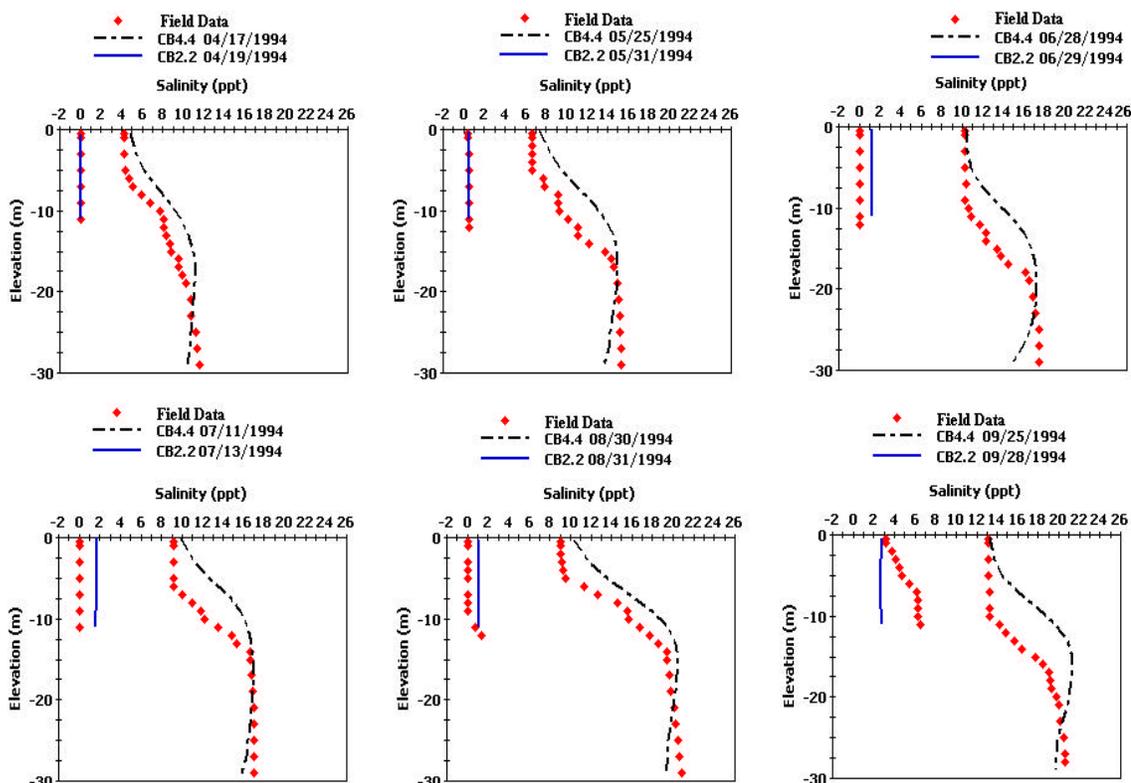
(c) Model Forcing and Boundary Conditions

The model is forced with meteorological influences, tidal energy, and freshwater inflows from the Susquehanna, Choptank, Chester, and Patapsco Rivers. The meteorological data, from NOAA’s Baltimore-Washington International Airport (BWI) station, includes wind speed, wind direction, solar radiation, cloud coverage, air temperature, wet bulb temperature, dew point temperature, and air pressure data. Tidal elevation measurements made at Poplar Island were obtained from “Tides and Currents for Windows” by Nautical Software. Vertical profile measurements of salinity and temperature from a station located close to the tidal boundary were obtained from the Chesapeake Bay Program and applied at the tidal boundary. Daily discharge data for the Susquehanna, Patapsco, and Choptank Rivers were obtained from the U.S. Geological Survey (USGS). Daily discharge data from the Chester River are unavailable for 1994 and were estimated from the watershed area ratio between the Chester River and Choptank River watersheds and the discharge data from the Choptank River. Atrazine loading is estimated from data reported by Foster and Lippa (1996) and the Agricultural Network Information Center (AgNIC).

(d) Calibration of the Upper Chesapeake Bay Model

The Upper Chesapeake Bay model is calibrated using field data for salinity and temperature. Figure 2 shows a comparison of salinity model results to field data (♦) for each month of the

simulation period at two locations; CB2.2 (—), which is close to the mouth of the Susquehanna River and CB4.4 (---), which is near the tidal boundary (see Figure 1). As seen in the figure, the qualitative agreement between model and field data for salinity is very good. The pycnocline, however, occurs at a shallower depth in the model results. Comparison of temperature data (not shown) follows a similar pattern with better quantitative agreement between field and model data. This suggests that the model may underestimate the concentration of atrazine in the deeper layers due to reduced mixing across the pycnocline. Mixing parameters, such as the Chezy coefficient, may be adjusted to acquire a more accurate location of the pycnocline. The general circulation pattern from the model simulations (not shown) is also in good agreement with typical estuarine circulation, with seaward flow in the surface layer and landward flow in the bottom layer.



Figures 2. Comparison of model results to field data (♦) at two locations.

RESULTS AND DISCUSSION

Model simulations are conducted for the time April 1 - October 1, 1994, as the most comprehensive data set for atrazine loading to the Upper Bay is available for this time. These months also capture the period of anoxia in the Chesapeake Bay when polysulfides are most likely to be present, hence the reaction between atrazine and polysulfides is most likely to occur. We also investigate the impact photolysis has on the concentration of atrazine in the Upper Bay.

Photolysis vs. Reaction with Polysulfides

Figures 3 and 4 show typical results from simulations using estimates of the photolysis rate constant (0.792 day^{-1}) and the pseudo-first order rate constant for the reaction between atrazine and polysulfides ($5.6 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$) from the literature. Figure 3 shows modeled atrazine

concentration in the surface layer at three locations; CB2.2, which is near the mouth of the Susquehanna River, CB3.2, which is in the middle of the Upper Bay, and CB4.4, which is near the tidal boundary (see Figure 1). This figure shows atrazine modeled as a conservative tracer in red and when photodegradation is incorporated in black, green, and blue for the different locations, respectively. The results in this figure demonstrate that the atrazine concentration in the surface layer is the same whether atrazine is modeled as a tracer or whether it is degraded via photolysis. Figure 4 shows modeled atrazine concentration in the bottom layer at the same three locations. This figure shows atrazine modeled as a conservative tracer in red and with the reaction in black, green, and blue for the three locations. As with the results in Figure 3, Figure 4 shows no appreciable differences between results from these two simulations. Although our limited field sampling showed that atrazine degradation products were present in both the surface and bottom layers, the present results indicate that the rates at which these reactions occur are too slow for these processes to be considered significant degradation pathways for atrazine in the Upper Bay.

Figures 3 and 4 show a steep decrease in atrazine concentration at stations CB2.2 and CB3.2. This suggests that the initial concentration of atrazine is too high for these regions and that the freshwater from the Susquehanna River significantly dilutes the concentration from 375 ng/L to 50 ng/L. The concentration of atrazine increases at approximately twenty days into the simulation, which corresponds to loading of atrazine through the Susquehanna River. The initial concentration of atrazine in the Upper Bay model is based on field samples taken at one location, near Kent Island, at one time during July 2001. The steep decrease in concentration suggests that the concentration of atrazine may not be homogeneous in space and time. The lunar cycle, which is approximately fifteen days, is also evident in Figures 3 and 4. The concentration of atrazine fluctuates with the tidal currents and, thus, the cycle of the moon.

Sensitivity of k_2

The sensitivity of this model to changes in reaction rate was investigated. Six values of k_2 ranging from $5.6 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ to $3.04 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$, a five order of magnitude range, were used in the Upper Chesapeake Bay model to investigate the impact of changing k_2 within a realistic range on the concentration of atrazine in the bottom layer. These values represent the reaction rates for other herbicides, including alachlor, metolachlor, and anilazine, which are also applied in the Chesapeake Bay watershed and react with polysulfides (Lippa and Roberts, in press). Results from these simulations are summarized in Figure 5, where it can be seen that the atrazine concentration in the main channel (shown in dark and light orange) is higher than in surrounding grid elements. Figure 5a and b show that increasing the value of k_2 by five orders of magnitude does not decrease the atrazine concentration in the bottom layer in any significant amount. Figure 5c shows that a decrease in atrazine concentration occurs in the southern region when k_2 is increased to approximately $10^{12} \text{ M}^{-1}\text{s}^{-1}$, which is the minimum value of this parameter required to change the atrazine concentration in the bottom layer. It is unlikely that a reaction between an herbicide or pesticide and polysulfides will proceed at such a fast rate.

CONCLUSION

Photolysis and a potential reaction between atrazine and naturally occurring polysulfides have been investigated as possible removal mechanisms for atrazine in the Upper Chesapeake Bay. Based on reaction rates reported in the literature, model results show that neither photolysis nor the potential reaction have an impact on the concentration of atrazine in the Upper Bay and, thus, are not considered to be significant sinks for atrazine. Our modeling study shows that the

minimum rate for the reaction between atrazine and polysulfides required to decrease the atrazine concentration in the bottom layer is $10^{12} \text{ M}^{-1}\text{s}^{-1}$. The wide range of reaction rates used to obtain these preliminary results suggests that a potential reaction between an herbicide and polysulfides is not a significant removal mechanism for agrochemicals in the Upper Chesapeake Bay.

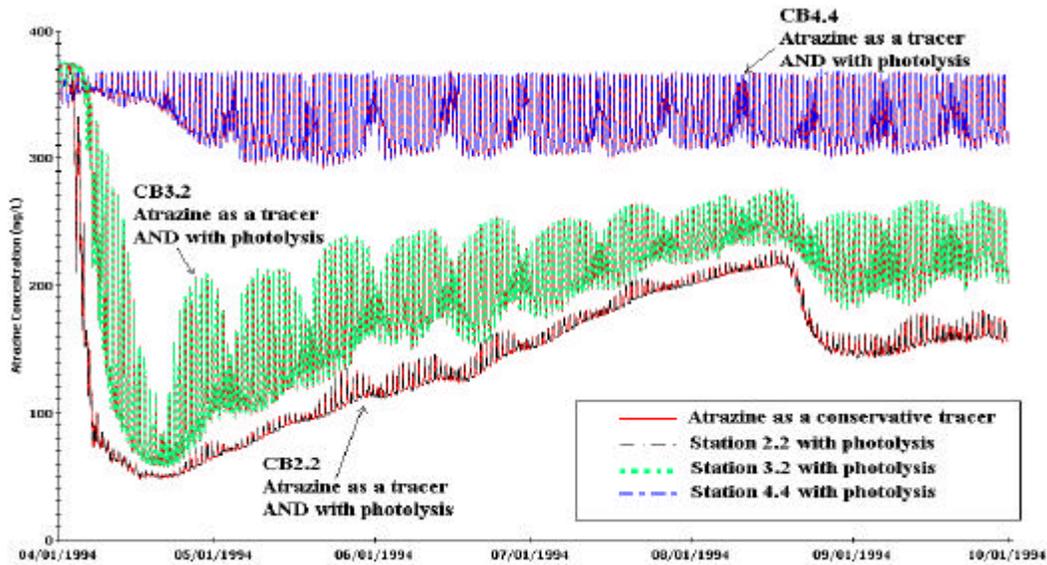


Figure 3. Model results for atrazine concentration as a conservative tracer and with photodegradation in the surface layer of three locations in the Upper Bay.

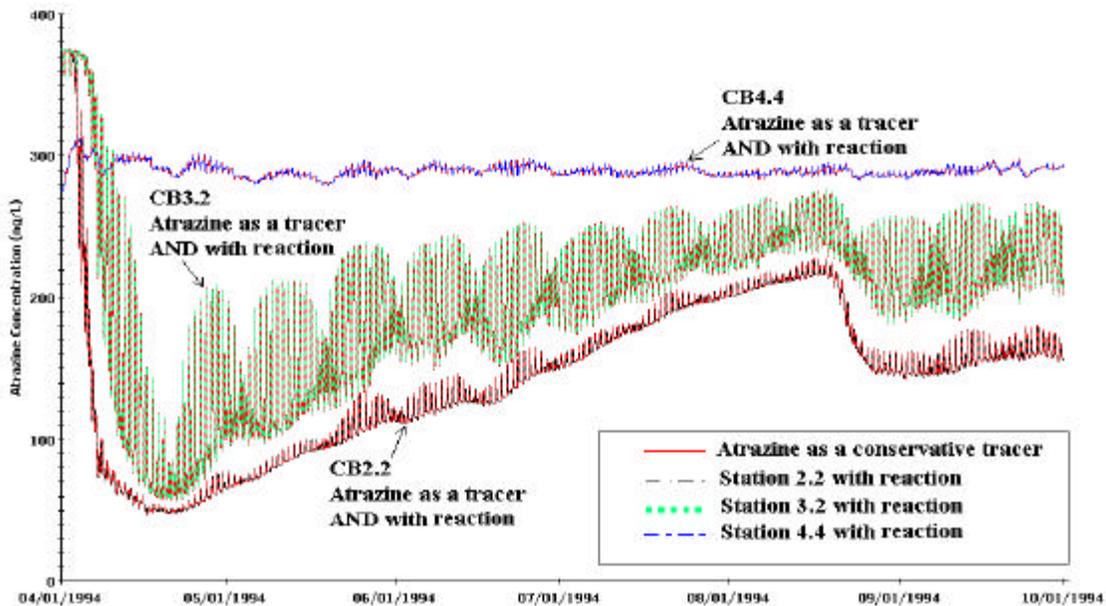


Figure 4. Model results for atrazine concentration as a conservative tracer and with the potential reaction between atrazine and polysulfides in the bottom layer of three locations in the Upper Bay.

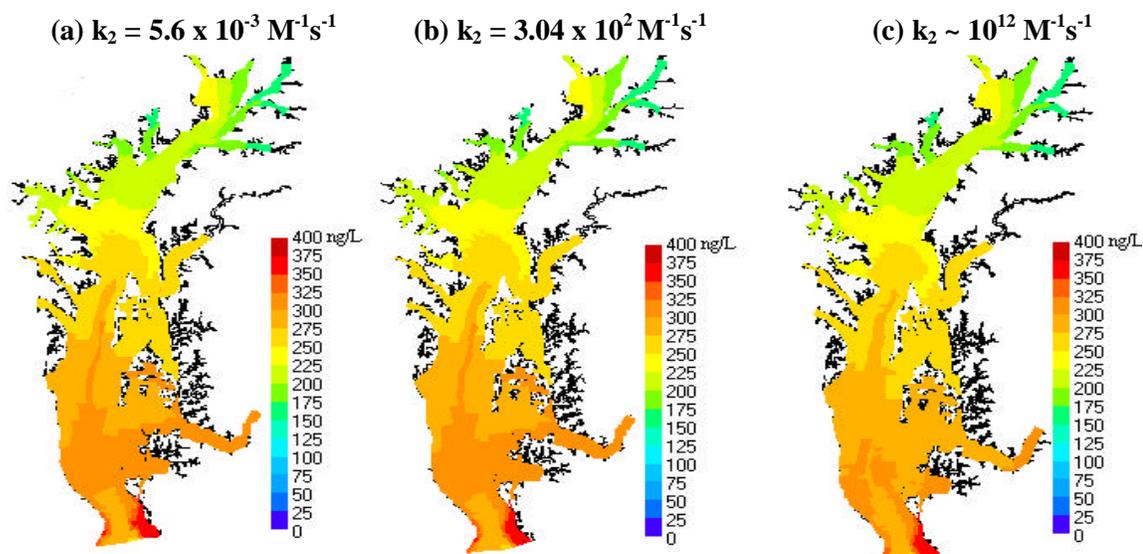


Figure 5. Atrazine concentration in the bottom layer of the Upper Bay corresponding to three values of k_2

ACKNOWLEDGMENTS

The authors would like to acknowledge the support provided by Venkat Kolluru and John Edinger with technical aspects this work. We are grateful to A. Lynn Roberts and Katrice Lippa for their help with the chemical aspects of our modeling effort. This research has been partially funded by the US Environmental Protection Agency through STAR Grant R826269-01-0.

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