Chapter IV
Implementation and Validation of Opus-SF

Description of Opus

Opus (Smith, 1992; Ferreira and Smith, 1992) is an integrated field-scale model developed for studying the effects of management and weather inputs on the movement of water and potential pollutants within and from a small catchment. Opus includes models for the growth of plants; development of cover; water use; uptake of nutrients; cycling of soil nitrogen, phosphorus, and carbon; transport of adsorbed pesticides and nutrients (nitrogen and phosphorus); interaction of surface water and soil water; runoff; and erosion. Simulations of runoff, plant growth, and movement of soil water are always included; at the user's option, any or all of the other processes may be simulated concurrently. The model allows the user to choose between a detailed simulation of the hydrologic process using rainfall rate information and a more lumped approach using either recorded or stochastically generated daily rainfall.

The daily hydrology option, which was used in this study, predicts runoff volume using a modification of the Soil Conservation Service (SCS) Curve Number (CN) runoff-estimation method, estimates peak runoff rates using a modification of the Rational formula, and calculates the amount of sediment produced using the modified universal soil loss equation (MUSLE) (Williams et al., 1984). When actual measurements of runoff volume and sediment loss are available, Opus allows the user to input them for a more direct assessment of the soil water, plant growth, or chemical components. Plant water use is a function of potential evapotranspiration (ET) and relative leaf area, as suggested by Ritchie (1972). Potential ET is estimated from weather information (net solar radiation and temperature) and estimated albedo, using Ritchie's (1972) simplification of Penman equation, which is essentially a Priestly-Taylor formula. Division of potential ET between soil and plant is a function of plant leaf area index (LAI) and soil mulch cover. Plant water use is distributed through the root zone according to the inverse of the total soil water potential H seen by the plant: $H = z - \psi$, where z is the depth from soil surface and ψ is the capillary head. The plant growth model in Opus simulates the growth of plants or crops in response to plant development factors, radiation, nutrients, temperature, and water availability.

The soil profile is assumed to consist of one or more soil horizons, with each horizon differing from adjacent horizons by its hydraulic or biochemical characteristics. A maximum of six horizons can be specified by the user. The program then divides the profile into smaller layers for computational purposes. Percolation is computed as the flow leaving the layer (ILBR) below the layer containing the rooting depth. Water and chemical balance is computed from the soil surface to this layer.

The Richards' equation (Richards, 1931), which assumes a one-dimensional vertical flow of water unaffected by the counterflow of air, is used to describe flow in the unsaturated soil profile. The functional relationship for soil water retention and hydraulic conductivity is a modification of the Brooks and Corey (1964) equation. Opus requires five parameters to describe the hydraulic and water retention characteristics of a soil horizon: saturated hydraulic conductivity (K_s or RC), saturated water content (θ_s or THS), residual water content (θ_r or B15), air entry pressure (ψ_b or PBUB), and a pore size distribution index (λ or ALAM).

Opus considers advective transport of partially soluble and partially adsorbed pesticides in soil and surface water. Ten pesticides can be considered simultaneously. Application modes can account for deposition on plants, deposition on surface soil and residue, or incorporation into soil at some depth. The depth of the interactive layer from which chemicals can be extracted into surface runoff and/or movement into the soil profile is user specified as a fraction of the 1-cm surface layer. The concentration on sediment is calculated from pesticide released into runoff from the surface soil and transported particles with adsorbed material. This concentration is then multiplied by an enrichment ratio and the sediment mass to obtain the total pesticide loss in sediment. Some pesticides may be susceptible to washoff from plants, and this portion is kept separate from interactions between runoff water and pesticides in soil.

Adsorption of pesticides may be described by a linear isotherm (equilibrium adsorption) or assumed to be kinetic with the rate of transfer between adsorbed and solution phases a linear function of the current phase ratio compared to the equilibrium ratio. The adsorbed to dissolved concentration ratio of pesticide, K_d, is calculated from the organic carbon partitioning coefficient of the pesticide, K_{oc}, and the fraction of organic carbon, which are specified by the user. The model considers first-order decay of pesticides from soil as well as plant foliage. Pesticide degradation rate in soil can be modified by temperature, according to the Arrhenius' equation, and water content by a power function (Walker, 1974). Pesticide degradation rate in the lower soil horizons is computed internally in the model by multiplying the pesticide degradation rate in the top horizon by the ratio of organic carbon in the subsurface horizon and the first horizon. Initial pesticide concentration can be specified for each soil horizon. Besides pesticides, Opus can also simulate the transport and transformations of plant nutrients, nitrogen and phosphorus; the interested reader may refer to the model documentation (Smith, 1992) for details.

The version of Opus used in this study was version 1.62 (March, 1995) with some modifications to the pesticide transport model. The modifications were: (i) organic carbon in the soil layers was calculated directly from the organic carbon content input by the user, instead of using the organic C partitioning in the nutrient model (into three layers); (ii) the user can specify the factor by which pesticide degradation is reduced in the ILBR layer, instead of using a fixed 0.1 factor; (iii) plant uptake of pesticides is included in the model, computed by multiplying the normal crop transpiration rate times the dissolved phase concentration with a user-specified plant uptake coefficient (PUPTK). A newer version of the model called R-Opus, and a Windows 95 version of R-Opus, called WinOpus, has been released in 1997 (R.E. Smith, personal communication, 1997).

IMPLEMENTING OPUS IN THE STOCHASTIC FRAMEWORK

As described in the previous chapter, implementation of a model in the stochastic framework consist of four steps: (i) Statistical/geostatistical analysis of spatially variable parameters; (ii) generation of input parameter sets; (iii) stochastic simulation of model; (iv) analysis of output. Selection of spatially-variable parameters and statistical/geostatistical analysis of spatially-variable parameters are site-specific, and therefore, are discussed separately for each field study in later sections. This section focuses on the other steps used to implement Opus in the stochastic framework (Opus-SF) using Monte Carlo simulation techniques.

The spatially variable input parameters were generated by the LHS method, using @RISK software (Palisade Corporation, 1996). Any known cross-correlation between these parameters was taken into account for generation of the random variates. Truncated distributions were used for spatially variable parameters that resulted in physically impossible values. In @RISK, random variates that follow a normal distribution are specified by the mean and standard deviation. For random variates that follow a lognormal distribution, there are two options to specify distribution parameters: (i) mean and standard deviation of the measured (raw) data, or (ii) mean and standard deviation of the log-transformed data. In this study, the first option was used. Random variates with exponential distributions are specified by the mean of the data, which is equal to the decay constant. Truncated distributions are specified by giving the minimum and maximum truncation limits.

In the case of soil properties with statistically significant and physically meaningful trends, the trends were added back to the zero-mean random variates. The trends were added back to the midpoints of square grids obtained by discretizing the agricultural field into the number of stream tubes, which is given by the number of trials. The input parameters generated by @RISK were output into Microsoft Excel (Microsoft, 1995a) spreadsheet, and the values of the spatially variable parameters for each trial were saved into a space-delimited text file. The number of trials was determined by testing the stability or convergence of the most variable output, pesticide leaching below the root zone.

The Opus source code comprises several programs and subprograms, interwoven in a complex manner (Ferreira and Smith, 1992) and distributed in 16 FORTRAN files. A thorough examination of the source code showed that considerable modification of the code was required to generate new model input parameter files, perform repeated executions of the model and obtain stochastic outputs in a manner conducive to analysis. Besides, modeling subsurface water flow and chemical transport was only one of the components of the model. Therefore, creating a general purpose module was not attempted and the Monte Carlo simulation was performed using an external model-specific routine (Appendix A).

The external routine generated new input parameter files and executed the model for each trial. The spatially variable parameters were denoted by a large negative number (-9999) in the base input parameter file. A new set of values was read in for each trial from the text file containing the values of all spatially variable parameters, instead of the large negative number in the base parameter file, and the model was executed using this modified input parameter file. Input and output files for the model were fixed (‘hard-wired’), which causes the model not to prompt for file names before executing.

Besides hard-wiring the input and output files, modification of the source code included writing IF-loops to the read statements of the (probable) spatially variable parameters in order to read in new values, and creating new routines to generate customized files of the output variables. The subroutine for creating customized soil water and chemical mass output files was added at the end of the subroutine SLFILE in the source file OSTAT.FOR, whereas customized water and chemical balance files were obtained by modifying the subroutine ANSTAT, which immediately succeeds SLFILE in the same file. A listing of the modifications made to create customized output files is given in Appendix A.

An alternate version of Opus-SF, where pesticide degradation rate for individual horizons could be read in, was also created. This version also allows the degradation rate in all soil horizons to be specified as random variables. The modified programs were compiled using a Microsoft FORTRAN PowerStation Compiler (Microsoft, 1995b) for operation in a DOS, Windows 95 or Windows NT environment. The execution of Opus-SF for a 3-year simulation using 50 spatially variable parameters and 1400 trials takes approximately five hours on a Pentium Pro-200 MHz personal computer with 64 Mb memory.

Modification of the source code was not without problems. Some ‘bugs’ were identified and corrected in the Opus code, and reported to the model developer. Another problem in modifying Opus for MCS was caused due to non-initialization of some parameters, functions, and variables in the code. This usually does not affect a deterministic simulation of the model, but can lead to mass balance errors and related problems when performing multiple executions of the model. All parameters, functions, and variables required in the simulation of subsurface water and chemical transport were initialized to resolve this problem. Besides these problems, multiple executions of Opus gave some run-time errors that could not be resolved. These errors were caused due to either non-convergence of the K-ψ solution, which was perhaps caused due to the combination of spatially variable parameters used in the solution, or negative chemical concentrations on certain dates. Run-time errors affected about 2% of the trials. These trials were discarded and not used in the analysis of output.

VERIFICATION AND VALIDATION OF OPUS-SF

The main objective of this part of the study was to ‘partially’ validate the performance of Opus-SF for predicting spatial variations in subsurface soil water content and pesticide mass under field conditions. Some model verification steps were also performed during the development of the stochastic framework. Since the deterministic model had already been verified extensively (Smith, 1992), a complete verification of the code was not performed here. However, the model components used for simulating subsurface water and pesticide transport under daily rainfall conditions were tested for errors using debugging techniques during the implementation of Opus-SF. A sensitivity analysis of the model was also performed to reveal any anomalies or unexpected effects using short, medium, and/or extreme perturbations of input parameters. The Opus-SF code was subjected to desk checking (the process of thoroughly examining one's work to ensure correctness, completeness, consistency, and unambiguity (Balci, 1998)) by a colleague (A.C. Bruggeman), familiar with the system. The internal consistency of the model was verified by numerical testing using mass-balance checks of the output variables.

The performance of Opus-SF in predicting subsurface water and pesticide transport in the root zone under field conditions was assessed using data from: (i) a 3.9-ha agricultural field in the Dougherty Plain region of Georgia; and (ii) an 18x27 m (0.0486 ha) field plot in the Nomini Creek watershed in Virginia. The first step in the validation process consisted of a review and evaluation of data, where the spatially variable input parameters were tested for spatial correlation across the field and cross-correlation among the various input parameters. This ensured that the assumptions in the stochastic framework regarding input data were met. The conceptual approach used to represent spatial variability in the stochastic framework, i.e., the field consisting of non-interacting, vertical one-dimensional stream tubes, could not be tested directly due to inadequate data. Finally, the results obtained from model predictions were compared with field-measured data. The following output variables from Opus-SF on the field sampling dates were considered for comparison with observed data: depth-averaged soil water content, depth-wise soil water content distribution, bromide mass, pesticide mass, and depth-wise pesticide mass distribution in the root zone.

Model Performance Criteria

The performance of Opus-SF was assessed using graphical displays, statistical estimators, and statistical tests. Graphical displays provided an overall subjective assessment of model performance, and included plotting mean and range of depth-averaged soil water content and chemical mass on several dates over the entire period of simulation and plotting mean and range of depth-wise distribution soil water content and chemical mass on specific field sampling dates. Mean was chosen as the appropriate location parameter because the output variables (soil water content and pesticide mass in soil) had no intrinsic identity (Parkin, 1993) and were defined by the size of the sample volume collected. In such cases, Parkin (1993) has suggested that the mean should be used as an estimator of the mass or volume of a constituent, and that the use of median will systematically underestimate the total mass of material.

Standard deviation and range were used as measures of dispersion. Standard deviation expresses the variation of the output variable, whereas the maximum and minimum values identify the extremes of the distribution. Standard deviation is a parametric estimator, and may not accurately describe the variability if the distribution is not Gaussian or log-Gaussian.

Quantitative assessment of model performance was based on the following three questions: (i) does the distribution of soil water content and pesticide mass predicted by the stochastic model match the corresponding observed distribution? (ii) can the stochastic model simulate average conditions of soil water content and pesticide mass in the field? (iii) does the observed range of soil water content and pesticide mass fall within the simulated range? The first question was answered by testing for significant differences between the observed and simulated EDFs by the two sample Kolmogorov-Smirnov (KS) test (Daniel, 1990). The EDF test provides the most rigorous and general way to assess the performance of a stochastic model. The two sample KS test is numerically equivalent to the one sample KS test (Stephens, 1974), a goodness-of-fit approach to test whether a given set of independent observations comes from a population with a specified distribution function, when the simulated EDF is regarded as the specified distribution function.

The second question was answered by testing for significant differences in the location parameter (median, in this case) by the Mann Whitney test (Minitab, 1995). The statistical test was performed on the median rather than the mean, because the distribution of outputs (soil water content and pesticide mass) on several dates was represented by a lognormal distribution. Besides, Mann-Whitney test can be applied to largely unequal sample sizes, unlike the t-test. The small sample size of the observed data may, however, adversely affect the results obtained from both KS and Mann-Whitney tests. EDF procedures are not effective for sample sizes less than 20 and may not be powerful for sample sizes less than 50 (Walter R. Pirie, Personal Communication, 1992).

Statistical tests of equality (for medians or EDFs) may be too rigorous for validating pesticide transport models (Hassanizadeh and Carrera, 1992; Zacharias et al., 1996), although there are not many alternatives available. The U.S. Environmental Protection Agency Workshop on Field Applicability Testing (EPA, 1982, unpublished data) recommended deterministic models to generally have an accuracy within a factor of two to four for site-specific applications. This criterion discards the variance information provided by a stochastic model and cannot be easily extended to stochastic models because of its asymmetric nature. Therefore, statistical tests of equality were used in this study, in conjunction with statistical estimators and graphical displays. Apart from mean, median, standard deviation, and range, a statistic termed “range statistic” was used to express the percentage of observations that fell within the simulated range. A range statistic of 100% means that all of the observations were contained within the simulated range.

Sensitivity Analysis

General Description

Sensitivity analysis provides insight into the sensitivity of the model to selected model parameters and identifies which parameters have the greatest effect on the model predictions. By subjecting the model to a wide range of (realistic) parameter values, sensitivity analysis helps to test the performance of the model under extreme conditions. In addition to identifying critical parameters, sensitivity analysis provides an initial evaluation of the model responses and can be used to guide any future modeling, model evaluation, and data collection efforts. In this research, sensitivity analysis of the deterministic model is also an important component of the stochastic framework as it helps in identifying the parameters that are to be treated as spatially variable.

Sensitivity analysis of models is conducted by varying input parameters that can affect the output of concern by a specified percentage and by calculating the relative sensitivity. Relative sensitivity gives the percent change in output with respect to the percentage change in input, and can be defined as (Haan et al., 1995):

$$S_R = \frac{\partial O}{O}\frac{I}{\partial I} \tag{20}$$

where S_R is the relative sensitivity, ∂O is the change in model output, ∂I is the change in model input, and O and I are the base output and base input values, respectively. Since S_R is dimensionless, parameters can be directly compared. If S_R is zero, the parameter has no effect on the model output. A negative value indicates an inverse relationship between the input parameter and the model output, whereas a positive value indicates a direct relationship between the two. The sensitivity analysis is conducted by changing one parameter at a time and by holding all other parameters as constant.

Sensitivity analysis of Opus was performed using input parameters that are capable of affecting subsurface water flow and chemical transport; the output variables of interest were percolation loss and pesticide leaching below the root zone, and soil water content and pesticide mass in the root zone. Sensitivity analysis was conducted using data from the Dougherty Plain field site, which is described in detail in the next section. This site was chosen over the Nomini Creek site because it had extensive field measurements of soil hydraulic and pesticide properties.

Relative sensitivities were computed by varying input parameters at different levels, as the model results were not linearly related to the parameters. All parameters were varied at a small percentage (± 5%) of the base value to reflect small changes in parameter values, and at a larger percentage (e.g., ± 50%) of the base value to approximate a realistic range of values for each parameter. For extremely variable parameters such as K_s, the parameter values were varied by an even larger amount in order to capture the effect of the occasional high or low value that occurs in the field.

In the sensitivity analysis of Opus, the model was used to simulate water flow and metolachlor mass in the 3.9-ha peanut field using actual rainfall, temperature, and radiation records from April 1 to September 30, 1985. The 1.2 m root zone was divided into five horizons, and a sixth horizon (1.2-1.5 m) was added to represent a plinthite layer found in the field. A listing of the input parameters used in the sensitivity analysis and their base values are given in Table 1. The base values of the input parameters represent average values calculated from field-measured soil physical, biological, and pesticide properties at the Dougherty Plain field site (Hook, 1987; Smith et al., 1987; Smith and Parrish, 1993).

Results of Sensitivity Analysis

Relative sensitivity of total percolation loss below root zone for the six months, average soil water content over the six month period, and resident metolachlor mass remaining in the root zone at the end of the six month period to soil physical parameters and root depth are shown in Figures 3, 4, and 5, respectively. Relative sensitivity of resident metolachlor mass to pesticide-related parameters is shown in Figure 6. The model did not predict any metolachlor loss in leaching, and hence, that output was not used for the sensitivity analysis. The results shown in these figures were obtained by varying input parameters by a larger percentage of their base value.

The relative sensitivity of percolation loss to initial water content (THST), THS, and B15 in the first horizon, and the moisture retention curve parameters (PBUB and ALAM) in the last horizon had an absolute value of over 1. The sensitivity of percolation below the fifth horizon (1.2 m) to soil physical parameters in the sixth horizon (1.2-1.5 m) were generally higher as compared to percolation from other horizons. This shows that upward movement from the plinthite layer, which forms a perched water table at the bottom, was considerable and had a strong influence on the amount of water leaching below 1.2 m. Besides, percolation loss was sensitive to most soil physical parameters in the first and fifth horizons and some in the fourth horizon, with absolute S_R exceeding 0.1. Percolation loss was also sensitive to potential maximum root depth (RDP), with an absolute S_R of over 0.5.

Average soil water content in the 1.2 m profile was most sensitive to root depth ($S_R > 1$) and residual water content in the first four horizons. Resident metolachlor mass in the 1.2 m profile was most sensitive to pore size index (ALAM) in the first horizon ($S_R > 1$) and saturated conductivity (RC) in the first horizon ($S_R \sim 1$). S_R of resident metolachlor mass to RC in the other horizons, THST, RDP, and PBUB and THS in the first horizon exceeded 0.1. Among the pesticide parameters, pesticide mass was sensitive to degradation rate (DKSOIL), with absolute S_R exceeding 4.0 when it was varied by -50% and with absolute S_R over 1.0 when it was varied by +50%. Absolute S_R of pesticide mass to adsorption coefficient (DKOC) and soil organic carbon content (ORGC) in the first horizon exceeded 0.1.

Although S_R quantifies the relative sensitivity of an output variable to changes in different parameters, it is hard to set a threshold or to consider a certain value of S_R to be significant. From the sensitivity analysis, it is evident that movement of water and pesticides in the vadose zone were sensitive to the soil hydraulic and retention properties, especially in the first, fifth, and sixth horizons. These soil properties were the least sensitive in the second and third horizons, with the exception of residual water content which was fairly sensitive in all the soil horizons. Other sensitive parameters include potential maximum root depth, initial water content and organic carbon content in the first horizon, pesticide degradation rate, and pesticide adsorption coefficient. Since there was no runoff observed at the Dougherty Plain site, runoff was not simulated. However, a sensitivity analysis using a 3-year dataset from the P3 catchment near Watkinsville, Georgia (data provided in Opus documentation) showed the runoff curve number (CN) to be sensitive to percolation loss, soil water content and pesticide mass. The sensitivity analysis using the Watkinsville data also showed that varying ORGC in all horizons by the same percentage of the base values gave the same relative sensitivity value as varying DKOC by the same percentage of its base values. This is expected as the depth variation of DKOC is simulated by varying the fraction of organic carbon content in each soil horizon.

MODELING FLOW AND TRANSPORT AT THE DOUGHERTY PLAIN SITE

Description of Field Study

A field study was conducted over four years (1984-1987) on a 3.9-ha agricultural field in the Dougherty Plain region of southwest Georgia, to quantify aldicarb, metolachlor, and bromide movement in unsaturated and saturated soil zones, with an emphasis on providing data of sufficient quality and quantity for use in model evaluation and testing (Smith and Parrish, 1993). The study site contained four soil series: Clarendon loamy sand (fine-loamy, siliceous, thermic Plinthaquic Paleudults), which comprised 45% of the field area, Ardilla fine sandy loam (fine-loamy, siliceous, thermic Fragiaquic Paleudults), 29% of the field area, Tifton loamy sand (fine-loamy, siliceous, thermic Plinthic Paleudults), 22% of the field area, and Lucy loamy sand (siliceous, thermic Arenic Paleudults), 4% of the field area (Fig. 7). Runoff potential was expected to be minimal due to the relatively level topography (average slope less than 1%) and high infiltration capacity; thus, runoff was not monitored. The water table at the site varied seasonally from 3 to 10 m below the surface.

Four distinct soil horizons in the root zone were identified, having depth ranges of approximately 0 to 0.30 m, 0.30 to 0.45 m, 0.45 to 0.75 m, and 0.75 to 1.10 m (J.E. Hook, personal communication, 1997). The field was planted with peanuts (*Arachis hypogea* L.) each year using modified, conventional tillage practices. The crop planting dates in each year, which also was the day on which pesticides were applied, were: May 5, 1984, May 7, 1985, Apr. 7, 1986, and June 1, 1987. The crop harvest dates were Sept. 20, 1984, Sept. 30, 1985, Sept. 10, 1986, and Sep. 10, 1987.

Twenty primary monitoring sites on a 15.24 m square grid network (Fig. 7) were used to measure soil properties, soil water content, and chemical concentrations. Sampling locations were proportionally allocated to the three dominant soil series on an area basis. Soil physical properties measured on samples from the four horizons included infiltration rate, saturated hydraulic conductivity, moisture retention curve, particle size analysis, and bulk density (Hook, 1987). Transformation rates and partition coefficients of aldicarb and metolachlor, and organic matter content, were measured from soil samples collected from the four horizons using laboratory techniques (Rao et al., 1986).

Aldicarb and metolachlor were applied to the site at the beginning of each cropping season, with application rates monitored using surface soil samples and filter disks. Residual pesticide concentrations were measured each year before tillage. Post-application monitoring of aldicarb (total carbamate residues, TCR) and metolachlor consisted of collecting soil samples around the twenty primary sites in 0.15 m depth increments, to a maximum depth of 1.2 m, on 2-3 days in each year. In the first two years, pesticides were monitored only to the depth to which they were estimated to move, but in 1987, pesticides were monitored throughout the entire 1.2 m profile. Gravimetric moisture content was also measured on the soil samples collected for pesticide analysis. Post-application monitoring of bromide consisted of collecting soil samples around the twenty primary sites at 0.15-m increments (to a maximum depth of 3.0-m), on 15 dates from May 1985 to July 1987 (825 days after application). A detailed description of the field study can be found in Smith and Parrish (1993).

Development of Base Parameters

The simulation period consisted of the three cropping seasons from April 1, 1985 to September 10, 1987. Weather data used in the simulation consisted of daily values of rainfall, minimum and maximum air temperature, and solar radiation. The rainfall and temperature data were from the Dougherty Plain site, and solar radiation data from Albany airport (EarthInfo, 1995), 16 kilometers from the site. Since the potential for runoff loss from the field was negligible and there was no runoff observed from the field (C.N. Smith, Personal Communication, 1998), runoff volume and sediment losses in the actual data file (third data file that allows the user to specify measured data) of Opus were entered as zero. Hence, there was no runoff or sediment loss simulated from the field.

The soil profile was divided into four horizons, 0-0.3, 0.3-0.45, 0.45-0.75, and 0.75-1.2 m, with the rooting depth for peanuts set at 1.0 m. All of the soil hydraulic and retention properties were either measured directly or estimated from two replicate soil cores (6.6 cm diameter, 10 cm long) sampled from the four horizons at the 20 primary monitoring sites in the field (Hook, 1987). The K_s values measured in the field and the θ_r values, measured as water content at 1500 kPa, were used directly. The values of θ_s, ψ_b and λ were estimated from the field-measured soil moisture retention values using the RETC computer code (van Genuchten et al., 1991) that fits the parametric models of Brooks-Corey and van Genuchten to represent the soil water retention curve. Porosity was estimated by dividing θ_s by the constant 0.95 (e.g., Mishra et al., 1989). In order to represent the effect of a plinthite layer present in the field below the fourth horizon, an additional horizon (1.2-1.5 m) was added with K_s set equal to one-fifth of its value in the fourth horizon. The fourth horizon was further divided into two horizons (0.75-1.05 m and 1.05-1.2 m) with the same properties in order to make the model assign 1.2 m as the depth to which solute transport calculations are made. (Opus has a constraint that solute transport calculations are made up to the layer below the maximum potential root depth. Therefore, with only the original five horizons, solute transport calculations and pesticide leaching would have been calculated based upon a 1.5 m profile instead of a 1.2 m profile.)

The initial soil water content (θ_i) in the first horizon was set to the values measured in the field on April 1, 1985. Initial concentrations of the pesticides/bromide were set to zero based on analysis of background concentrations in the field. The planting and harvest dates of the peanuts for the three study years were set according to field observations, and crop parameters specific to the site (C.K. Kvien, personal communication, 1997) were used. Organic carbon content was calculated by dividing the field-measured organic matter content values by the constant 1.732 (van Bemmelen factor).

Pesticide degradation rate in the first horizon, calculated from laboratory measurements of half-life (Rao et al., 1986; Smith et al., 1987), and an average value of K_{oc} for each horizon, calculated from adsorption distribution coefficients (K_D) and organic carbon content (Rao et al., 1986; Smith et al., 1987), were used in the simulations. Parameters used to modify degradation rate with moisture content and temperature were calculated from the average soil moisture content and average air temperature at which soil samples for laboratory measurements of degradation rate were taken (Ou et al., 1986), and Arrhenius equation activation energy constants of aldicarb and metolachlor were obtained from the literature. The estimated relative soil moisture content (DKTHE) was 0.37, temperature (DKTEMP) was 24.3°C, and Arrhenius constant (ARRHC) for aldicarb was assumed as 14.7 kcal $mole^{-1}$ (Lemley et al., 1988, pg.413) and ARRHC for metolachlor was assumed as 12.4 kcal $mole^{-1}$ (Walker and Brown, 1985, pg.145).

Coefficients of uptake for the two pesticides were calculated using a regression equation (Briggs et al., 1982) that relates plant uptake to the logarithm of the octanol-water partitioning coefficient (log K_{ow}) of the pesticide. The midpoints of the log K_{ow} ranges of aldicarb and metolachlor, given in the Agrochemicals Desk Reference (Montgomery, 1993), were used in the calculation of plant uptake. Other pesticide properties, such as solubility, were obtained from the SCS/ARS/CES pesticide property database (Wauchope et al., 1992), whereas plant-washable fraction of the pesticide and foliar degradation rates, computed from foliar half-life, were obtained from the GLEAMS user manual (Knisel et al., 1992). Pesticide application rates measured in the field were used in the simulation.

Bromide was simulated as a non-conservative, non-reactive tracer with a zero degradation rate and a zero adsorption coefficient. Solubility of 1000 mg L^{-1}, washoff fraction of 0.75, and plant uptake coefficient of 0.6 were assumed for the tracer. Bromide application rates measured in the field were used in the simulation.

Selection of Spatially Variable Parameters

Selection of the spatially-variable parameters to be used in the simulations was based on the sensitivity of the model to the parameter, physical considerations and availability of data. The five soil hydraulic and water retention parameters (RC, PBUB, ALAM, THS, B15) were selected to be spatially variable parameters. Since residual water content was fairly sensitive in all horizons and since correlations between these soil properties were to be considered, it was decided to treat all these parameters variable in all horizons. Since porosity was estimated from saturated water content, porosity in all horizons was also treated as spatially variable. Initial water content in the top horizon was treated as spatially variable. Even though root depth was found to be a sensitive parameter, there were no data available to describe its spatial variability and therefore it was treated as a fixed parameter. Among the pesticide parameters, pesticide degradation rate in the first horizon (DKSOIL), soil organic carbon content in the upper 1.2 m (5 horizons), and pesticide application rate(s) were selected to be spatially-variable. Spatial variability of pesticide degradation rate in the lower horizons (up to 1.2 m) was represented by spatial variations in DKSOIL and spatial variations in organic carbon content. Spatial variability of pesticide sorption was represented by spatial variations in organic carbon content.

Statistical/Geostatistical Analysis of Spatially Variable Parameters

An initial PDF analysis on the soil hydraulic and retention properties from the two replicate soil cores at the 20 sites showed that they generally followed a normal or lognormal distribution. Arithmetic mean was used to average the two replicates at one site for all the normally-distributed parameters, whereas a geometric mean was used for all the lognormally distributed parameters. Further analysis was performed on the averaged values from the two replicates (Table 2). Truncated distributions were used in most cases so that all parameter values would be physically meaningful. Cross-correlation analysis of the soil physical properties in each horizon indicated several of the properties to be correlated. Even though the correlation coefficients calculated from field data did not always match the physical relationships between the properties, it was decided to use the computed correlation coefficients for the generation of input parameters instead of literature values or expert knowledge. The rationale behind such a decision was that correlation coefficients computed from field measured values are site-specific estimates that reflect the effect of spatial variability on these properties. Correlation between soil physical properties in adjacent horizons was not used as property measurements were not calculated from the entire horizon and hence, were not continuous.

The soil properties were then examined for spatial trends. Due to paucity of data, spatial structure was analyzed using the simpler method described in Chapter III. Trend surface analysis indicated statistically significant trends ($\alpha = 0.05$) in soil physical properties in some of the soil horizons (Table 2). RC and PBUB in the first horizon indicated a linear trend in the north-south direction, with RC increasing from south to north and PBUB increasing in the opposite direction. ALAM, THS, and B15 in the second horizon also showed linear trends, with the trends of ALAM and B15 in the north-south direction and the THS trend in the east-west direction. B15 increased in the north direction whereas ALAM increased in the south direction. THS values showed an increase from west to east. ALAM and B15 in the third horizon showed parabolic trends with ALAM values increasing from the edges to the center of the field and B15 values increasing in the opposite direction. Due to the small sample size (*n* = 20) used to calculate the trend coefficients, it was decided to use only linear (first order) trends for input parameter generation and, hence, the parabolic (second order) trends were not considered in the input parameter generation. Semivariogram analysis of the detrended residuals of all the above parameters resulted in linear models with a pure nugget effect, indicating spatial independence.

PDF and correlation analyses of the soil parameters with trends were conducted again on the detrended residuals. The PDFs of the detrended residuals turned out to be normal, even in the case of log-normally distributed raw data (Table 2). As expected, the detrended residuals had a zero (constant) mean and their standard deviation were, in many cases, less than that of the raw data (Table 2). Correlation coefficients calculated considering the detrended residuals for variables that exhibited spatial trends (Table 3a) were comparable to correlation coefficients calculated using the raw data for all variables.

Organic carbon values were estimated from randomly generated organic matter content using the van Bemmelen factor. Depth-wise correlation was considered in the generation of organic matter values, as it was measured continuously throughout the profile. These correlation coefficients are given in Table 3b.

Among pesticide parameters, pesticide degradation rates were assumed to follow a lognormal distribution as the sample size was not large enough for a proper PDF analysis. Aldicarb degradation rates were measured at 10 sites, whereas metolachlor degradation rates were measured at 6 sites in the top and bottom horizons and at 3 sites in the middle horizons (Rao et al., 1986; Smith et al., 1987). Application rates of the chemicals, on the other hand, were measured at 60 sites when they were sampled using surface soil samples (aldicarb and metolachlor) and at 100 sites when they were sampled using filter papers (metolachlor and bromide). Metolachlor application rates measured from filter papers in 1987 showed a linear trend as a function of distance along the application spray (tractor) path. Analysis of the 1987 metolachlor application rates was conducted on the residuals obtained after subtracting the trend. Application rates were not examined for spatial trends as there was no physical justification for such a trend. Statistical characteristics of the spatially variable pesticide parameters, along with values of the important fixed pesticide parameters at the Dougherty Plain site are given in Table 4.

Number of Trials

The required number of trials for a Monte Carlo simulation can be determined from the computed confidence intervals of the model results or by graphically checking the convergence of the model results (Law and Kelton, 1991). For the former method, the required number of trials is reached when the computed confidence interval for the selected model output falls below a specified error. Because the pesticide mass and leaching data are non-normal, the graphical approach was used here. The median, 10^{th} and 90^{th} percentiles of percolation loss predicted by Opus-SF at the end of the 1985, 1986, and 1987 cropping season as a function of the number of trials are given in Figure 8a, whereas corresponding values for aldicarb leaching as a function of the number of trials are given in Figure 8b. With both percolation losses and aldicarb leaching, the output variables converged by 1000 trials with the exception of 10^{th} and 90^{th} percentile values in some years. The 10^{th} percentile of water percolation loss in 1985 and the 90^{th} percentile of aldicarb leaching loss in 1987 show fluctuations close to 1400 trials. Based on these results, it was decided to run Opus for approximately 1400 trials. The execution of Opus-SF for a 3-year simulation for 1400 trials using 50 spatially variable parameters takes approximately five hours on a Pentium Pro-200 MHz personal computer with 64 Mb memory.

Generation of Spatially Variable Parameters

The spatially variable input parameters were generated with @RISK software (Palisade Corporation, 1996) using the LHS method. Input parameters that exhibit spatial trends were generated using the PDF and distribution parameters estimated from the detrended residuals (Table 2), while the other parameters were generated using the PDF and distribution parameters estimated from the measured data (Table 2, Table 4). The spatial trends were added back to each of the zero mean (detrended) random variates, by using a 4.7x4.7 m grid (which resulted in a total of 1410 cells covering the field area). Correlated variates of soil physical properties in each horizon were generated using the correlation matrix in Table 3a. Correlated variates of soil organic matter content in the different horizons were generated using the correlation matrix in Table 3b. All other spatially variable parameters were generated assuming no correlation.

Truncation limits for the soil properties were set to physically reasonable values, by considering the minimum and maximum values observed in the field. Minimum values for RC, PBUB and B15 were set to very low positive values so as to avoid negative values. Minimum values for other properties were set to be less than the minimum value of the property measured in the field. Maximum values for all spatially variable soil properties were set to be greater than the field-measured maximum for the property. Truncation limits for detrended residuals were computed by inserting the minimum and maximum values into the trend equation.

There were a total of 22 trials that gave run-time errors (as discussed earlier) for the soil water and pesticide simulation, and 32 trials that gave run-time errors for the bromide simulation. Therefore, output analysis of soil water and pesticides were based on 1388 trials out of the 1410 trials, whereas output analysis of bromide was based on 1378 trials.

Comparison with Observed Data

Water Balance

Since runoff was assumed to be zero in the Opus-SF simulation, the water balance consisted of ET, percolation below the root zone, and soil water in the root zone. Mean monthly ET and percolation predicted by Opus-SF over the simulation period are given in Table 5, along with monthly rainfall measured at the site, and ET and percolation amounts predicted by the deterministic version of Opus. The seasonal variations of ET, i.e., high values in the summer months and low values in the winter months, were predicted correctly. Soil moisture in the root zone was generally low in the summer, because of the low rainfall and high ET demand. This resulted in negative percolation values in the summer months, i.e., water was being drawn into the 1.05-1.2 m layer from the layers below the root zone. In the winter months, however, percolation loss from the root zone was positive with larger percolation loss occurring in months with high rainfall. Over the whole year, there was not much net soil water loss from the root zone, as most of the water deficit in the summer was made up by recharge in the winter.

The monthly ET and percolation amounts predicted by a deterministic simulation of Opus, using average values of the stochastic input parameters, were slightly different from the mean monthly ET and percolation values predicted by Opus-SF. In some months, deterministic Opus predicted higher ET than the mean predicted by Opus-SF, while in other months the opposite was true. There was very little difference between the monthly ET predicted by Opus-SF (mean) and Opus for nearly 6 months in 1986-87. The highest difference in monthly ET predictions by Opus-SF (mean) and Opus was about 10 mm in July 1986. A summation of the differences in monthly ET over the entire simulation period showed that deterministic Opus predicted higher ET than Opus-SF (mean) by about 11 mm. Monthly percolation predicted by Opus-SF (mean) and Opus were never the same, and the greatest difference between the two was about 17 mm in November 1986. A summation of the differences in monthly percolation over the entire simulation period showed that Opus-SF (mean) predicted about 4 mm higher percolation than deterministic Opus. Such differences are a result of the characterization of the spatially variable parameters as well as the effect of nonlinear components in the model.

Soil Water Content

Depth-averaged soil water content predicted by Opus-SF on the field-measurement dates and at the end of each month are shown in Figure 9, along with corresponding depth-averaged soil water content predicted by deterministic Opus and daily rainfall measured at the site. Observed data are given only for sampling dates in which the field measurements were made for most of the root zone (≥ 0.9m). Summary statistics and statistical tests (Table 6), however, were computed on all dates where observed data were available considering simulated data from only the depths at which the measurements were made. The effect of seasonal fluctuations on the water balance can be seen from the mean, minimum, and maximum values of depth-averaged soil water content predicted by Opus-SF. The response of simulated soil water content to rainfall can also be seen clearly from the increase in mean soil water content on June 28, 1987.

Opus-SF generally over-predicted the mean and maximum values of depth-averaged soil water content observed in the field on most dates (Fig. 9). The Mann-Whitney test results showed that the observed and simulated median depth-averaged soil water content were significantly different (at significance level, $\alpha = 0.05$) on all dates except July 22, 1985, July 8, 1986, and July 27, 1987 (Table 6). The simulated standard deviation was less than observed standard deviation on most sampling dates, except in the drought period of 1986 when the simulated values were consistently greater than observed values. The KS test showed that the distribution of observed and simulated depth-averaged soil water content were significantly different on all the field sampling dates, except July 22, 1985 and July 8, 1986 at $\alpha = 0.05$ (Table 6). On July 27, 1987, the differences between the distribution of observed and simulated depth-averaged soil water content were not significantly different at the 0.01 level.

The simulated range, however, was larger than the observed range on all six sampling dates. The range statistics indicated that a majority of the depth-averaged soil water content observations fell within the simulated range (Table 6). Except on April 30, 1986 (when soil water measurements were made only from the upper 0.15 m), at least sixty-five percent (13/20) of the observations were within the simulated range. On all dates including April 30, 1986, the observed mean was within the simulated range. On the other hand, the simulated mean was within the observed range on all except two dates (April 30, 1986 and June 28, 1987).

Simulated depth-wise distribution of soil water content on four dates are compared with observed data in Figure 10. These dates are spread over the three years, and had different rainfall patterns in the weeks preceding them. July 22, 1985 represented a dry date preceded by no rainfall for more than a week; March 24, 1986 had one storm of 43 mm four days earlier; June 28, 1987 represented a wet date, with some rain almost every day in the previous two weeks, producing a total rainfall of 35 mm in the previous week and 100 mm in the previous 2 weeks; July 27, 1987, which had some rain every day in the previous two weeks, with rainfall totals of 35 mm in the previous week and 50 mm in the previous two weeks. Opus-SF predicted the shape of the observed soil water profile well on all dates. While Opus-SF predicted mean depth-wise soil water content on July 22, 1985 and July 27, 1987, it overpredicted mean soil water content throughout the soil profile by about 0.05 mm mm^{-1} on March 24, 1986 and June 28, 1987. While rainfall may have had an influence on the overpredictions on March 24, 1986 and June 28, 1987, rainfall alone cannot be used to explain these results as all of these dates occurred in months with moderate or high rainfall (Table 5). A more thorough explanation of these results would be possible only if measurements on additional dates were available.

Opus-SF overpredicted the observed ranges of soil water content on almost all the depths on the four dates (Fig. 10). This result is expected, as variations of soil properties include information on spatial variability and parameter uncertainty. The range and standard deviation of initial soil water content simulated by Opus-SF were larger than the observed range and standard deviation (Fig. 9, Table 6). The increase in simulated range may also come from a simplification in the Opus model by which it estimates initial water content for the lower horizons from the initial water content of the first horizon (user-specified) based on static equilibrium conditions.

The mean soil water content obtained from Opus-SF was also compared to a deterministic simulation of Opus, which used average values of spatially variable parameters. The depth-averaged values (Fig. 9) as well as depth-wise distribution of soil water content (Fig. 10) show that there were noticeable differences between the two, after the end of September of 1985. The differences were about 4-8% of the mean soil water content from Opus-SF from January to June of 1986 and 1987. Such differences reflect the differences in characterization of the spatially variable parameters as well as the effect of nonlinear components in the model. The deterministic predictions were also closer to observed data than the mean from Opus-SF, on most dates where observed data were available.

Bromide Mass

The observed mean and range of bromide mass in the field on 14 sampling dates over two and a half years (April 1985 to July 1987) are shown along with mean and range predicted by Opus-SF in Figure 11. The observed data showed bromide to remain in the profile in appreciable amounts throughout the study period. Less than 20 kg ha^{-1} of bromide was detected on the first three sampling dates (until Aug. 26, 1985), after which the bromide mass detected increased to nearly 40 kg ha^{-1} and then gradually decreased. The lower observed bromide mass on the first three dates may have been due to incomplete recovery of bromide, as soil samples were taken only up to 0.3 m on June 12 and up to 0.9 m on July 22. Bromide mass on Aug. 26, 1985 was, however, taken from 1.2 m and had lower mean and range of bromide mass than the previous sampling dates. These and other inconsistencies in observed bromide mass values may be due to spatial variability of bromide mass being not well represented in the sample size of 20.

Opus-SF predicted the initial loss of bromide as in the field, as indicated by the mean, maximum, and minimum values it predicted on June 12, 1985 (Fig. 11, Table 7). However, Opus-SF predicted most of the bromide to be lost by plant uptake (in the cropping season) and leaching, and the simulated maximum was less than the observed minimum by Nov. 26, 1985. By January 1986, mean bromide mass in the 1.2 m profile had gone below 0.1 kg ha^{-1} and the maximum value had gone below 1 kg ha^{-1}. Plant uptake accounted for most of the bromide losses during the cropping season of 1985 (approximately 48 kg ha^{-1}), as there was not much rainfall for leaching. The remaining bromide was lost by leaching as a result of the high rainfall in October, November, and December of 1985 (Table 5, Fig. 9).

Bromide losses due to plant uptake in the field is not exactly known, and the validity of the uptake coefficient assumed in this study (0.6) should be investigated further. Only a few studies have examined bromide uptake by plants. Owens et al. (1985) found approximately 10% and 20% of applied bromide (168 kg ha^{-1}) to be lost to plant uptake from a permanent pasture in the first two years of its application. Gish and Jury (1982) found bromide uptake by plants to be only 2 to 3% of total bromide applied continuously in irrigation water.

In this study, simulation runs with a zero uptake coefficient (data not shown) also showed very little bromide remaining in the 1.2 m soil profile by February of 1986, with most of the bromide lost by leaching in October, November, and December of 1985. The difference in observed and simulated bromide leaching is because Opus simulates all of the bromide to move with downward movement of water, whereas substantial amounts of field-applied bromide is retained in the soil profile. A model that divides the soil matrix into mobile and immobile regions (e.g., Nicholls et al., 1982; Wagenet and Hutson, 1993) may have predicted the observed leaching of bromide better. Including the dispersion process may also improve predictions, as dispersion also can retard the movement of bromide. In an experiment to determine the movement of bromide tracer through a no-till corn field, Gish and Coffman (1987), however, found that convection was the dominant transport mechanism and that most of the variability associated with chemical dispersion could be attributed to the water velocity.

Retention of bromide in field soils has also been found in other field studies (Owens et al., 1985; Gish and Coffman, 1987; Heatwole et al., 1997). Long-term bromide data from three monolith, grassed lysimeters, and two watersheds on a silt loam soil in Ohio (Owens et al., 1985) showed that 39-78% of total bromide recovered were retained in the upper 1.5 m profile after one year of application. Bromide retained in the 1.5 m profile after the second, third, and fourth years were 24-44%, 15-24%, and 18-25%, respectively, of the total bromide recovered from the lysimeters and watersheds. The above values of bromide retention show that bromide may not be a truly conservative, non-reactive tracer in field soils, even though it may be chemically inert. If this is the case, then the inaccurate description of bromide as a conservative, non-reactive tracer is partially responsible for the poor model predictions.

Bromide, like soil water content and pesticides, was simulated only in the upper 1.2 m of the soil profile as detailed soil property measurements were not available beyond that depth. Since the model showed little bromide left in the root zone after Feb. 26, 1986, statistical tests beyond this date do not have much meaning. The Mann-Whitney test showed that the medians of observed and simulated bromide mass were significantly different at $\alpha = 0.05$ (Table 7) on all seven sampling dates, except Aug. 26, 1985. The observed and simulated EDFs of observed and simulated bromide mass were not significantly different at $\alpha = 0.01$. The range statistics showed that at least 45% of the observations on the first three dates were in the simulated range (Table 7). As noted earlier, the observed data from the first two dates seem to reflect incomplete recovery of bromide and, therefore, the range statistics and statistical test results from these dates may not be sound. From Nov. 26, 1985 until Mar. 24, 1986, none of the bromide mass observations were within the simulated range.

An interesting observation is that Opus-SF predicted an increase in bromide mass in the summer of 1986 and 1987 (Fig. 11, Table 7). For example, after predicting less than 0.005 kg ha^{-1} on March 24, 1986, Opus-SF predicted mean bromide mass of approximately 0.01 kg ha^{-1} and 0.17 kg ha^{-1} in the 1.2 m profile on May 5 and Nov. 19, 1986, respectively. This increase is because Opus predicts upward movement of solutes from below the lower boundary when there is an upward movement of water due to plant and/or evaporation gradients (R.E. Smith, Personal Communication, 1997). In other words, Opus assumes that all of the solute below the lower boundary (the layer below the maximum rooting depth – 1.2 m, in this case) is leached into a "reservoir", and allowed to move up if there is upward movement of water into the root zone from below the lower boundary. In reality, this may not happen as the solute will continue to leach and may not remain in the reservoir, as conceptualized in Opus. This assumption may lead to unrealistic values of solute mass in the lower layers, in soils like the one found at the Dougherty Plain site, where upward movement of water is significant.

Aldicarb Mass

The simulated mean and range of aldicarb mass in the field on a monthly interval are shown in Figure 12, along with observed and simulated data on the field sampling dates. Even though pesticide mass was simulated in the upper 1.2 m of the soil profile, simulated pesticide mass on the field measurement dates in Figure 12 were summed over the depths at which the observed data were available. Aldicarb mass in 1986 was greater than aldicarb mass in 1985 and 1987 because the pesticide was applied at a higher application rate (target rate of 12.6 kg ha^{-1}) in 1986 to the easternmost 36 rows of the field. Summary statistics and results of statistical tests between observed and simulated aldicarb mass are given in Table 8.

The mean and maximum values of aldicarb mass were overpredicted on most of the post-application dates in each cropping season. While there was only approximately 2%, 5%, and 5% of mean aldicarb mass remaining in the 1.2 m profile on the last sampling date before crop harvest in each year, the corresponding figures predicted by Opus-SF were 11%, 15%, and 27%.

Mean and median of simulated aldicarb mass were different on most dates (Table 8), like the observed data, showing that aldicarb mass distribution was skewed. The Mann-Whitney test showed that, except on Apr. 30, 1986, observed and simulated medians of aldicarb mass were significantly different ($\alpha = 0.01$) on all the field sampling dates in the three years (Table 8). The simulated standard deviations were greater than the observed standard deviations on all dates except the first sampling dates in 1985 and 1986: June 12, 1985 (35 days after application) and April 30, 1986 (23 days after application). The KS test showed that observed and simulated EDFs of aldicarb mass on these dates were not significantly different at $\alpha = 0.01$. The range statistics showed that almost all of the observations were within the simulated range except on July 27, 1987 when 30% (6/20) of the observations were outside the simulated range (Table 8). The simulated range was, however, much larger than the observed range in some of the later post-application sampling dates (e.g., July 22, 1985, July 8, 1986, July 27, 1987), and the simulated mean was not even contained in the observed range. Thus, the variation in aldicarb mass was overpredicted on most dates.

The overprediction of aldicarb mass by Opus-SF is also evident from Figure 13, where the observed and simulated depth-wise distribution of aldicarb mass on four dates are shown. Aldicarb mass predicted by Opus-SF was greater than observed mass in the top 0.6 m on July 22, 1985 (76 days after application) and July 27, 1987 (56 days after application), and in the top 0.3 m on June 28, 1987 (27 days after application). This indicates that the predicted degradation and/or leaching was lower than what occurred in the field. Besides potential inaccuracies in the model, the lower degradation and/or leaching predicted by the model may have been the result of inaccurate degradation and/or adsorption parameters. Although the adsorption coefficients and degradation rates available at the site were more detailed than what is available in most field studies, they were measured using laboratory techniques and may not have reflected the *in-situ* values. Other possible reasons for the increased persistence of aldicarb mass predicted by Opus-SF, as compared to observed data, are the computation of degradation rate for subsurface horizons using organic carbon ratio and the adjustment of the degradation rate in Opus with respect to temperature and soil moisture content to better match the *in-situ* degradation rate. The overprediction of aldicarb mass in the lower depths with increasing time after application (Fig. 13) shows that degradation rate in the lower depths were overpredicted. This overprediction was caused because degradation rates for subsurface horizons, computed internally in the model, were lower than the actual degradation rate in the field.

There were some differences between deterministic predictions and mean values of aldicarb mass predicted by Opus-SF, although the differences were smaller than that of soil water content. The depth-wise aldicarb mass distribution predicted by the two model versions on July 22, 1985 (Fig. 13a) showed that the mean of aldicarb mass predicted by Opus-SF was 0.1 kg ha^{-1} more than deterministic Opus at the 0-0.3 m depth, and less than deterministic Opus by approximately the same amount at the 0.45-0.75 m depth. There were no noticeable differences in predictions between the two model versions on the other three dates shown in Figure 13.

Metolachlor Mass

The observed and simulated mean and range of metolachlor mass in the 1.2 m profile over the entire simulation period are shown in Figure 14. Opus-SF overpredicted mean metolachlor mass earlier in 1985 and 1987, whereas it underpredicted metolachlor mass in all dates in 1986. Even though observed and simulated median metolachlor mass were very different on June 12, 1985, the Mann-Whitney test showed that they were not significantly different at $\alpha = 0.01$. The observed and simulated medians on the other sampling dates in 1985, July 22 and Aug. 26, were also not significantly different at $\alpha = 0.01$.

Unlike aldicarb, standard deviation and range of metolachlor were underpredicted by Opus-SF on most dates. The observed mean was, however, within the simulated range on all dates. The simulated mean was within the observed range on all dates except June 17, 1986. Range statistics showed that, except on June 12, 1985, March 24, 1986, and June 17, 1987, more than 80% of the observations were within the simulated range. The KS tests showed that the EDFs of metolachlor mass were significantly different (α = 0.01) on all of the post application sampling dates in the three cropping seasons, except July 22, 1985 (Table 9).

The depth-wise distribution of metolachlor mass (Fig. 15) showed that most of the pesticide remained in the upper 0.3 m, where most of the differences between observed and simulated mean metolachlor mass also occurred. The mean metolachlor mass in the upper 0.3 m was overpredicted in the 1987 dates, and underpredicted on April 30, 1986 (23 days after application). On the two 1987 dates, Opus-SF overpredicted the observed range considerably.

Once again, the mean metolachlor mass predictions show that Opus-SF may not have predicted leaching and degradation of the herbicide well. The underprediction in 1986 was due to greater loss of the herbicide than what occurred in the field, as most of the herbicide remained in the top horizon and was subjected to a higher degradation rate. The reduced leaching of metolachlor may also be responsible for the lower standard deviation and range of metolachlor mass. Unlike aldicarb, lower metolachlor degradation rate in the subsurface horizons did not affect the results much as most of the metolachlor remained in the top horizon. Metolachlor, with a higher K_{oc} and a lower half-life (Table 4), leached much slower than aldicarb and, therefore, was subject to greater degradation early in the season.

There were some differences between predictions of metolachlor by the deterministic version of Opus and the mean predicted by Opus-SF, but they were smaller compared to the differences seen in soil water content predictions and comparable to the differences seen in aldicarb mass predictions. The two 1987 dates show that deterministic Opus predicted more metolachlor mass than the mean predicted by Opus-SF and was farther away from the observed data (Fig. 15c,d).

Comparison with Traditional Monte-Carlo Simulation

Results from the proposed stochastic framework (Opus-SF) were compared with results from the traditional Monte-Carlo approach (Opus-MC), where spatial trends are not considered and all variation is described as a random component. The major difference between the two approaches is conceptual: Opus-MC assumes all spatially variable parameters to have a constant mean over the entire field, whereas Opus-SF describes the parameters that exhibit spatial trends as the sum of the deterministic trend and the random variations. Although theoretically there is no comparison between the two approaches as they solve the same problem using different assumptions, they can be compared numerically to determine if the differences between their outputs were significant and to examine how each compared with the observed data.

Statistical tests were performed to determine if the output variables (depth-averaged soil water content, bromide, aldicarb, and metolachlor mass) predicted by the two approaches were the same, and to compare the Opus-MC predictions with observed data. The KS two sample test was used to test for significant differences between EDFs predicted by Opus-SF and Opus-MC, and the observed EDF and the EDF predicted by Opus-MC. The Mann-Whitney test was used to test for significant differences between medians predicted by Opus-SF and Opus-MC, and the observed median and the median predicted by Opus-MC. Comparisons between outputs from the two models were made considering the entire 1.2 m profile, whereas comparison with observed data on the field sampling dates were made using model output from the depths from which field measurements were taken.

Water Balance and Soil Water Content

Overall, the water balance predicted by Opus-MC was comparable to that of Opus-SF (Table 10), with the seasonal variations in mean ET and percolation amounts predicted by both models in a similar fashion. The difference between the two models was small, except between July and September, when Opus-MC predicted lower ET and greater percolation losses than Opus-SF. The difference in summer months obviously resulted from the differences in the soil parameters used in the two models. Over the entire simulation period, Opus-MC predicted approximately 30 mm of ET less than Opus-SF, with the maximum difference in one month (July 1986) being approximately 10 mm. Opus-MC predicted approximately 31 mm of percolation more than Opus-SF over the simulation period, with the maximum difference in one month (July 1986) being approximately 7.5 mm.

The Mann-Whitney and two sample KS tests showed that the median and the EDFs of depth-averaged soil water content EDFs predicted by Opus-MC and Opus-SF were significantly different (α = 0.01), with the exception of the simulation start date, June 12, 1985, and July 27, 1987 (Table 11). These results indicated that including spatial trends of the five soil hydraulic and retention properties in either of the first two soil horizons (Table 2) had some impact on soil water results from the stochastic simulation of Opus, especially after the first 150 days of the simulation period (Table 11).

The results obtained from the KS test comparing Opus-MC predictions and observed data were the same as the KS test results comparing Opus-SF predictions and observed data (Table 6), except for July 27, 1987 when the Opus-MC p-value was 0.1-0.2 and the Opus-SF p-value was 0.02-0.05. The Mann Whitney test comparing Opus-MC and observed data gave the same results as the Mann Whitney test comparing Opus-SF and observed data (Table 6). Barring few exceptions, the p-values and test statistics showed that Opus-MC predicted the EDF slightly better than Opus-SF, whereas Opus-SF predicted the median slightly better than Opus-MC.

Bromide Mass

Differences between bromide leaching predicted by the two models was small (data not shown). There were some differences between model predictions in November-December, when most of the leaching took place. There were some differences in model predictions from July to September of 1986 too. However, it must be noted that the bromide amounts remaining in the profile in 1986 were caused due to uptake of the chemical from below the lower boundary which is unlikely to happen in the field. The net difference in bromide leaching predicted by the two models was approximately 0.19 kg/ha (0.3% of applied amount), with Opus-SF predicting more leaching than Opus-MC.

The distributions as well as the medians of bromide mass predicted by Opus-MC and Opus-SF were not significantly different ($\alpha = 0.05$) on the application date (data not shown) and the first three sampling dates (Table 12). On these dates, the mean and range of bromide mass predicted by the models were almost the same as that of the application date. After these dates, there was a rapid decrease in bromide mass in the 1.2 m profile (Fig. 11), and the predictions by Opus-MC and Opus-SF were significantly different ($\alpha = 0.05$). The model predictions continued to be significantly different after that, with the exception of Nov. 19, 1986, when bromide mass in the profile had once again risen due to upward water gradient. Since bromide was simulated only up to 1.2 m and the differences between the models occurred when the solute was present in the profile in low quantities, it is hard to say whether there was any real difference between model predictions. One thing is clear: if there was difference in bromide mass predictions by Opus-SF and Opus-MC, it occurred only when there was very little solute left in the profile.

On the few dates where observed versus simulated bromide mass comparisons were possible, the p-values and the test statistics obtained from the KS and the Mann-Whitney tests from Opus-MC were not much different than the p-values obtained from Opus-SF (Table 7). It was difficult to determine which was closer to observed data, as the Opus-MC predictions were closer to observed data on some sampling dates, and the Opus-SF predictions were closer to observed data on other dates.

Pesticide Mass

Aldicarb leaching losses from the 1.2 m profile, predicted by Opus-MC and Opus-SF, were similar (data not shown), with some differences in November-December of 1985 and 1986, when most of the leaching occurred. The differences between leaching predicted by the two models were never more than 0.01 kg ha^{-1} in any month. The net difference in aldicarb leaching predicted by the two models was approximately 0.016 kg ha^{-1} (0.07% of the total application amount), with Opus-MC predicting more leaching than Opus-SF.

The distributions as well as the medians of aldicarb mass predicted by Opus-MC and Opus-SF were not significantly different ($\alpha = 0.05$) on all of the post-application dates within the cropping season (Table 13). The only two cases that resulted in rejection of the null hypothesis were on Mar. 24, 1986 (321 days after application) and on Apr. 28, 1987 (386 days after application), when hardly any of the pesticide remained in the profile. With metolachlor, however, the statistical tests showed significant differences ($\alpha = 0.05$) between the distributions as well as the medians predicted by Opus-MC and Opus-SF on the last post-application date in 1986 (92 days after application) and on all three sampling dates in 1987 (Table 14).

The p-values obtained from the KS and the Mann-Whitney tests by comparing aldicarb and metolachlor mass predictions from Opus-MC and observed data were very close to the p-values obtained by comparing Opus-SF predictions and observed data (Tables 8 and 9). At $\alpha = 0.05$ and 0.01, Opus-MC resulted in rejection of the null hypothesis on the same dates as Opus-SF for both aldicarb and metolachlor mass. From this it can be concluded that although there were some differences between pesticide mass predicted by Opus-MC and Opus-SF, these differences were small and did not change the results from the statistical tests used for comparing simulated data with observed data. Overall, the small differences may be due to the fact that spatial trends in the soil physical properties were weak, i.e., trends of one soil property were not found in multiple horizons nor did all properties in one horizon possess a trend.

Summary

Soil hydraulic and retention properties and organic carbon content in the four horizons and the plinthite layer, initial water content in the surface horizon, pesticide degradation rate in the four horizons, and pesticide application rates in the three years were selected as the spatially variable input parameters for the stochastic simulation of water flow and pesticide transport at the Dougherty Plain site using Opus-SF. In the stochastic simulation of bromide, all of the above parameters except organic carbon content and degradation rates were considered spatially variable. Bromide was also applied only once in 1985. The spatially variable parameters were described by their PDFs, after analyzing them for spatial trends. For the variables with physically meaningful and statistically significant trends, the trends were removed before PDF analysis and later reinstated after generation of random variates. Correlation between the soil properties within a horizon was also considered in input parameter generation.

There were considerable seasonal variations in the water balance components predicted by Opus-SF. High water demand (ET) and low rainfall in the summer months led to low soil water content in the root zone and resulted in upward movement of soil water from the layer below the root zone. High rainfall in the fall and winter months recharged the soil water content in the root zone and led to increased percolation from the root zone.

Comparison between observed and simulated data on the 14 field sampling dates showed that Opus-SF generally overpredicted the mean of depth-averaged soil water content in the root zone. Spatial variability of simulated soil water content was less than the observed variability except on the 1986 dates, although the simulated maximum values were greater than the observed maximum. The observed and simulated medians and EDFs were significantly different ($\alpha = 0.01$) on all dates, except the three dates in July of each year. The fact that there were no significant differences between observed and simulated EDFs of soil water content on at least one date in each cropping season shows that there was no decline in performance of Opus-SF over the three year period. Range statistics of soil water content showed that at least 65% of the observations fell within the simulated range on all except one sampling date, and at least 85% of the observations fell within the simulated range on all except three sampling dates. Opus-SF was also able to predict the depth-wise distribution of soil water content in the soil profile fairly well.

Opus-SF was not able to predict the field-scale movement of bromide well. The inaccuracies in bromide predictions could not be explained fully due to inconsistency in observed data and unexplained retention of bromide in the root zone of the Dougherty Plain site. Opus-SF overpredicted bromide mass in the field for the first two months after application, after which it predicted extensive loss of bromide from the root zone due to plant uptake and leaching. The simulated maximum was less than the observed minimum after about 225 days after application. The mean bromide mass simulated by Opus-SF was less than 0.2 kg ha^{-1} within 260 days after application, whereas mean bromide mass observed in the field was never below 10 kg ha^{-1} for over 700 days after application. Simulating plant uptake of bromide and the value of the plant uptake coefficient assumed in this study must be investigated further. Dividing the soil water regime into mobile/immobile regions and/or including the dispersion process may improve the predictions of solute transport in Opus-SF.

The observed median of total aldicarb mass in the root zone were overpredicted by the model, and were significantly different ($\alpha = 0.01$) on all dates except on the first sampling date in 1986 (23 days after application). Most of the overprediction of aldicarb mass occurred in the lower depths, and increased with time after application. Overprediction in the lower depths was because aldicarb degradation rate in the subsurface horizons, computed internally in the model, was lower than the laboratory measured degradation rates. The observed spatial variations in aldicarb mass were overpredicted by the model, and the observed and simulated EDFs were significantly different ($\alpha = 0.01$) on all dates except the first sampling dates in 1985 and 1986. Except for the last date in 1987, more than 90% of the aldicarb mass observations were contained in the simulated range.

Opus-SF overpredicted mean metolachlor mass in the earlier dates in 1985 and in 1987, whereas it underpredicted metolachlor mass for all dates in 1986. The observed and simulated medians were significantly different ($\alpha = 0.01$) on all post application sampling dates in 1986 and 1987. Unlike aldicarb, the spatial variations of metolachlor mass in the field were underpredicted by Opus-SF, and the observed and simulated distributions were significantly different on all except one field sampling date. Range statistics showed that more than 80% of the metolachlor mass observations were contained in the simulated range on seven of the ten post-application dates. Overall, Opus-SF was able to predict pesticide mass much better than bromide mass.

The deterministic version of Opus, which used average values for spatially variable parameters, predicted water balance and soil water content, bromide and pesticide mass similar, but not equal to the mean values obtained from the stochastic simulation of Opus. Over the entire simulation period, the deterministic Opus predicted about 11 mm less ET than Opus-SF (mean), and predicted about 4 mm more percolation than Opus-SF (mean). The deterministic Opus also predicted lower soil water content than Opus-SF (mean), after the end of September 1985, and was closer to observed data. These differences reflect the differences in characterization of the spatially variable parameters as well as the effect of nonlinear components in the model. The differences in pesticide mass between the two versions were smaller than the differences in soil water content.

A comparison of stochastic outputs from Opus-SF and Opus-MC, in which spatial trends were not considered in the description of the spatially variable parameters, showed that soil water contents predicted by the two models were significantly different ($\alpha = 0.01$), especially after 150 days from the simulation start date. Depth-averaged soil water content predicted by Opus-MC was closer to observed data than that predicted by Opus-SF. The difference between bromide and pesticide mass predictions from the two models was significant only after most of the solute was leached/degraded/lost by uptake from the 1.2 m profile. The small differences between bromide and pesticide mass predicted by Opus-MC and Opus-SF did not change the results from the statistical tests used for comparing simulated data with observed data. Overall, the small differences between Opus-SF and Opus-MC may be due to the fact that spatial trends in the soil physical properties were weak, i.e., trends of one soil property were not found in multiple horizons nor did all properties in one horizon possess a trend.

MODELING FLOW AND TRANSPORT AT THE NOMINI CREEK SITE

Description of Field Study

Heatwole et al. (1992) used surface runoff monitoring and soil core sampling to characterize the fate and transport of atrazine, metolachlor, and bromide from two field plots in the Nomini Creek watershed in the Coastal Plain region of Virginia (Westmoreland County). The soil is a Suffolk sandy loam (coarse-loamy, siliceous, thermic Typic Hapludult), characterized as deep and well-drained. Depth to water table at the site ranges from 8 to 10 m. The two 18x27 m plots, separated by a 6-m buffer (Fig. 16), were located in a field that was in the second year of a two year no-till wheat-soybean-corn rotation typical of the region. One plot (TP) was plowed and disked before corn was planted and herbicides (atrazine and metolachlor) were applied, while the other plot (NT) remained no-till with a heavy soybean-wheat residue.

Atrazine, metolachlor, and bromide were applied on April 25, 1990. Forty hours following pesticide application, a rainfall simulator was used to apply 37 mm of rainfall to the plots in 1 h. Surface runoff quantity and quality measurements from the no-till and tilled plot were made over the five month corn season, from April 25 (day 115) to September 29 (day 272). Soil core samples were collected up to 1.5 m depth at 20 random locations in the plot, 6 times following chemical application. The six sampling dates were days 118, 128, 145, 167, 209, and 272. Soil cores were collected at intervals of 0-0.01, 0.01-0.15, 0.15-0.3, 0.3-0.45, 0.45-0.6, 0.6-0.9, 0.9-1.2, and 1.2-1.5 m. On the last sampling date (day 272), the top 0.15 m was sampled as one layer. The soil core samples were analyzed for atrazine, metolachlor, and bromide concentrations, as well as for organic matter content, pH, and gravimetric moisture content. A detailed description of the field study can be found in Heatwole et al. (1992; 1997).

Spatial variability of soil texture at the site was characterized in 1994 by taking soil (auger) samples on a 8x8 m grid, covering an area of 48x32 m (Fig. 16). The soil samples from the 35 grid points were taken at 0.15 m increments to a depth of 0.9 m, and particle size analyses from these samples are summarized in Table C1 of Appendix B. Soil texture data showed a distinct trend across the study site, with the clay content increasing from the south-west quadrant to the north and to the east of the study area (Zacharias et al., 1997). Saturated hydraulic conductivity, water retention, and bulk density were also measured at the site using undisturbed soil cores (5 cm diameter, 5 cm long), from 12 locations at four depths (0-0.05, 0.15-0.3, 0.3-0.35, and 0.45-0.5 m); the data are presented in Table C2 of Appendix B.

Development of Base Parameters

The simulation period started on the day before corn planting, April 22, 1990 (day 112), and ended on the harvest date, September 30, 1990 (day 273). Weather data used in the simulation consisted of daily values of rainfall, minimum and maximum air temperature, and solar radiation. Daily rainfall amounts recorded using a raingage close to the plots were used in the simulation. Air temperature and solar radiation data were obtained from the LN3 weather station of the watershed (Mostaghimi et al., 1989b), which is approximately 500 m from the plots. The option of using measured data for runoff and sediment losses in Opus was invoked; runoff volume and sediment loss on runoff-producing events were set to the values measured in the NT plot. Initial soil water content was set to the mean soil water content in the NT plot measured on day 114.

The soil profile was characterized into six depth layers, 0-0.15, 0.15-0.3, 0.3-0.45, 0.45-0.6, 0.6-0.9, and 0.9-1.2 m. These soil layers did not exactly match the morphological horizons given in the soil survey manual (SCS, 1981), but were representative of the depthwise variation in soil texture, and to some extent, depthwise variation in other soil physical properties. Because soil hydraulic and retention properties measured at the site were limited, the soil water parameters, RC, PBUB, ALAM, and B15, for the stochastic simulation were estimated using field-measured texture and porosity data in the regression equation of Rawls and Brakensiek (1985). THS was estimated from porosity by multiplying by the reduction factor 0.95 (e.g., Mishra et al., 1989).

Porosity (ϕ) was estimated from bulk density measured at the study site (Table C2), by the expression (Mishra et al., 1989):

$$\phi = 1 - \frac{\rho_b}{\rho_s} \qquad (21)$$

where ρ_b is the bulk density of the soil (g cm^{-3}) and ρ_s is the particle density of the soil, assumed to be 2.65 g cm^{-3}. Organic carbon content in the six horizons was estimated from organic matter content measured in the NT plot on day 118, using the van Bemmelen factor (1.732). Soil properties used to estimate soil hydraulic and retention properties are summarized in Table 15.

The amount of wheat-bean residue at the start of the simulation (day 112) was assumed to be 1800 kg ha^{-1}, 75% of which was on the soil surface and the remaining 25% was on dead plant dry matter standing above soil. Crop parameters for the simulation were based on values given for the Iowa short season corn in the Opus User Manual (Ferreira and Smith, 1992), with the following changes. The potential total dry matter for the crop was assumed to be 17920 kg ha^{-1} and potential yield of fruit and seed was assumed to be 8400 kg ha^{-1}. The potential maximum rooting depth for corn was set at 0.9 m.

Initial concentrations of bromide, atrazine and metolachlor were set to zero, as there was no residue left from previous applications. Pesticide and bromide application rates measured in the NT plot using filter papers (Heatwole et al., 1997) were used in the simulation. Other pesticide properties used in the simulations were derived from the literature. Pesticide properties not affected by soil type, such as solubility and K_{oc}, were obtained from the SCS/ARS/CES pesticide property database (Wauchope et al., 1992). Plant-washable fraction of the pesticide and foliar degradation rates, computed from foliar half-life, were obtained from the GLEAMS user manual (Knisel et al., 1992).

Estimates of pesticide half-life in soil were obtained from studies with similar soil type and comparable organic carbon, as degradation estimates are influenced by these soil properties. The soil at the Dougherty Plain site was an *Udult* soil, like the soil at the Nomini Creek site, and had similar texture and comparable organic carbon content. Therefore, first-order degradation rate of metolachlor, computed from the average half-life (18 days) measured in the surface soil at Dougherty Plain site, was used in this simulation. For atrazine, studies with laboratory measurements of degradation rate/half-life on soils similar to that of Nomini Creek site were unavailable. Therefore, a half-life of 60 days, recommended in the SCS/ARS/CES pesticide property database (Wauchope et al., 1992), was used to calculate the first-order degradation rate in the surface soil. Atrazine half-life of 60 days was also reported by Ritter et al. (1994) from atrazine concentration in the upper 0.3 m of a field (Evesboro loamy sand soil) under no-till corn in the Coastal Plain region of Delaware. Parameters used to modify degradation rate with moisture content and temperature were assumed as the average soil moisture content and average soil temperature over the cropping season at the Nomini Creek site (obtained from sensors placed at 0.1 m depth), and Arrhenius constants of atrazine and metolachlor were obtained from the literature. The estimated relative soil moisture content (DKTHE) was 0.38, temperature (DKTEMP) was 23.6°C, and Arrhenius constant (ARRHC) for atrazine was assumed as

16.7 kcal mole^{-1} (Walker, 1978, pg.308) and ARRHC for metolachlor was assumed as 12.4 kcal mole^{-1} (Walker and Brown, 1985, pg.145).

Coefficients of uptake for atrazine and metolachlor were calculated using the regression equation of Briggs et al. (1982) that relates plant uptake to the logarithm of the octanol-water partitioning coefficient (log K_{ow}) of the pesticide. The midpoints of the log K_{ow} ranges of atrazine and metolachlor, given in the Agrochemicals Desk Reference (Montgomery, 1993), were used in the calculation of plant uptake. Bromide was simulated as a conservative, non-reactive tracer with a zero degradation rate and a zero adsorption coefficient. Solubility of 1000 mg L^{-1}, washoff fraction of 0.75, and plant uptake coefficient of 0.6 were assumed for the tracer.

Even though soil properties were described only to 1.2 m, solute transport calculations in Opus was made based on a 1.5 m profile. Opus assumes the soil properties in the 1.2-1.5 m depth to be equal to values in the 0.9-1.2 m depth. Pesticide degradation rate in the 1.2-1.5 m depth was calculated by multiplying the degradation rate of the surface soil with the ratio of organic carbon in the two layers (in other words, the reduction factor ZDGR was set to 1.0). The simulation domain, therefore, consisted of the top 1.5 m of the NT plot area (Fig. 16). The simulation was performed with the entire domain (18x27x1.5 m) as no-till, and simulated data were compared with observed data from the 1.5 m profile in the no-till plot.

Selection of Spatially Variable Parameters

Selection of the spatially variable parameters to be used in the simulations was based on the sensitivity of the model to the parameters, physical considerations and availability of data. Due to their sensitivity to water flow and/or chemical transport, the five soil hydraulic and water retention parameters (RC, PBUB, ALAM, THS, B15) were selected as spatially variable parameters. Because porosity was estimated from saturated water content, porosity in all horizons was also treated as spatially variable. The soil hydraulic and retention properties were not sensitive to water flow and solute transport predictions by the model beyond the upper 0.6 m, as there was very little resistance to water flow due to the marked increase in the sand content and a corresponding decrease in the clay content of the soil (Table C1). Therefore, soil hydraulic and retention properties below 0.6 m were assumed to be not spatially variable. Even though initial water content in the top horizon was a sensitive parameter, there were not enough data to specify the distribution parameter. Among the pesticide parameters, pesticide degradation rate in the surface soil (DKSOIL) and soil organic carbon content in upper 0.6 m, and the pesticide application rate(s) were selected to be spatially-variable. Spatial variability of pesticide degradation rate in the lower horizons (up to 0.6 m) was represented by spatial variations in DKSOIL and spatial variations in organic carbon content. Spatial variability of pesticide sorption was represented by spatial variations in organic carbon content.

Statistical/Geostatistical Analysis of Spatially Variable Parameters

Soil hydraulic and water retention parameters for the Nomini Creek site were estimated using the Rawls and Brakensiek (1985) regression equation with sand and clay content and porosity measured at the site. The method used to estimate soil water properties at the site consisted of: (i) generate the required number of trials (1350 trials) of sand and clay content and porosity from the field-measured data; and (ii) calculate the soil water parameters for each trial from the generated sand, clay, and porosity values using the regression equation.

Distribution analysis of sand and clay content in the first four soil layers (up to 0.6 m) from 35 locations in the 48x32 m area (Fig. 16), showed normal distribution to be the best fit (Table 15). As expected, cross-correlation analysis of sand and clay content in each depth layer showed a strong negative correlation.

Trend surface analysis performed on depth-averaged sand and clay content showed a strong parabolic trend (Zacharias et al., 1997), with sand content increasing from the north-east quadrant to the south-west quadrant of the study area (Fig. 16) and clay content increasing in the opposite direction. The planar trends were attributed to fluvial and marine action in the soil formation process. Trend surface analysis of sand content in individual soil layers (0-0.9 m) indicated statistically significant trends (α = 0.05) in all except the second layer (Table 15), and the trends were in the same direction as above. Trend surface analysis of clay content in individual soil layers (0-0.9 m) indicated statistically significant trends (α = 0.05) in all except the third and fourth layers (Table 15), and the trends were in the same direction as the depth-averaged clay content. Semivariogram analysis of the detrended residuals of all the sand and clay resulted in linear models with a pure nugget effect, indicating lack of spatial correlation or that the correlation scale was below the 8 m grid spacing used.

PDF and correlation analyses of sand and clay content with trends were conducted again on the detrended residuals. The PDFs of the detrended residuals were all, once again, normal (Table 15). As expected, the detrended residuals had a zero (constant) mean and standard deviation similar to but less than that of the raw data (Table 15). Correlation coefficients calculated considering the detrended residuals of sand and clay content that exhibited spatial trends (Table 16a) were comparable to correlation coefficients calculated using the raw data for all variables. PDF analysis of porosity and organic matter content in all four layers showed that they followed a normal distribution. Depth-wise correlation of organic matter content (Table 16b) was used in the random input generation. Soil hydraulic and retention parameters for each of the four soil layers were then estimated from sand, clay, and porosity values, and are summarized in Table 17. Organic carbon values were estimated from randomly generated organic matter content for the soil layers by using the van Bemmelen factor (1.732), and are presented in Table 17.

Among pesticide parameters, soil degradation rates were assumed to follow a lognormal distribution (Table 18). Application rates of bromide, atrazine, and metolachlor, were measured using 20 filter papers, placed diagonally across the field. PDF analysis of application data showed lognormal distribution to be the best fit for all three chemicals. Statistical characteristics of the spatially variable pesticide parameters, along with values of the important fixed pesticide parameters at the Nomini Creek site, are given in Table 18.

Generation of Spatially Variable Parameters

Sand, clay, and porosity values were generated with @RISK software (Palisade Corporation, 1996) using the LHS method. Sand and clay content that exhibited spatial trends were generated using the PDF and distribution parameters estimated from the detrended residuals (Table 15), while the other parameters were generated using the PDF and distribution parameters estimated from the measured data (Table 15, Table 18). The spatial trends were added back to each of the zero mean (detrended) random variates, by using a 0.6x0.6 m grid (which resulted in a total of 1350 cells covering the field area). Correlated variates of soil physical properties in each horizon were generated using the correlation matrix in Table 16a.

Truncation limits for sand and clay content were set such that their total did not exceed 100%. Truncation limits for detrended residuals were computed by inserting the minimum and maximum values into the trend equation. There were also five other trials where the saturated water content was low and less than field capacity. These six trials were not included in the stochastic simulation.

Simulation of Opus-SF resulted in run-time errors for a total of six trials. Only one trial resulted in a convergence error (more than 20 iterations were required in the RBHF subroutine), and affected soil water as well as solute transport results. The remaining five trials with runtime errors were caused due to negative concentrations of bromide around July 1. Therefore, a total of 1343 trials were available for analysis of soil water and pesticide outputs, while a total of 1340 trials were available for analysis of bromide outputs.

Comparison with Observed Data

Water Balance

Mean monthly ET and percolation predicted by Opus-SF and Opus over the simulation period are given in Table 19, along with monthly rainfall and runoff measured at the plot. As discussed earlier, runoff volume measured from the plot was provided as an input to the model (in the measured data file) for a more direct evaluation of the subsurface component. In the model, runoff is subtracted from rainfall giving a direct (rather than predicted) estimate of infiltration. There was substantial rainfall, totaling 353 mm, in the first 34 days of the study period including 37 mm from the rainfall simulator application on day 116 (Fig. 17). Because of the heavy residue on the no-till plot, only the large rainfall events produced substantial runoff from the plot. The rainfall events on day 146 (104 mm) and 149 (105 mm) resulted in a total runoff of 38 mm, whereas the rainfall event on day 235 (91 mm) resulted in 12 mm lost in runoff. The remaining rainfall events resulted in only about 5 mm of runoff.

The high rainfall in May resulted in Opus predicting over 200 mm of water percolating below 1.2 m. Monthly ET was close to or higher than 100 mm from June through September. The high ET resulted in a decrease in soil water content in the root zone and negative percolation in these months (Table 19). The total runoff, ET, and percolation values indicate that there was a net loss in soil water storage of approximately 120 mm from the 1.2 m soil profile over the simulation period.

Monthly ET predicted by the deterministic version of Opus was slightly lower than the mean values predicted by Opus-SF on all months, whereas monthly percolation predicted by deterministic Opus was slightly higher than Opus-SF mean except in April and June. The differences, however, were small. The total difference in monthly ET predictions by Opus-SF (mean) and Opus was 7 mm, with the maximum difference of approximately 3 mm in June. The total difference in monthly percolation was negligible, with the maximum difference of 4 mm in May (Table 19). Spatial characterization of soil parameters and non-linearities in the model had some effect on monthly water balance.

Soil Water Content

The mean, minimum and maximum values of depth-averaged soil water content predicted by Opus-SF on a 15-day interval and on the field sampling dates are shown in Figure 17, along with corresponding deterministic values and the observed mean and range on the field sampling dates. The daily rainfall measured at the site is also given in Figure 17. Results from the statistical comparison of observed and simulated (Opus-SF) depth-averaged soil water content are given in Table 20. The summary statistics, p-values from the Mann-Whitney test for equality of medians and Kolmogorov-Smirnov (KS) test for equality of EDFs, as well as the range statistic, i.e., the percentage of observations in simulated range, are given in Table 20. For the Nomini Creek simulation, all statistical comparisons between observed and simulated data were conducted on output variables from the root zone (0.9 m). Observed and simulated (Opus-SF) mean and range of soil water content in each of the soil layers in the root zone on day 118 (preceded by 37 mm of rain in the previous week) and day 209 (preceded by 0.5 mm of rain in the previous week) are shown in Figure 17.

Opus-SF predicted the seasonal fluctuations in soil water, as reflected by the mean, minimum, and maximum values of depth-averaged soil water content in Figure 17. The mean and maximum values predicted by Opus-SF were, however, lower than the observed mean on days 209 and 272. The mean and median of depth-averaged soil water content on all field sampling dates were almost identical (Table 20), implying that their distributions were symmetrical. Soil water content medians predicted by Opus-SF were significantly different than the observed medians on all dates except day 167 at the 0.05 level of significance and on all dates except days 128 and 167 at the 0.01 level of significance. The depth-wise distribution of soil water content on days 118 and 209 (Fig. 18) showed that the simulated mean was consistently less than the observed mean at almost all depths.

The simulated range was greater earlier in the season when there was high rainfall and was lower in the low rainfall period in July-August. The simulated variation in depth-averaged soil water content was much lower than what was observed in the field. This is evident from the smaller standard deviation (Table 20) and range (Fig. 17) on all the six dates. The smaller variation in depth-averaged soil water content in the root zone is attributed to two reasons: (a) soil physical properties derived from texture data are less variable than their field-measured values; and (b) there was very little variation in the 0.6-0.9 m depth (Fig. 18), as spatial variability of soil physical properties were considered only up to 0.6 m. Simulated range and standard deviation of depth-averaged soil water content from the upper 0.6 m was still lower than the corresponding observed range and standard deviation (data not shown), indicating that point (a) was the dominant cause for the reduced simulated variation. The above statement can also be substantiated by the fact that the simulated range was smaller than the observed range of soil water content in the first four soil layers (0-0.6 m) on days 118 and 209 (Fig. 18).

The KS test showed that the observed and simulated EDFs of depth-averaged soil water content were significantly different on all dates at $\alpha = 0.05$ and on all dates except day 167 at $\alpha = 0.01$ (Table 20). The range statistic indicates that except for days 145 and 167, less than 50% of the observations were within the simulated range. The observed mean was within the simulated range on days 128, 145, and 167, whereas the simulated mean was within the observed range on all six dates.

Depth-wise distribution of observed and simulated soil water content (Fig. 18) showed that Opus-SF predicted the depth-wise variation in soil water well except for the 0.6-0.9 m depth on day 118. This may have been partially due to not including the variation in soil hydraulic and retention properties beyond 0.6 m. The observed mean was within the simulated range on all depths except 0.6-0.9 m, whereas the simulated mean was always within the observed range.

A comparison of the mean depth-averaged soil water content predicted by Opus-SF and corresponding predictions by deterministic Opus show that there were small differences (less than 3.5% of the predictions from deterministic Opus) between the two for the first four months of the simulation period (until the end of August). The differences were higher earlier, perhaps due to the differences in initial water content assumed by the two models and the high rainfall. The depth-wise distribution of soil water content showed that the main difference on day 118 was in the 30-60 cm soil layers whereas the differences on day 209, which were smaller, was greatest in the 15-30 cm layer. Such differences reflect the effect of how the spatially variable parameters were defined as well as the effect of nonlinear components in the model.

Bromide Mass

Mean of observed total bromide mass in the root zone showed that there was nearly 10 kg ha^{-1} of the applied bromide lost or not recovered from the no-till plot on day 118, 3 days after application (Fig. 19, Table 21). While part of the unaccounted bromide may have been due to incomplete recovery of the tracer from soil (as explained in the Dougherty Plain simulation section), a major portion of bromide loss from the root zone may have occurred due to preferential flow as a result of the rainfall simulator application (37 mm of rain in one hour) on day 116. Bromide concentrations in the 0.9-1.2 m and 1.2-1.5 m depth layers on day 118 (Fig. 20a) and simulation results from a one-dimensional flow and transport (CDE) model (Heatwole et al., 1997, pg. 1272) showed that preferential movement of chemicals occurred in the plot. In a tracer study conducted on the same plots in 1991, Bruggeman (1997) attributed more than 50% of the solute transport to preferential flow. Since Opus deals with only matrix flow and not preferential flow of chemicals, the drop in bromide mass could not be predicted by the model. This led to the overprediction of bromide mass in the field in the first month after application.

Opus-SF also predicted a little over 0.7 kg ha^{-1} of bromide to be lost in runoff, based on the field-measured runoff provided as input to the model. Bromide losses in runoff were not monitored in the field; so there was no comparison made. The large range of bromide application rate generated in Opus-SF resulted in the model overpredicting the observed maximum and minimum on day 118 (Fig. 19). Opus-SF predicted large amount of bromide loss after the two large rainfall events on day 146 and 149 (Fig. 19), after which it consistently underpredicted bromide mass. Observed bromide mean in the root zone, and to some extent, its standard deviation and range, remained steady on the last three sampling dates, days 167, 209, and 272. Opus-SF predictions were also steady, but the maximum bromide mass simulated was less than the mean observed mass on these dates.

As explained earlier, the difference in observed and simulated bromide mass may be partly due to inaccurate description of the chemical as a tracer with zero adsorption and partly due to model errors (increased plant uptake and/or leaching). The effect of the plant uptake coefficient must be investigated further. With regard to leaching, Opus simulates all of the bromide to move with downward movement of water – in other words, none of the bromide is retained in the soil matrix. A model that divides the soil matrix into mobile and immobile regions may have predicted the observed leaching of bromide better. Simulating dispersion, which retards the movement of a solute, may also improve bromide prediction.

Mean and median of bromide mass simulated by Opus-SF differed by less than 4% (Table 21). Such differences were also found between observed mean and median, and indicated that bromide mass distribution in soil was only slightly skewed. The Mann-Whitney test showed that observed and simulated medians of total bromide mass in the root zone were significantly different ($\alpha = 0.05$) on all dates (Table 21).

Simulated standard deviation of total bromide mass in the root zone (Table 21) was comparable but lower than observed standard deviations on all field sampling dates. Thus, bromide variability was underpredicted even though maximum bromide mass was higher than the observed maximum values on the application date and the first three sampling dates. As with soil water variability, the underprediction may be caused by the reduced variation in soil physical properties derived from texture data. The KS test showed that the observed and simulated EDFs of total bromide mass in the root zone were significantly different on all dates at $\alpha = 0.05$, and on all dates except day 128 at $\alpha = 0.01$ (Table 21). Range statistics show that over 80% of the observations were contained within the simulated range on the first three sampling dates, while less than 10% of the observations were contained within the simulated range on the last two dates (Table 21).

Depth-wise distribution of observed and simulated bromide mass on day 118 (Fig. 20a) showed that the overprediction of total mass on day 118 was because bromide remaining in the 0-0.3 m depth in the field was only about half of the bromide mass simulated by Opus-SF. Depth-wise distribution of observed and simulated bromide mass on day 209 (Fig. 20b) showed that while Opus-SF simulated most of the bromide to have left the 0-0.3 m depth, there was still an average of 3 kg ha^{-1} left in the field. By day 209, Opus-SF also predicted substantial amounts of bromide to move to the 1.5 m depth, as was observed in the field. There were some differences between Opus-SF mean and deterministic predictions of bromide mass, although these differences were small, as in the case of soil water content.

Atrazine Mass

Mean of observed atrazine mass on the application date (Table 18) and day 118 (Fig. 21, Table 22) showed that approximately 0.07 kg ha^{-1} left the root zone as a result of leaching below 0.9 m, degradation, and to a small extent, runoff and volatilization. Leaching below the root zone by preferential movement was perhaps the major loss pathway before day 118, since only 0.02 kg ha^{-1} of atrazine was lost during the next 10 days (day 118 to day 128) even though there was about 40 mm of rainfall. By day 145 (17 days later), the mean atrazine mass was reduced by approximately 0.46 kg ha^{-1}. This rapid decrease in mean atrazine mass may be attributed to losses in leaching and runoff (57 mm rainfall during the period), degradation and, perhaps, incomplete recovery of atrazine from the soil and crop residue.

Opus-SF, on the other hand, predicted the mean atrazine mass to constantly decrease with time. The simulated mean leaching loss below the root zone (0.9 m) by day 145 was approximately 0.002 kg ha^{-1} and atrazine loss in runoff was approximately 0.011 kg ha^{-1}; therefore, the majority of atrazine loss was because of degradation. By the end of the simulation period, degradation and plant uptake accounted for more than 95% of atrazine losses predicted by Opus-SF whereas mean leaching losses were only about 0.015 kg ha^{-1}. Opus-SF predicted 0.2 kg ha^{-1} of atrazine mass (mean) to remain in the field as compared to a mean atrazine mass of 0.3 kg ha^{-1} observed in the field (Table 22).

Mean and median of atrazine mass simulated by Opus-SF differed by less than 7% (Table 22). Such differences were also found between observed mean and median, and indicate that the atrazine mass distribution in soil was skewed. The Mann-Whitney test showed that observed and simulated medians of total atrazine mass in the root zone were not significantly different ($\alpha = 0.05$) on days 118, 128, and 209 (Table 21), but were significantly different on days 145 and 272. Observed data from day 167 were excluded from analysis, due to anomalous data (Heatwole et al., 1997, pg.1273).

Simulated standard deviation of total atrazine mass in the root zone (Table 22) was somewhat less, but comparable, to observed standard deviation for all five sampling dates. Thus, atrazine variability was underpredicted even though maximum atrazine mass was higher than the observed maximum values on all dates except day 209. The simulated minimum atrazine mass was lower than the observed minimum on day 118, but coincided with observed minimum on all other dates. The KS test showed that the observed and simulated EDFs of total atrazine mass in the root zone were not significantly different on days 118 and 128 at $\alpha = 0.05$, and on day 209 also at $\alpha = 0.01$ (Table 21). Range statistic showed that over 85% of the observations were contained within the simulated range on all sampling dates (Table 21).

Depth-wise distribution of observed and simulated atrazine mass on day 118 (Fig. 22a) showed that Opus-SF overpredicted atrazine mass in the 0-0.15 m and underpredicted atrazine mass in the remaining depths. Depth-wise distribution of observed and simulated atrazine mass on day 209 (Fig. 22b) showed that while atrazine was distributed evenly throughout the 0.9 m profile, Opus-SF predicted more herbicide in the 0.15-0.45 m depths. The simulated means, however, were still within the observed range for all depths. Overall, Opus-SF predicted total atrazine mass in the root zone over the entire simulation period better than bromide mass in the root zone.

Metolachlor Mass

Observed metolachlor mass on the application date (Table 18) and day 118 (Fig. 23, Table 23) show that there was a difference of 0.45 kg ha^{-1}. The difference between metolachlor mass on days 118 and 128 was much lower (approximately 0.05 kg ha^{-1}). Even though part of this difference may have been due to incomplete recovery of herbicide from the soil and crop residue, most of the difference reflects the loss of the herbicide as a result of leaching below 0.9 m, degradation, volatilization and runoff. As in the case of bromide and atrazine, leaching below the root zone by preferential movement may have been one of the loss pathways following the rainfall simulator application on day 118. Total metolachlor loss in runoff was less than 1% of the herbicide applied (0.006 kg ha^{-1}).

Predicted leaching losses of metolachlor was lower than that of atrazine due to its higher adsorption rate and higher degradation rate (Table 18). By the end of the simulation period, degradation and plant uptake accounted for more than 99% of metolachlor losses predicted by Opus-SF, whereas metolachlor losses in leaching and runoff were 0.001 kg ha^{-1} and 0.009 kg ha^{-1}, respectively. Opus-SF predicted a mean metolachlor mass of 0.022 kg ha^{-1} to remain in the root zone on day 272 (157 days after application) as compared to 0.070 kg ha^{-1} observed in the field.

With the exception of day 118 and day 272, Opus-SF was able to predict the mean and median of total metolachlor mass in the root zone well (Table 23). The Mann-Whitney test showed that observed and simulated medians of total metolachlor mass were not significantly different ($\alpha = 0.05$) on days 128, 145, and 209 (Table 23). Observed data from day 167 were excluded from analysis, due to anomalous data (Heatwole et al., 1997, pg.1273).

Simulated standard deviation of total metolachlor mass in the root zone (Table 23) was comparable to observed standard deviation, but lower on all sampling dates except day 118. Thus, metolachlor variability was underpredicted even though maximum metolachlor mass was higher than the observed maximum values on all sampling dates. The KS test showed that the observed and simulated EDFs of total metolachlor mass in the root zone were not significantly different ($\alpha = 0.01$) on days 128, 145, and 209 (Table 23). Range statistic indicated that over 90% of the observations were contained within the simulated range on all sampling dates (Table 23).

Depth-wise distribution of observed and simulated metolachlor mass on day 118 (Fig. 24a) showed that Opus-SF overpredicted metolachlor mass in the 0-0.15 m and underpredicted metolachlor mass in the remaining depths. Depth-wise distribution of observed and simulated metolachlor mass on day 209 (Fig. 24b) showed that Opus-SF predicted more of the herbicide in the 0.15-0.3 m depth. The simulated mean of metolachlor mass was always within the observed range in most depths, and the observed mean was always within the simulated range.

Like atrazine, Opus-SF predicted metolachlor mass in the root zone over the entire simulation period well and better than the non-reactive tracer, bromide. As with the results from the Dougherty Plain study, this once again shows that even though the model predictions for bromide did not match closely with observed data, the model did predict fate and transport of pesticides (solutes that adsorb and degrade) reasonably well [provided reasonably good estimates of adsorption and degradation parameters were available.]

Comparison with Traditional Monte-Carlo Simulation

The Nomini Creek site was simulated using the traditional Monte-Carlo approach with Opus (Opus-MC) and its results were compared with results from the proposed stochastic framework (Opus-SF). The difference between the two approaches is that Opus-SF describes spatially variable input parameters that exhibit spatial trends as a sum of the deterministic trend and the random variations, whereas Opus-MC treats all spatially input parameters to be random, and describes the parameters by its PDF.

Statistical tests were performed to determine if the output variables (depth-averaged soil water content, bromide, atrazine, and metolachlor mass) predicted by the two approaches were the same, and to compare the Opus-MC predictions with observed data. The two sample KS test was used to test for significant differences between EDFs predicted by Opus-SF and Opus-MC, and the observed EDF and the EDF predicted by Opus-MC. The Mann-Whitney test was used to test for significant differences between medians predicted by Opus-SF and Opus-MC, and the observed median and the median predicted by Opus-MC. Comparisons between outputs from the two models and comparisons between observed and Opus-MC predictions were made based on the root zone (upper 0.9 m of the profile).

Water Balance and Soil Water Content

Overall, the water balance predicted by Opus-MC was comparable to that of Opus-SF (Table 24), with the seasonal variations in mean ET and percolation amounts predicted by both models in a similar fashion. Opus-SF predicted 5 mm of total ET more than Opus-MC over the simulation period, with almost all of the differences occurring in the months of June and July. The difference in total percolation losses over the simulation period was less than 1 mm, even though monthly fluctuations were a little more with the maximum difference being 1.6 mm in April. These small differences in ET and percolation resulted from the differences in the soil parameters used in the two models.

The differences in mean and median depth-averaged soil water content predicted by Opus-SF and Opus-MC on the simulation start date, day 112, were approximately 2% (Table 25). This difference between the models was due to the different set of values used for parameters exhibiting spatial trends. These differences carried over for most of the season. The Mann-Whitney test, however, showed that the depth-averaged soil water content medians predicted by Opus-MC and Opus-SF were significantly different ($\alpha = 0.05$) on all dates except day 272 (Table 25). The KS test on the depth-averaged soil water content EDFs predicted by Opus-SF and Opus-MC, also gave similar results, with the distributions not significantly different on only day 272 at $\alpha = 0.01$. It must be noted that with a large sample, tests are likely to detect statistically significant differences for small departures from the null hypothesis that might be quite unimportant in practice (Snedecor and Cochran, 1980, pg.67).

However, it is fair to say that calculating soil hydraulic and retention properties by including spatial trends of sand and clay content in some of the soil layers (Table 15) in the upper 0.6 m profile had some impact on soil water predictions from the stochastic simulation of Opus (Table 25).

The Mann Whitney test comparing observed and simulated (Opus-MC) depth-averaged soil water content gave the same results as the Mann Whitney test comparing Opus-SF and observed data at α = 0.05 (Table 20). On all dates except day 118, Opus-MC means and medians were a little closer to observed means and medians than Opus-SF means and medians. The KS tests comparing Opus-MC predictions and observed data and the KS tests comparing Opus-SF predictions and observed data, also gave the same results at α = 0.01 (Table 20). The test statistics show that EDF predicted by Opus-MC was closer to observed EDF on days 128, 145, and 272, whereas EDF predicted by Opus-SF was closer to observed EDF on days 118, 167, and 209. Therefore, it is difficult to say whether Opus-MC or Opus-SF did a better job of predicting observed data.

Bromide Mass

The mean and median of bromide mass predicted by Opus-MC on all the sampling dates were lower than the mean and median predicted by Opus-SF. However, the Mann-Whitney test did not show any significant differences (α = 0.05) between the two medians until day 167 (Table 26). Bromide mass values predicted by the two models on day 209 were also not significantly different at α = 0.05. The standard deviation of bromide mass predicted by Opus-MC was slightly greater than Opus-SF on the application date and the first two sampling dates, whereas the opposite was true for the remaining dates. The KS test for the EDFs predicted by Opus-SF and Opus-MC also gave the same result. The above result showed that there were differences between the models only after substantial amounts of bromide had leached out of the root zone.

Comparison between observed median and medians predicted by Opus-MC and Opus-SF gave the exact same results at α = 0.05. It was difficult to determine which model predicted observed data better, as the Opus-MC medians were closer to observed data on days 128 and 145 and the Opus-SF predictions were closer to observed data on the last three dates. Comparison between observed EDF and EDFs from Opus-MC and Opus-SF also gave the same results at α = 0.05. The test statistics indicated that the Opus-MC EDFs were closer to observed EDFs on all dates as compared to Opus-SF, although the difference was very small.

Pesticide Mass

There was very little difference between mean and median of atrazine mass predicted by Opus-MC and Opus-SF, especially until day 167 (Table 27). On days 209 and 272, there were some differences but the Mann-Whitney test still showed that the medians were not significantly different at $\alpha = 0.05$. There was very little difference in the standard deviation of atrazine mass predicted by the two models on all of the sampling dates. In the case of metolachlor mass also, there was very little difference between the mean, median, and standard deviation predicted by Opus-MC and Opus-SF (Table 28). The medians as well as the EDFs of atrazine and metolachlor mass predicted by Opus-MC and Opus-SF were not significantly different ($\alpha = 0.05$) on all sampling dates (Tables 27 and 28).

The p-values obtained from the KS and the Mann-Whitney tests by comparing atrazine and metolachlor mass predictions from Opus-MC and observed data were very close to the p-values obtained by comparing Opus-SF predictions and observed data (Tables 22 and 23). Atrazine medians predicted by Opus-SF were closer to observed data on days 118, 167, and 209, whereas those predicted by Opus-MC were closer to observed data on days 128 and 272, with equal medians predicted by the two models on day 145. The test statistics from the KS tests indicated that atrazine mass EDFs from Opus-SF were closer to observed EDFs than Opus-MC on all sampling dates. With metolachlor mass, the medians predicted by Opus-SF were closer to observed medians on all dates than the medians predicted by Opus-MC. Metolachlor mass EDFs predicted by Opus-SF were closer to observed EDFs on days 145, 209, and 272, whereas the opposite was true on days 128 and 167. Overall, Opus-SF predicted field-measured herbicide mass in the root zone slightly better than Opus-MC. However, these differences were small and did not change the results from the statistical tests conducted for comparing simulated data with observed data.

Summary

Soil hydraulic and retention properties and organic carbon content in the upper 0.6 m of the soil profile (four soil layers), pesticide degradation rate in the four layers, and chemical application rates were selected as the spatially variable input parameters for the stochastic simulation of water flow and pesticide transport at the Nomini Creek site using Opus-SF. The soil hydraulic and retention properties were derived from texture and porosity data measured at the site. Spatial variability of sand and clay content was described by PDFs, after analyzing them for spatial trends. Soil hydraulic and retention properties for the four layers were computed from correlated random variates of sand and clay content and independent random variates of porosity, using the regression equations of Rawls and Brakensiek (1985).

Opus-SF predicted high ET during the summer months and high percolation during the high rainfall events in April and May. Soil water content was overpredicted during the high rainfall months of April and May, with the exception of the first 5-10 days of the simulation when it was underpredicted because of the lower initial water content in the subsurface horizons computed by the model. Opus-SF also underpredicted the soil water content during the dry periods in the latter part of the cropping season. The simulated medians were not significantly different ($\alpha = 0.01$) from the observed medians on days 128 and 167, whereas simulated EDFs were not significantly different on only day 167. Spatial variability of simulated soil water content was much less than the observed variability on all sampling dates, and there were only two out of the six sampling dates where at least 50% of the observations fell within the simulated range. The reduced variation of simulated soil water content was primarily due to the reduced variability in soil water properties derived from texture. Variation in soil water content in the layers beyond 0.6 m was very low, as spatial variability of soil water properties were not considered beyond that depth.

As with the Dougherty Plain simulation, Opus-SF was not able to predict the field-scale movement of bromide well. Opus-SF overpredicted bromide mass in the field in the first month after application and underpredicted bromide mass for the remainder of the simulation period. Opus-SF could not simulate preferential movement of chemicals, which had resulted in considerable amount of bromide loss from the field soon after application. Two large rainfall events of approximately 105 mm each at the end of May caused extensive movement of bromide from the root zone, which resulted in the underprediction of the tracer thereafter. Spatial variations in bromide mass predicted by Opus-SF was comparable but less than the observed variation until the majority of the bromide leached out of the root zone. More than 80% of the observations were contained in the simulated range in the first 30 days of application (until day 145). Before bromide predictions by the model can be evaluated, retention of the tracer in field soils for prolonged time will have to be better explained. In order to improve solute transport predictions at the Nomini Creek site, the model will have to simulate preferential movement of solutes and may have to provide better description of the solute's transport and uptake by plants.

The mean and median of total atrazine mass in the root zone was predicted well initially, overpredicted after the first few weeks of application, and underpredicted in the latter stages of the cropping season. The observed and simulated medians and EDFs were not significantly different ($\alpha = 0.01$) on days 118, 128, and 209. Spatial variations in atrazine mass were comparable, but less than the spatial variations in the field. More than 80% of the atrazine mass observations on all field sampling dates were within the simulated range. Opus-SF was, however, not able to predict the depth-wise distribution of atrazine mass as well.

Except for the first sampling date when metolachlor mass in the field was low because of incomplete recovery or preferential movement, Opus-SF predicted the mean and median of total metolachlor mass in the root zone well during the cropping season. The observed and simulated medians and EDFs were not significantly different ($\alpha = 0.01$) on days 128, 145, and 209. Spatial variations in metolachlor mass were comparable, but less than the observed spatial variation. More than 90% of the metolachlor mass observations on all field sampling dates were within the simulated range. Like atrazine, Opus-SF was not able to predict the depth-wise distribution of metolachlor mass as well as the total mass in the root zone. Therefore, Opus-SF was not able to predict pesticide transport as well as its fate.

The water balance, soil water content, bromide and pesticide mass predicted by the deterministic version of Opus were similar, but not equal to the mean values predicted by Opus-SF. Over the 5-month simulation period, the deterministic Opus predicted about 7 mm less ET than Opus-SF (mean). The differences in percolation between the two model versions were averaged out over the simulation period and the total difference was less than 1 mm. The deterministic Opus predicted lower soil water content than Opus-SF (mean) until the end of June, after which it predicted slightly higher soil water content than Opus-SF (mean). These differences reflect the differences in characterization of the spatially variable parameters as well as the effect of nonlinear components in the model. The differences between pesticide mass predictions by the two versions were less distinct than the differences in soil water content and bromide mass predictions.

A comparison of stochastic outputs from Opus-SF and Opus-MC showed that soil water contents predicted by the two models were significantly different (α = 0.01) for nearly 150 days after the simulation start date, like in the Dougherty Plain simulation. It was difficult to determine which model performed better, as soil water predictions by both models were closer to the observed data on three of the six sampling dates. The difference between bromide mass predictions from the two models was significant only after most of the solute had moved out of the root zone. There were no significant differences (α = 0.01) between pesticide mass predictions by Opus-SF and Opus-MC. The small differences between bromide and pesticide mass predicted by Opus-MC and Opus-SF did not change the results from the statistical tests used for comparing simulated data with observed data.

Table 1. Model parameters and base values used in the sensitivity analysis of Opus.

Parameter description	Identifier	Base values†
Soil parameters		
Initial water content (mm/mm)	THST	0.110
Clay content	PCLAY()	0.04,0.11,0.17,0.20,0.20,0.25
Porosity	POR()	0.404,0.374,0.374,0.374,0.374,0.398
Sat. hydraulic conductivity (mm/hr)	RC()	213.5,364.9,288.9,70.5,70.5,14.1
Air entry pressure (mm)	PBUB()	171.7,159.5,152.0,195.6,195.6,280.8
Pore size distribution index	ALAM()	0.336,0.249,0.162,0.145,0.145,0.250
Saturated water content (mm/mm)	THS()	0.384,0.355,0.355,0.355,0.355,0.378
Residual water content (mm/mm)	B15()	0.034,0.069,0.117,0.132,0.132,0.148
Root depth (mm)	RDP	1000.0
Pesticide (Metolachlor) parameters		
Degradation rate in soil (days)	DKSOIL	0.0254
Adsorption coefficient(mL/g)	DKOC	200
Organic carbon content in soil (%)	ORGC()	0.74,0.27,0.26,0.26,0.26,0.26
Solubility in water (ppm)	PSOLUB	530

† Base values listed are for the six horizons simulated at the Dougherty Plain field site.

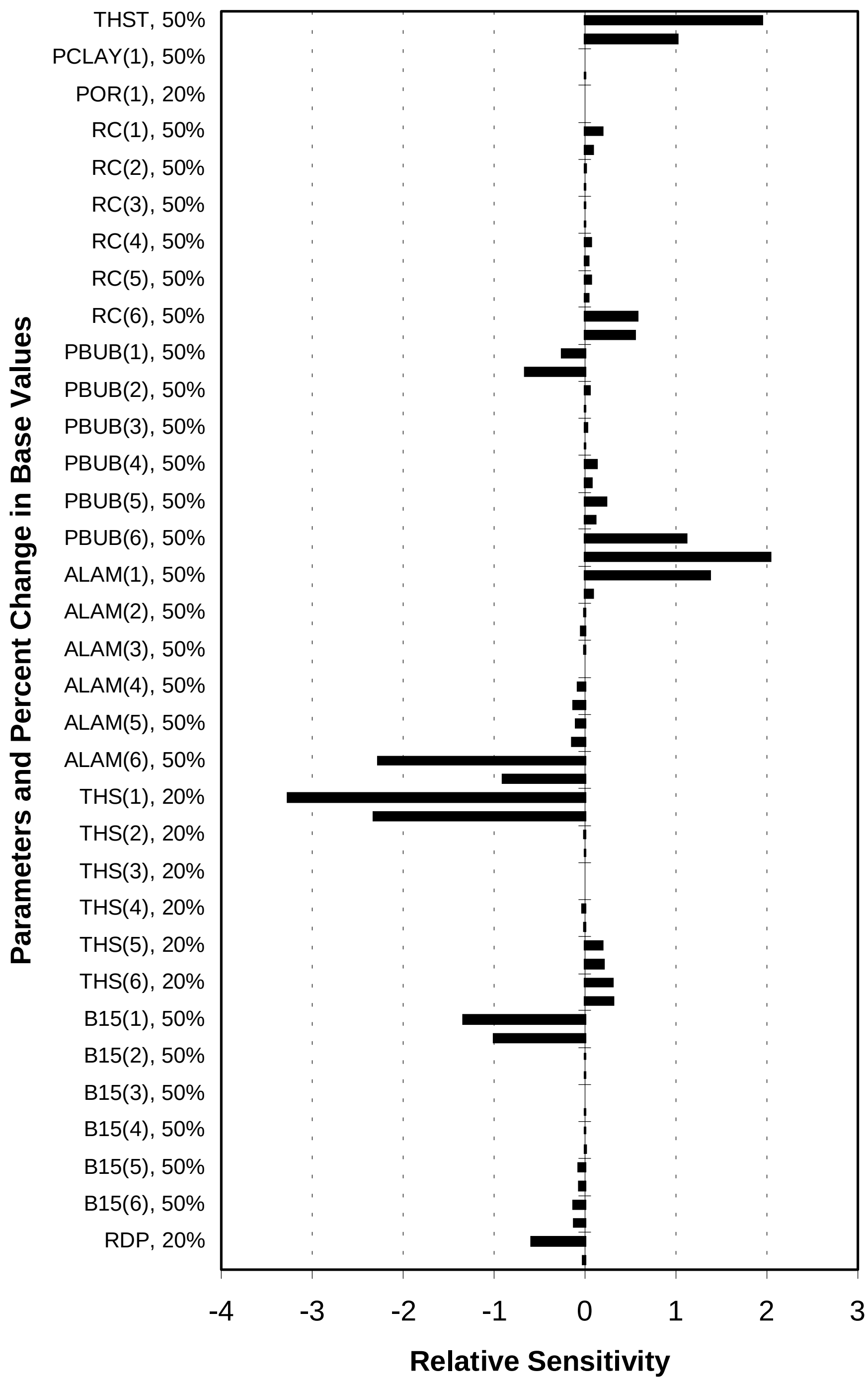


Figure 3. Relative sensitivity of total percolation below the top 1.2 m profile of the Dougherty Plain field, predicted by Opus, to soil parameters (The two bars for each parameter denote sensitivity to negative and positive change in base values).

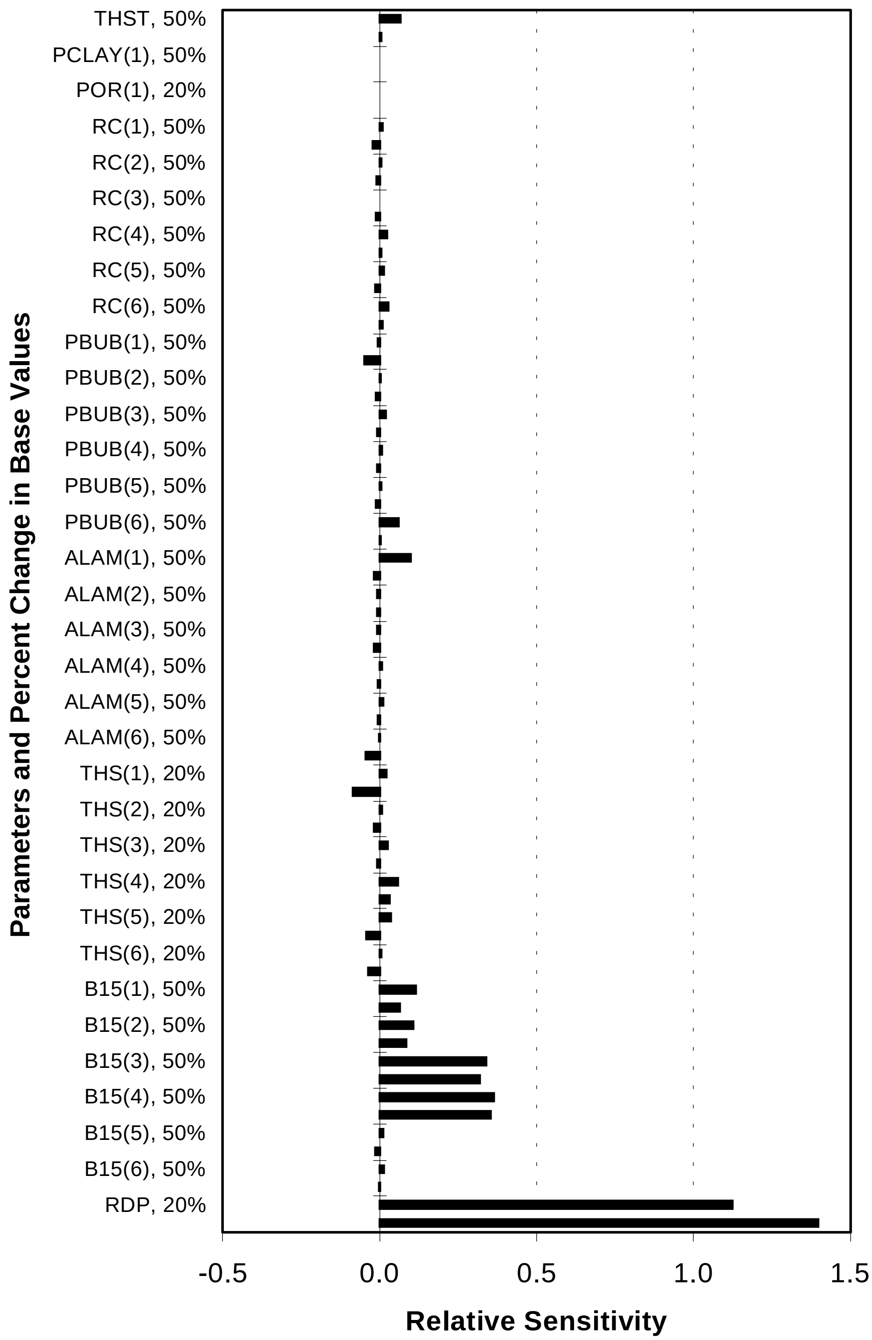


Figure 4. Relative sensitivity of average soil water content in the top 1.2 m profile of the Dougherty Plain field, predicted by Opus, to soil parameters (The two bars for each parameter denote sensitivity to negative and positive change in base values).

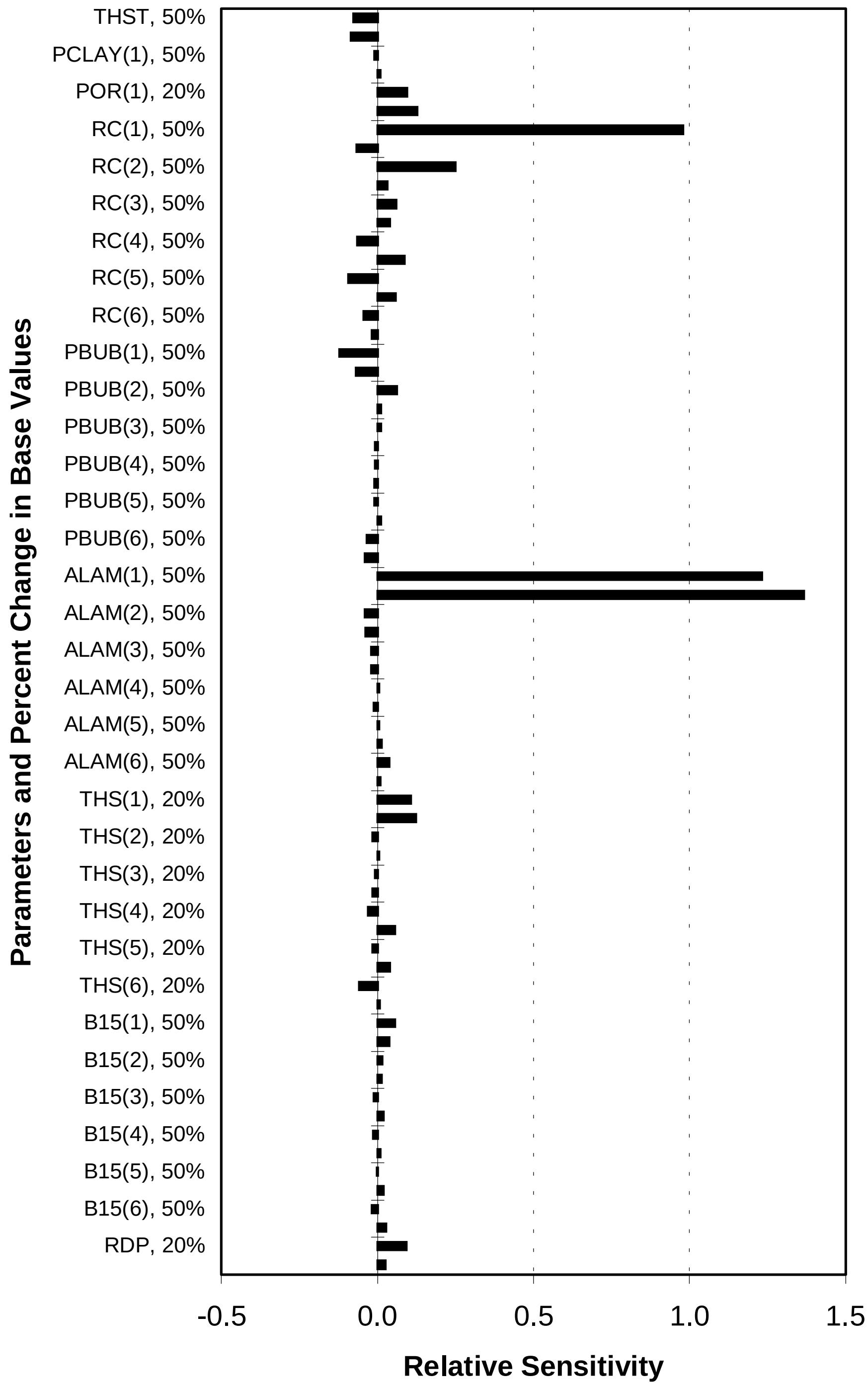


Figure 5. Relative sensitivity of resident metolachlor mass in the top 1.2 m profile of the Dougherty Plain field, predicted by Opus, to soil parameters (The two bars for each parameter denote sensitivity to negative and positive change in base values).

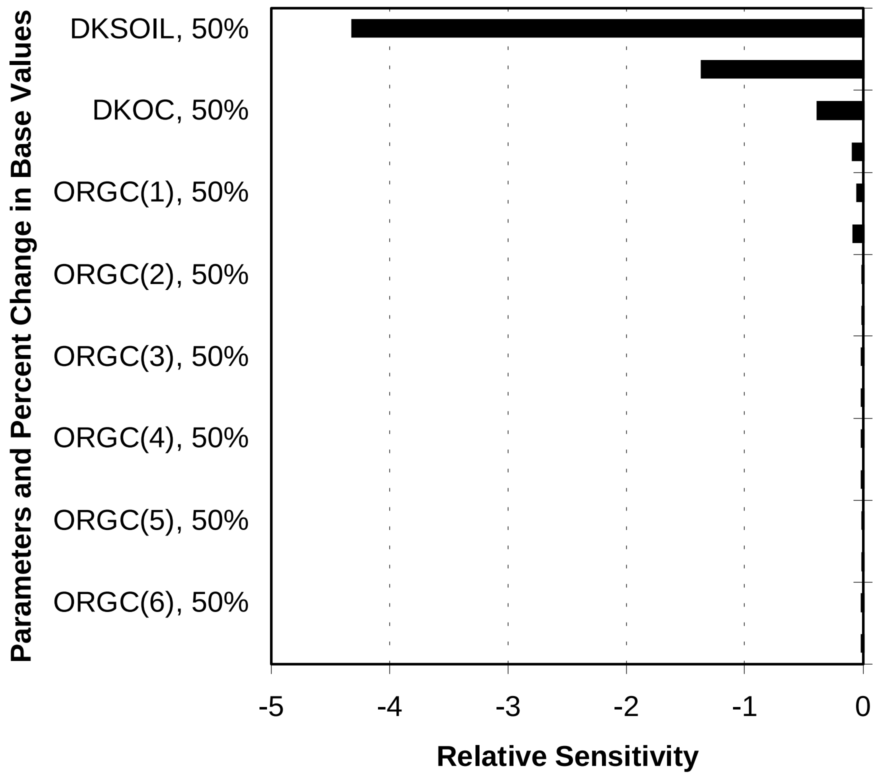


Figure 6. Relative sensitivity of resident metolachlor mass in the top 1.2 m profile of the Dougherty Plain field, predicted by Opus, to pesticide parameters (The two bars for each parameter denote sensitivity to negative and positive change in base values).

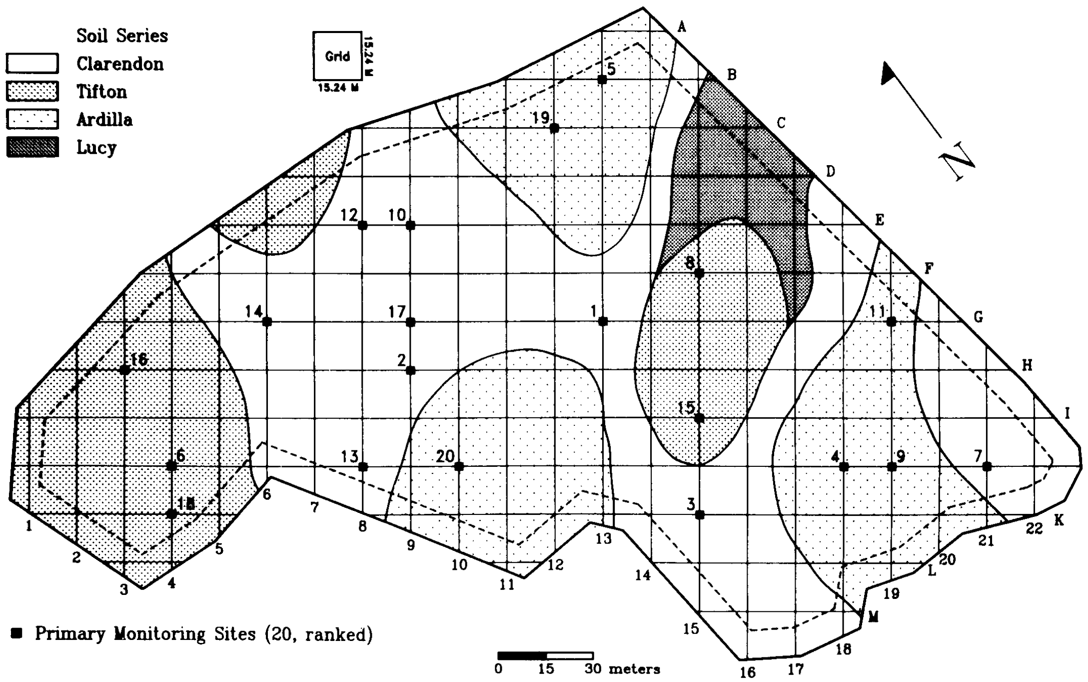


Figure 7. Dougherty Plain field site with grid pattern (15.24x15.24 m) and monitoring sites (adapted with permission from Smith and Parrish (1993)).

Table 2. Statistical characteristics of spatially variable soil properties at the Dougherty Plain site used in Opus-SF.

Soil property	Measured data			Order of	Detrended data†		
	Mean	St.dev.	PDF	Trend Surface†	Mean	St.dev.	PDF
Init. water content (THST), mm mm^{-1}	0.11	0.031	LogNormal				
Sat. conductivity (K_s or RC), mm hr^{-1}							
Horizon 1 (0-0.3 m)	213.5	109.8	Normal	First[1]	0	84.8	Normal
Horizon 2 (0.3-0.45 m)	364.9	217.2	LogNormal				
Horizon 3 (0.45-0.75 m)	288.9	179.4	LogNormal				
Horizon 4 & 5 (0.75-1.2 m)	70.5	87.2	Exponential				
Horizon 6 (1.2-1.5 m)	14.1	65.4	Exponential				
Air entry pressure (ψ_b or PBUB), mm							
Horizon 1 (0-0.3 m)	171.7	64.7	LogNormal	First[2]	0	0.32	Normal
Horizon 2 (0.3-0.45 m)	159.5	67.1	LogNormal				
Horizon 3 (0.45-0.75 m)	152	98.5	LogNormal				
Horizon 4 & 5 (0.75-1.2 m)	195.6	151.7	LogNormal				
Horizon 6 (1.2-1.5 m)	280.8	151.7	LogNormal				
Pore size index (λ or ALAM)							
Horizon 1 (0-0.3 m)	0.336	0.069	LogNormal				
Horizon 2 (0.3-0.45 m)	0.249	0.08	LogNormal	First[3]	0	0.287	Normal
Horizon 3 (0.45-0.75 m)	0.162	0.049	LogNormal				
Horizon 4 & 5 (0.75-1.2 m)	0.145	0.045	LogNormal				
Horizon 6 (1.2-1.5 m)	0.25	0.06	LogNormal				
Sat. water content (θ_s or THS), mm mm^{-1}							
Horizon 1 (0-0.3 m)	0.384	0.03	Normal				
Horizon 2 (0.3-0.45 m)	0.355	0.026	Normal	First[4]	0	0.021	Normal
Horizon 3 (0.45-0.75 m)	0.355	0.029	Normal				
Horizon 4 & 5 (0.75-1.2 m)	0.355	0.026	Normal				
Horizon 6 (1.2-1.5 m)	0.378	0.024	Normal				
Residual water content (θ_r or B15), mm mm^{-1}							
Horizon 1 (0-0.3 m)	0.031	0.009	LogNormal				
Horizon 2 (0.3-0.45 m)	0.069	0.033	LogNormal	First[5]	0	0.420	Normal
Horizon 3 (0.45-0.75 m)	0.117	0.036	Normal				
Horizon 4 & 5 (0.75-1.2 m)	0.132	0.039	Normal				
Horizon 6 (1.2-1.5 m)	0.148	0.024	Normal				
Organic carbon content (ORGC), %							
Horizon 1 (0-0.3 m)	0.54	0.23	Normal				
Horizon 2 (0.3-0.45 m)	0.18	0.08	Normal				
Horizon 3 (0.45-0.75 m)	0.14	0.06	Normal				
Horizon 4 & 5 (0.75-1.2 m)	0.09	0.07	Normal				
Horizon 6 (1.2-1.5 m)	0.09	0.07	Normal				

† Only for properties that exhibited spatial trend

[1]Trend coefficients of K_s: β_0=454.97, β_1=-0.87, β_2=-0.71

[2]Trend coefficients of ln(ψ_b): β_0=4.415, β_1=0.002, β_2=0.002

[3]Trend coefficients of ln(λ): β_0=-1.902, β_1=0.0004, β_2=0.002

[4]Trend coefficients of θ_s: β_0=0.347, β_1=-0.0002, β_2=0.0002

[5]Trend coefficients of ln(θ_r): β_0=-1.868, β_1=-0.003, β_2=-0.003

Table 3. Correlation between soil properties measured at the Dougherty Plain site.

(a) Correlation† between soil hydraulic and retention properties in each horizon

Horizon 1	θ_i	K_s	ψ_b	λ	θ_s	θ_r
θ_i	1.00					
K_s	0.00	1.00				
ψ_b	-0.13	-0.21	1.00			
λ	-0.40	0.05	0.57	1.00		
θ_s	0.08	0.24	0.26	0.07	1.00	
θ_r	0.67	0.22	-0.18	-0.58	0.38	1.00

Horizon 2	K_s	ψ_b	λ	θ_s	θ_r
K_s	1.00				
ψ_b	0.00	1.00			
λ	-0.08	0.48	1.00		
θ_s	0.10	-0.21	0.33	1.00	
θ_r	0.14	-0.23	0.48	0.00	1.00

Horizon 3	K_s	ψ_b	λ	θ_s	θ_r
K_s	1.00				
ψ_b	0.09	1.00			
λ	-0.11	0.49	1.00		
θ_s	0.32	-0.55	-0.38	1.00	
θ_r	0.08	-0.50	-0.93	0.51	1.00

Horizon 4&5	K_s	ψ_b	λ	θ_s	θ_r
K_s	1.00				
ψ_b	-0.51	1.00			
λ	0.30	0.42	1.00		
θ_s	0.47	-0.53	-0.33	1.00	
θ_r	-0.28	-0.29	-0.97	0.32	1.00

† Correlation coefficients were calculated on log-transformations for log-normally distributed variables, and on detrended residuals for variables that exhibited spatial trends.

(b) Correlation between organic matter content in different horizons

Depth (m)	0-0.3	0.3-0.45	0.45-0.75	0.75-1.2
0-0.3	1.00			
0.3-0.45	0.71	1.00		
0.45-0.75	0.76	0.76	1.00	
0.75-1.2	0.46	0.92	0.70	0.00

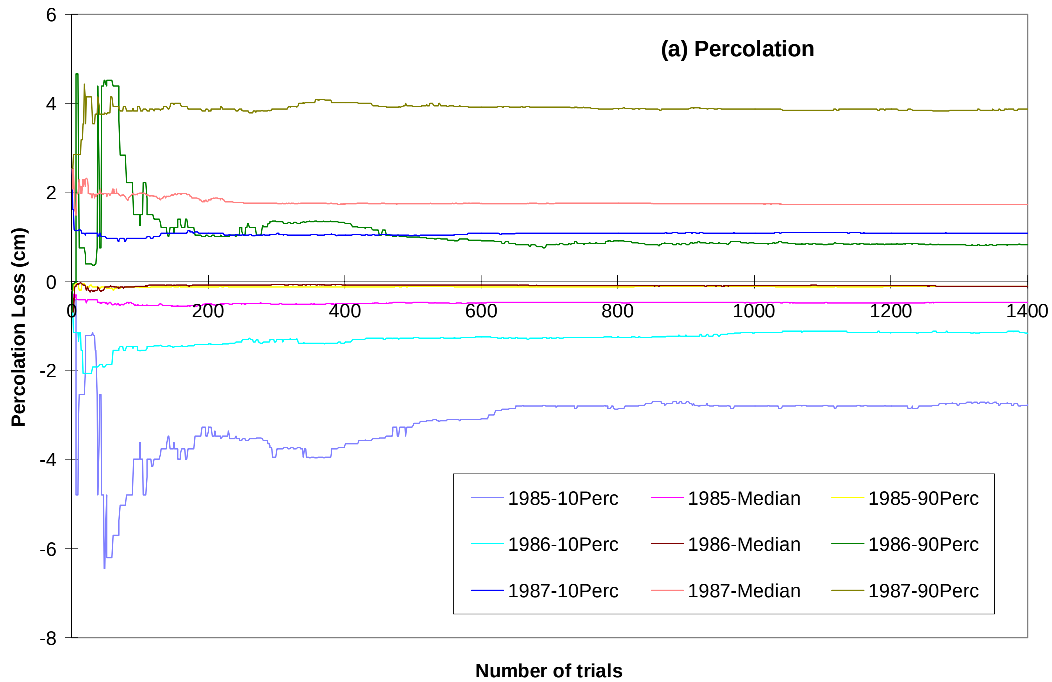
Table 4. Estimates of important pesticide parameters used in Opus-SF simulation of the Dougherty Plain site.

Property	Aldicarb			Metolachlor		
	Mean	**St.dev.†**	**PDF†**	**Mean**	**St.dev.†**	**PDF†**
Solubility in water (PSOLUB), mg L^{-1}	6000			530		
Adsorption coefficient (DKOC), $cm^3\ g^{-1}$	24.4			153.0		
Washoff fraction (FWASH)	0.5			0.6		
Foliar degradation rate (DKFL), day^{-1}	0.1386			0.1386		
Soil degradation rate (DKSOIL), day^{-1}	0.0165	0.0035	LogNormal	0.0392	0.0040	LogNormal
Plant uptake coefficient (PUPTK)	0.60			0.32		
Application rate (QPEST), kg ha^{-1}						
1985 (May 7)	2.96	1.05	Normal	2.49	0.48	LogNormal
1986 (April 7)	3.04	1.47	Normal	2.96	0.62	LogNormal
1986 (April 7) - High application rate‡	11.63	5.05	Normal			
1987 (June 1)	2.67	1.27	Normal	3.36	1.26	Normal
Bromide§ - 1985 (April 17)	58.83	14.94	Normal			

† Standard deviation and PDF's are given only for spatially variable parameters

‡ Aldicarb was applied at two target rates in 1986: a higher rate was applied to the easternmost 36 rows (22% of total area) and a lower (regular) rate to the rest of the field.

§ Other bromide properties used in the simulation are: PSOLUB = 1000 mg L^{-1}; DKOC = 0 $cm^3\ g^{-1}$; FWASH=0.75; DKFL = DKSOIL = 0 day^{-1}; PUPTK = 0.6.



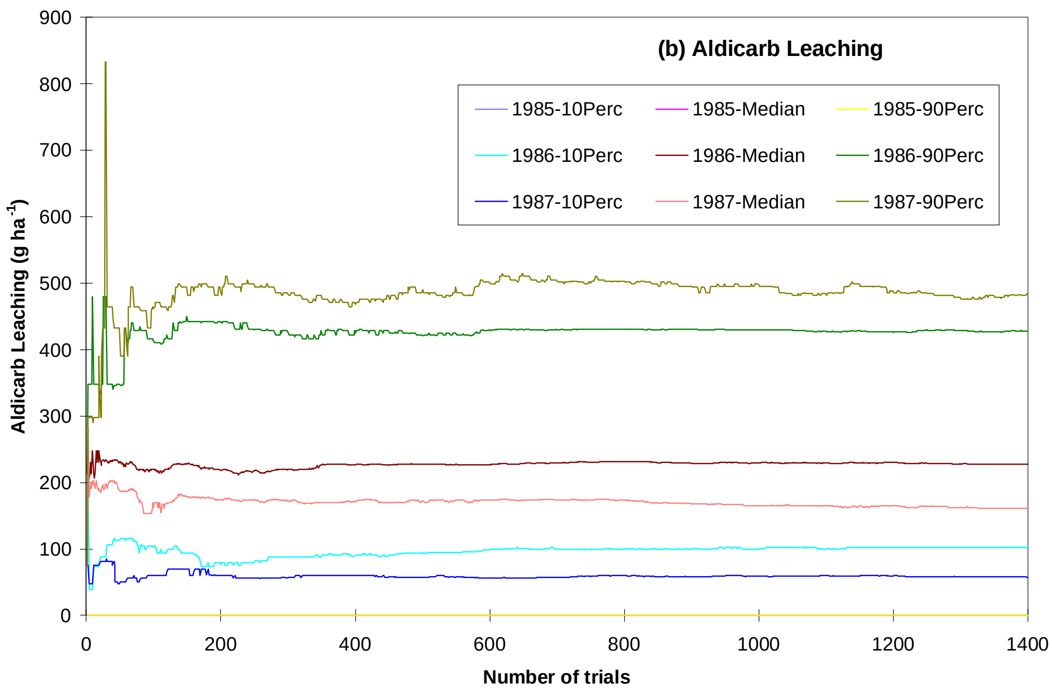


Figure 8. Simulated median, 10th and 90th percentile of (a) percolation loss and (b) aldicarb leaching loss predicted by Opus-SF at the end of each cropping season at the Dougherty Plain site, as a function of the number of trials. (Note: Aldicarb leaching losses in 1985 was zero or close to zero).

Table 5. Mean monthly evapotranspiration (ET) and percolation predicted by Opus-SF at the Dougherty Plain site, along with ET and percolation predicted by deterministic Opus.

Month-	Rainfall,	....ET, mm.…		....Percolation, mm.…	
Year	mm	Opus-SF	Opus	Opus-SF	Opus
Apr-85	47.2	60.9	65.9	1.3	-3.7
May-85	81.5	76.8	77.9	1.0	-0.5
Jun-85	106.1	132.0	135.6	-12.3	-18.1
Jul-85	94.3	150.2	158.7	-14.2	-16.0
Aug-85	100.9	60.1	55.0	-13.4	-12.3
Sep-85	31.1	102.0	103.2	-10.7	-9.9
Oct-85	176.0	17.7	18.4	9.1	15.6
Nov-85	187.3	18.2	18.3	170.2	176.7
Dec-85	149.9	18.2	18.3	152.3	150.3
Total-85	974.3	636.1	651.2	283.4	282.1
Jan-86	76.3	22.8	22.9	70.5	68.8
Feb-86	133.7	28.7	28.6	101.7	102.0
Mar-86	89.8	44.0	44.0	44.7	45.8
Apr-86	14.9	33.2	32.5	3.3	-0.3
May-86	4.4	25.9	36.4	-5.3	-8.9
Jun-86	65.4	161.0	159.4	-25.5	-31.5
Jul-86	63.3	94.8	85.4	-27.3	-24.3
Aug-86	108.6	93.8	92.3	-21.7	-21.9
Sep-86	57.5	64.8	64.7	-9.2	-13.1
Oct-86	77.8	25.6	24.9	6.5	6.1
Nov-86	150.1	18.4	18.5	49.3	66.9
Dec-86	110.8	16.4	16.4	124.0	125.4
Total-86	952.6	629.5	626.0	310.9	315.1
Jan-87	177.3	20.0	20.0	165.1	165.3
Feb-87	142.5	22.2	22.2	89.4	91.7
Mar-87	62.7	46.0	46.0	60.7	57.8
Apr-87	28.9	55.9	55.8	5.9	1.0
May-87	79.2	78.8	80.7	1.9	1.1
Jun-87	135.1	94.2	91.6	21.4	25.2
Jul-87	165.7	203.3	203.5	-21.6	-28.6
Aug-87	204.7	180.2	180.0	-6.2	-6.9
Sep-87†	12.7	35.2	35.1	6.6	9.9
Total-87	1008.8	735.7	734.8	323.1	316.4

† September 1-10 only

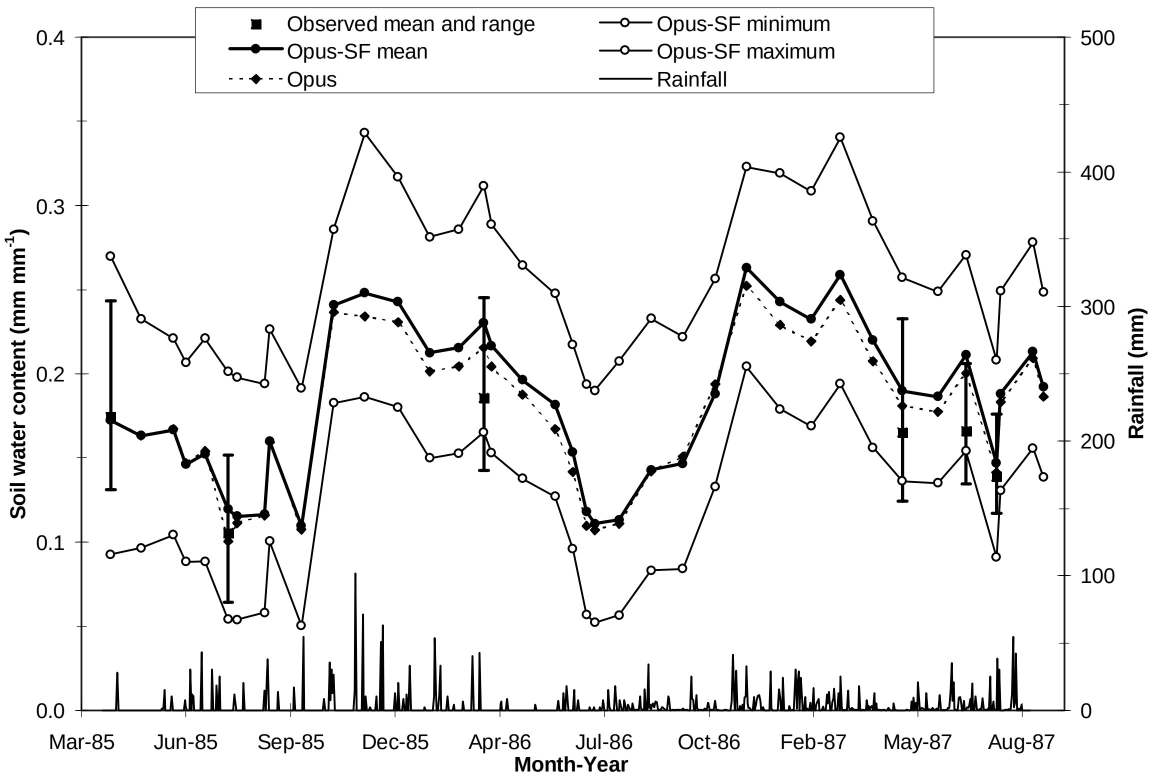


Figure 9. Observed and simulated (Opus-SF) mean and range of depth-averaged soil water content in the root zone (1.2 m) at the Dougherty Plain site, along with depth-averaged soil water content predicted by deterministic Opus.

Table 6. Statistical comparison of observed and simulated (Opus-SF) depth-averaged soil water content in the root zone at the Dougherty Plain site.

	Soil	Observed			Opus-SF			p-value†		Range
Date	depth (m)	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistics‡
6/12/85	0-0.30	0.066	0.062	0.015	0.077	0.075	0.017	0-0.01	0.0033	100
7/22/85	0-0.90	0.105	0.108	0.026	0.103	0.101	0.019	0.2-1.0	0.4683	100
8/26/85	0-0.60	0.076	0.073	0.021	0.092	0.091	0.015	0-0.01	0.0001	85
3/24/86	0-1.20	0.186	0.181	0.033	0.230	0.230	0.020	0-0.01	0.0000	70
4/30/86	0-0.15	0.043	0.034	0.028	0.125	0.128	0.035	0-0.01	0.0000	35
6/17/86	0-0.30	0.048	0.048	0.009	0.077	0.075	0.024	0-0.01	0.0000	100
7/8/86	0-0.30	0.040	0.039	0.012	0.039	0.036	0.016	0.2-1.0	0.3786	100
4/28/87	0-1.20	0.165	0.152	0.032	0.190	0.189	0.018	0-0.01	0.0001	95
6/28/87	0-1.20	0.166	0.167	0.030	0.211	0.210	0.017	0-0.01	0.0000	65
7/27/87	0-1.20	0.139	0.135	0.029	0.147	0.146	0.017	0.02-0.05	0.0753	95

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

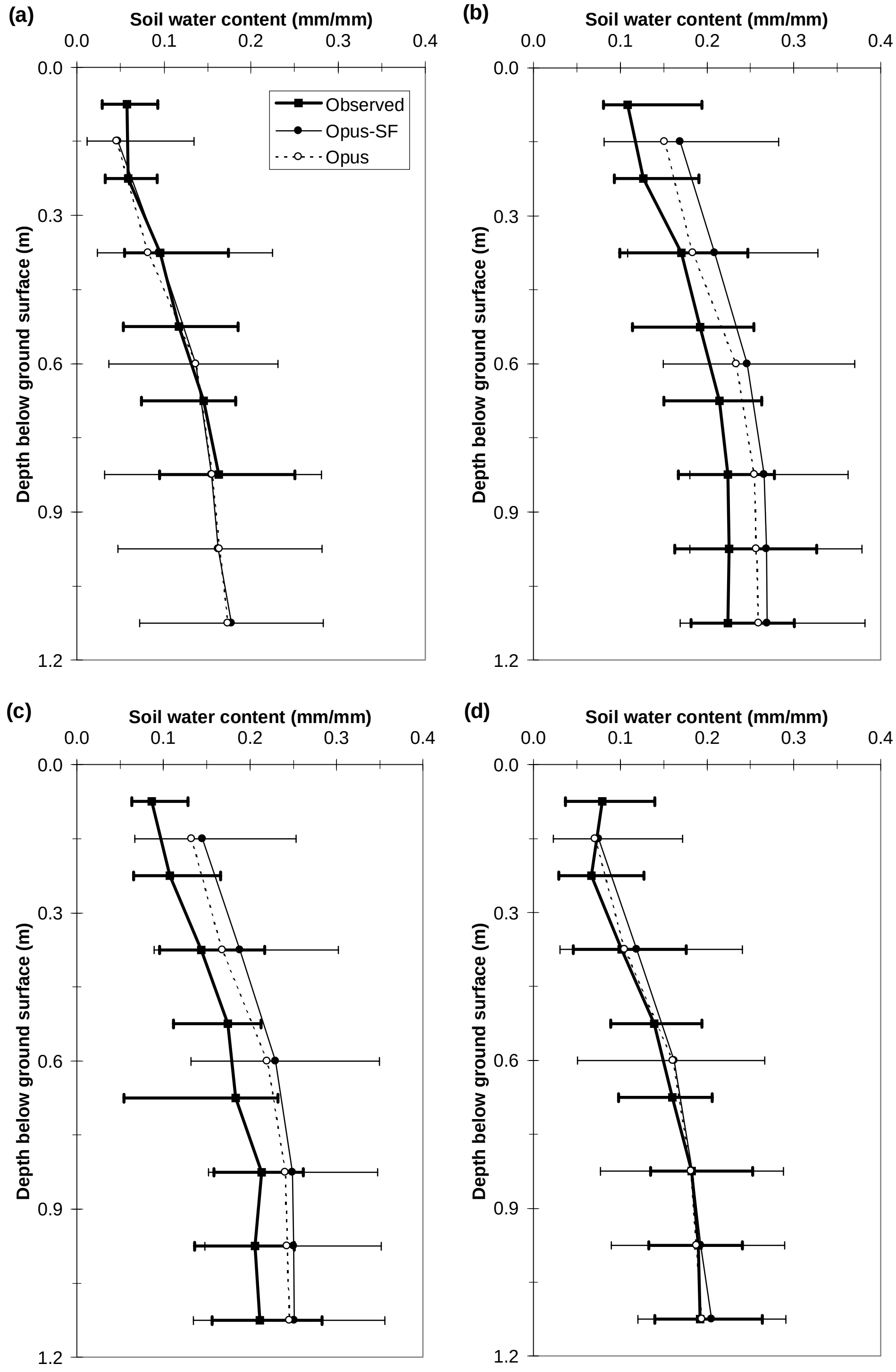


Figure 10. Observed and simulated (Opus-SF) mean and range of soil water content in the root zone at the Dougherty Plain site, along with soil water content predicted by deterministic Opus, on: a) July 22, 1985, b) March 24, 1986, c) June 28, 1987, and d) July 27, 1987.

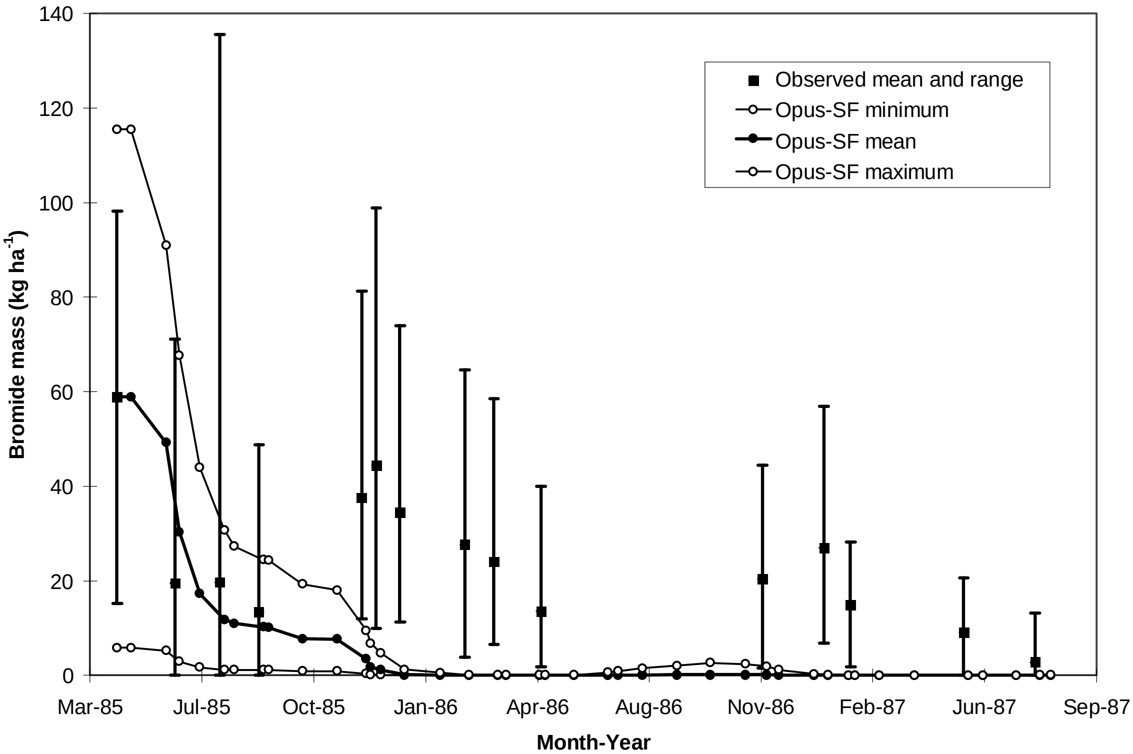


Figure 11. Observed and simulated (Opus-SF) mean and range of total bromide mass in the root zone (1.2 m) at the Dougherty Plain site.

Table 7. Statistical comparison of observed and simulated (Opus-SF) total bromide mass in the root zone at the Dougherty Plain site.

Date	Soil depth (m)	Observed Mean	Observed Median	Observed St.dev.	Opus-SF Mean	Opus-SF Median	Opus-SF St.dev.	p-value† KS Test	p-value† MW Test	Range Statistics‡
6/12/85	0-0.30	19.57	11.29	23.68	30.37	30.02	9.89	0-0.01	0.0069	70
7/22/85	0-0.90	19.69	4.89	35.80	11.82	11.41	4.27	0-0.01	0.0012	45
8/26/85	0-1.20	13.36	10.05	12.68	10.20	9.89	3.46	0.02-0.05	0.8871	75
11/26/85	0-1.20	37.57	38.73	17.42	3.40	3.15	1.56	0-0.01	0.0020	0
12/9/85	0.30-1.20	44.47	40.77	23.99	1.13	0.97	0.69	0-0.01	0.0000	0
12/30/85	0.30-1.20	34.48	35.81	16.53	0.19	0.14	0.16	0-0.01	0.0000	0
2/26/86	0.15-1.20	27.69	27.92	15.74	0.01	0.01	0.01	0-0.01	0.0000	0
3/24/86	0-1.20	24.00	18.30	16.28	0.00	0.00	0.01	0-0.01	0.0000	0
5/5/86	0-1.20	13.59	13.07	8.70	0.01	0.00	0.01	0-0.01	0.0000	0
11/19/86	0-1.20	20.40	19.55	13.03	0.17	0.09	0.20	0-0.01	0.0000	6
1/13/87	0-1.20	26.94	26.54	13.89	0.01	0.00	0.01	0-0.01	0.0000	0
2/6/97	0-1.20	14.85	14.21	8.41	0.00	0.00	0.00	0-0.01	0.0000	0
5/18/97	0-1.20	9.04	9.12	6.55	0.00	0.00	0.00	0-0.01	0.0000	10
7/21/87	0-1.20	2.85	1.21	3.64	0.00	0.00	0.00	0-0.01	0.0000	20

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

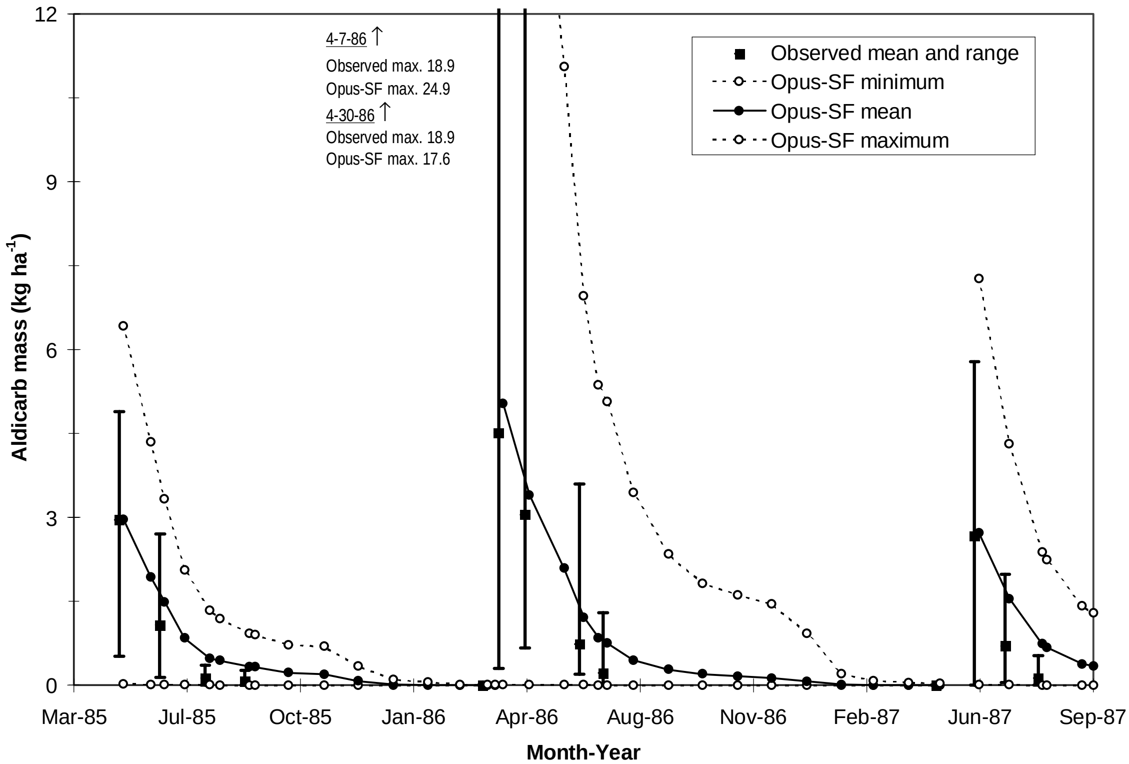


Figure 12. Observed and simulated (Opus-SF) mean and range of total aldicarb mass in the root zone (1.2 m) at the Dougherty Plain site.

Table 8. Statistical comparison of observed and simulated (Opus-SF) total aldicarb mass in the root zone at the Dougherty Plain site.

Date	Soil depth (m)	Observed Mean	Observed Median	Observed St.dev.	Opus-SF Mean	Opus-SF Median	Opus-SF St.dev.	p-value† KS Test	p-value† MW Test	Range Statistics‡
6/12/85	0-0.30	1.082	0.936	0.657	1.490	1.474	0.560	0.01-0.02	0.0031	100
7/22/85	0-0.60	0.124	0.098	0.102	0.487	0.464	0.222	0-0.01	0.0000	90
8/26/85	0-0.60	0.067	0.043	0.066	0.334	0.315	0.162	0-0.01	0.0000	90
3/24/86	0-1.20	0.000	0.000	0.000	0.001	0.000	0.001	—§	—	100
4/30/86	0-0.15	3.047	1.791	4.235	3.399	2.404	2.990	0.02-0.05	0.0487	95
6/17/86	0-0.30	0.737	0.405	0.883	1.209	0.850	1.131	0-0.01	0.0006	100
7/8/86	0-0.30	0.214	0.095	0.306	0.749	0.506	0.733	0-0.01	0.0000	100
4/28/87	0-1.20	0.000	0.000	0.000	0.001	0.000	0.002	—	—	100
6/28/87	0-1.20	0.707	0.715	0.459	1.550	1.502	0.717	0-0.01	0.0000	100
7/27/87	0-1.20	0.128	0.104	0.135	0.738	0.700	0.368	0-0.01	0.0000	70

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

§ The test could not be performed as all observed or simulated values were zero

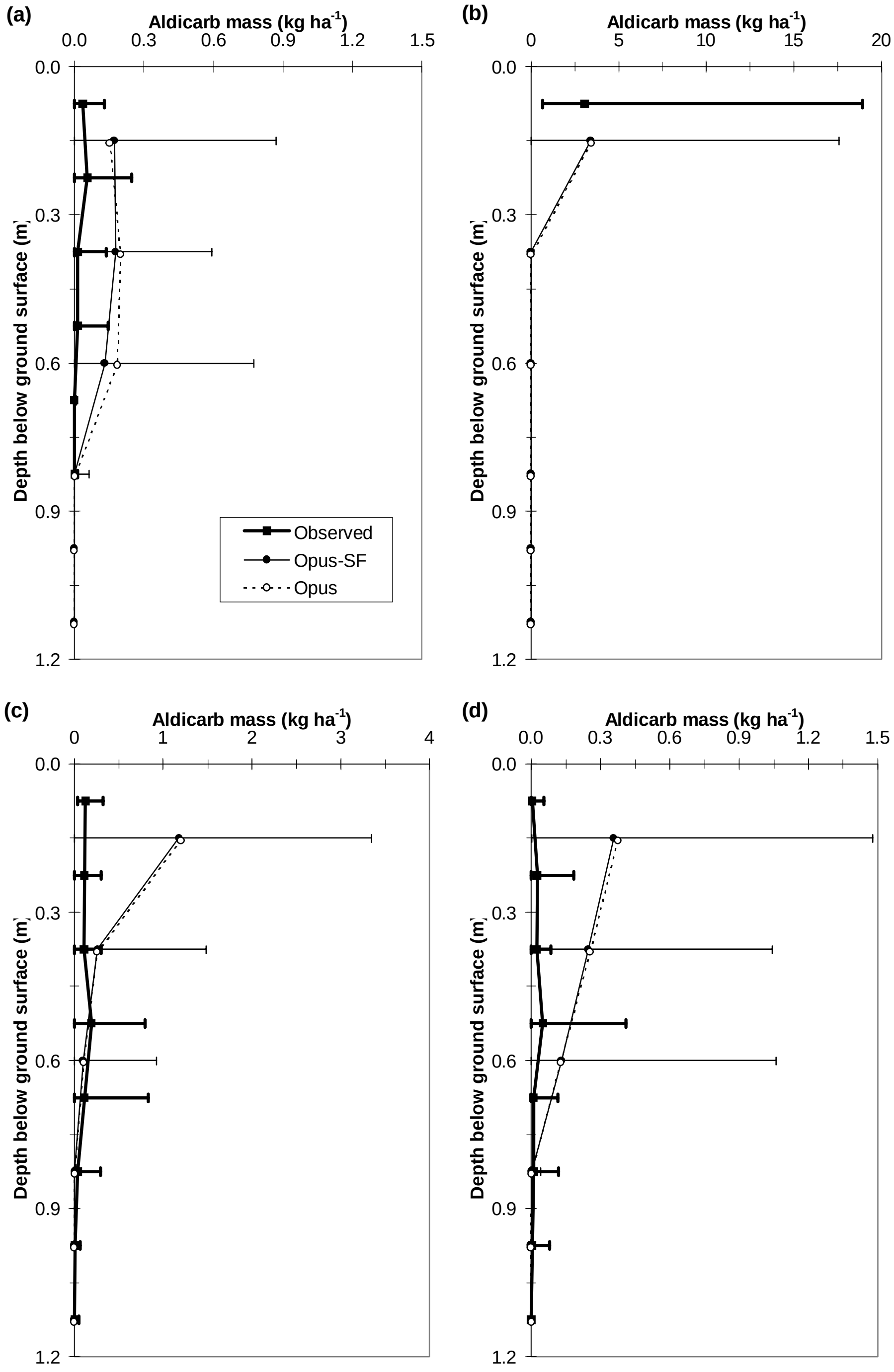


Figure 13. Observed and simulated (Opus-SF) mean and range of aldicarb mass in the root zone at the Dougherty Plain site, along with aldicarb mass predicted by deterministic Opus, on: a) July 22, 1985, b) April 30, 1986, c) June 28, 1987, and d) July 27, 1987. (Note difference in scales).

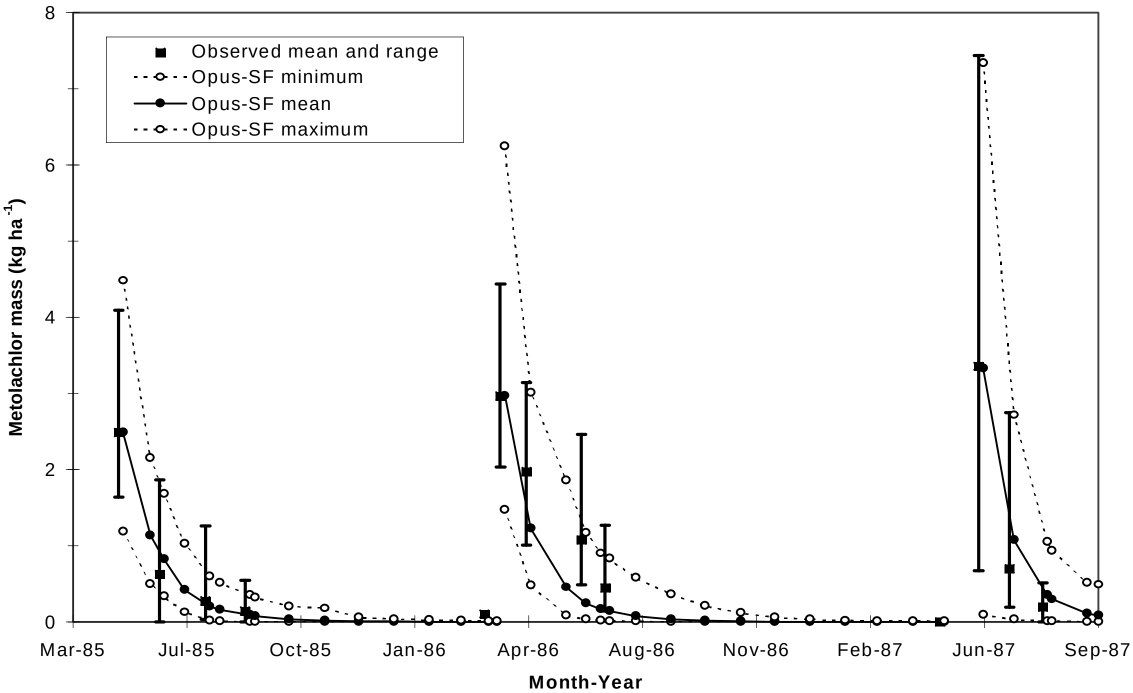


Figure 14. Observed and simulated (Opus-SF) mean and range of total metolachlor mass (1.2 m) in the root zone at the Dougherty Plain site.

Table 9. Statistical comparison of observed and simulated (Opus-SF) metolachlor mass in the root zone at the Dougherty Plain site.

	Soil	Observed			Opus-SF			p-value†		Range
Date	depth (m)	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistics‡
6/12/85	0-0.30	0.623	0.498	0.549	0.824	0.804	0.211	0-0.01	0.0368	45
7/22/85	0-0.60	0.272	0.149	0.342	0.200	0.188	0.081	0.01-0.02	0.2308	90
8/26/85	0-0.60	0.139	0.145	0.121	0.088	0.079	0.048	0-0.01	0.0319	90
3/24/86	0-1.20	0.106	0.045	0.291	0.001	0.000	0.001	0-0.01	0.0020	30
4/30/86	0-0.15	1.975	2.077	0.620	1.227	1.179	0.343	0-0.01	0.0000	90
6/17/86	0-0.30	1.074	0.860	0.539	0.244	0.200	0.149	0-0.01	0.0000	60
7/8/86	0-0.30	0.448	0.401	0.268	0.139	0.110	0.098	0-0.01	0.0000	90
4/28/87	0-1.20	0.000	0.000	0.000	0.000	0.000	0.000	—§	—	100
6/28/87	0-1.20	0.701	0.590	0.532	1.076	1.065	0.431	0-0.01	0.0000	95
7/27/87	0-1.20	0.192	0.196	0.140	0.354	0.331	0.175	0-0.01	0.0000	80

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

§ The test could not be performed as all observed or simulated values were zero

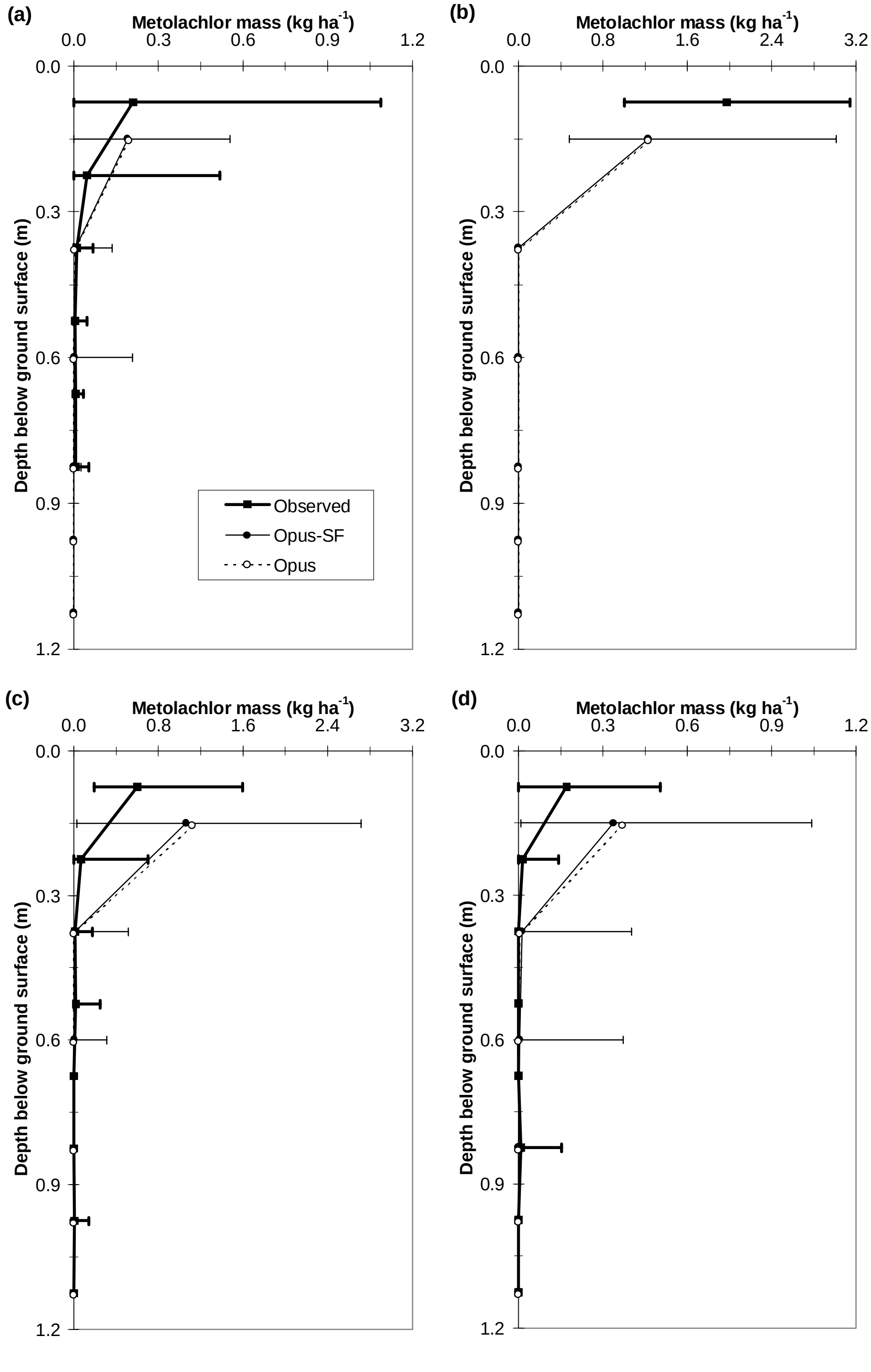


Figure 15. Observed and simulated (Opus-SF) mean and range of metolachlor mass in the root zone at the Dougherty Plain site, along with metolachlor mass predicted by deterministic Opus, on: a) July 22, 1985, b) April 30, 1986, c) June 28, 1987, and d) July 27, 1987. (Note difference in scales).

Table 10. Mean monthly evapotranspiration (ET) and percolation predicted by Opus-SF and Opus-MC at the Dougherty Plain site.

Month-Year	Rainfall, mm	....ET, mm....		....Percolation, mm....	
		Opus-SF	Opus-MC	Opus-SF	Opus-MC
Apr-85	47.2	60.9	59.7	1.3	1.4
May-85	81.5	76.8	75.5	1.0	1.8
Jun-85	106.1	132.0	132.4	-12.3	-11.8
Jul-85	94.3	150.2	149.8	-14.2	-12.2
Aug-85	100.9	60.1	55.3	-13.4	-10.1
Sep-85	31.1	102.0	99.9	-10.7	-7.7
Oct-85	176.0	17.7	17.6	9.1	7.2
Nov-85	187.3	18.2	18.2	170.2	171.6
Dec-85	149.9	18.2	18.3	152.3	153.5
Total-85	974.3	636.1	626.7	283.4	293.7
Jan-86	76.3	22.8	22.8	70.5	70.7
Feb-86	133.7	28.7	28.7	101.7	101.6
Mar-86	89.8	44.0	44.0	44.7	45.1
Apr-86	14.9	33.2	33.1	3.3	3.6
May-86	4.4	25.9	25.8	-5.3	-4.9
Jun-86	65.4	161.0	160.3	-25.5	-23.2
Jul-86	63.3	94.8	84.8	-27.3	-19.8
Aug-86	108.6	93.8	88.3	-21.7	-15.9
Sep-86	57.5	64.8	64.6	-9.2	-9.4
Oct-86	77.8	25.6	25.1	6.5	4.8
Nov-86	150.1	18.4	18.4	49.3	50.9
Dec-86	110.8	16.4	16.4	124.0	124.8
Total-86	952.6	629.5	612.4	310.9	328.3
Jan-87	177.3	20.0	20.0	165.1	164.7
Feb-87	142.5	22.2	22.2	89.4	89.7
Mar-87	62.7	46.0	46.1	60.7	61.2
Apr-87	28.9	55.9	55.5	5.9	6.1
May-87	79.2	78.8	77.7	1.9	2.6
Jun-87	135.1	94.2	92.9	21.4	23.1
Jul-87	165.7	203.3	203.2	-21.6	-21.4
Aug-87	204.7	180.2	179.6	-6.2	-5.6
Sep-87†	12.7	35.2	35.2	6.6	6.1
Total-87	1008.8	735.7	732.4	323.1	326.6

† September 1-10 only

Table 11. Statistical comparison of depth-averaged soil water content in the root zone predicted by Opus-SF and Opus-MC at the Dougherty Plain site.

Date	K-S Test p-value	M-W Test p-value
4/1/85	0.05-0.10	0.1045
6/12/85	0-0.01	0.0047
7/22/85	0.01-0.02	0.0160
8/26/85	0-0.01	0.0000
3/24/86	0-0.01	0.0000
4/30/86	0-0.01	0.0000
6/17/86	0-0.01	0.0000
7/8/86	0-0.01	0.0000
4/28/87	0-0.01	0.0000
6/28/87	0-0.01	0.0000
7/27/87	0.05-0.10	0.0195

Table 12. Statistical comparison of total bromide mass in the root zone predicted by Opus-SF and Opus-MC at the Dougherty Plain site.

Date	K-S Test p-value	M-W Test p-value
6/12/85	0.2-1.0	0.9578
7/22/85	0.2-1.0	0.9578
8/26/85	0.2-1.0	0.9577
11/26/85	0-0.01	0.0000
12/9/85	0-0.01	0.0000
12/30/85	0-0.01	0.0000
2/26/86	0-0.01	0.0000
3/24/86	0-0.01	0.0000
5/5/86	0-0.01	0.0000
11/19/86	0-0.01	0.1378
1/13/87	0-0.01	0.0000
2/6/87	0-0.01	0.0000
5/18/87	0-0.01	0.0005
7/21/87	0-0.01	0.0026

Table 13. Statistical comparison of total aldicarb mass in the root zone predicted by Opus-SF and Opus-MC at the Dougherty Plain site.

Date	K-S Test p-value	M-W Test p-value
6/12/85	0.2-1.0	0.8200
7/22/85	0.2-1.0	0.8294
8/26/85	0.2-1.0	0.9225
3/24/86	0-0.01	0.0000
4/30/86	0.2-1.0	0.9528
6/17/86	0.2-1.0	0.8628
7/8/86	0.2-1.0	0.8135
4/28/87	0.01-0.02	0.0673
6/28/87	0.2-1.0	0.9281
7/27/87	0.2-1.0	0.7777

Table 14. Statistical comparison of total metolachlor mass in the root zone predicted by Opus-SF and Opus-MC at the Dougherty Plain site.

Date	K-S Test p-value	M-W Test p-value
6/12/85	0.2-1.0	0.6253
7/22/85	0.1-0.2	0.3515
8/26/85	0.1-0.2	0.4155
3/24/86	0.2-1.0	0.9053
4/30/86	0.2-1.0	0.4795
6/17/86	0.2-1.0	0.2855
7/8/86	0-0.01	0.0000
4/28/87	0.01-0.02	0.0094
6/28/87	0.01-0.02	0.0048
7/27/87	0-0.01	0.0000

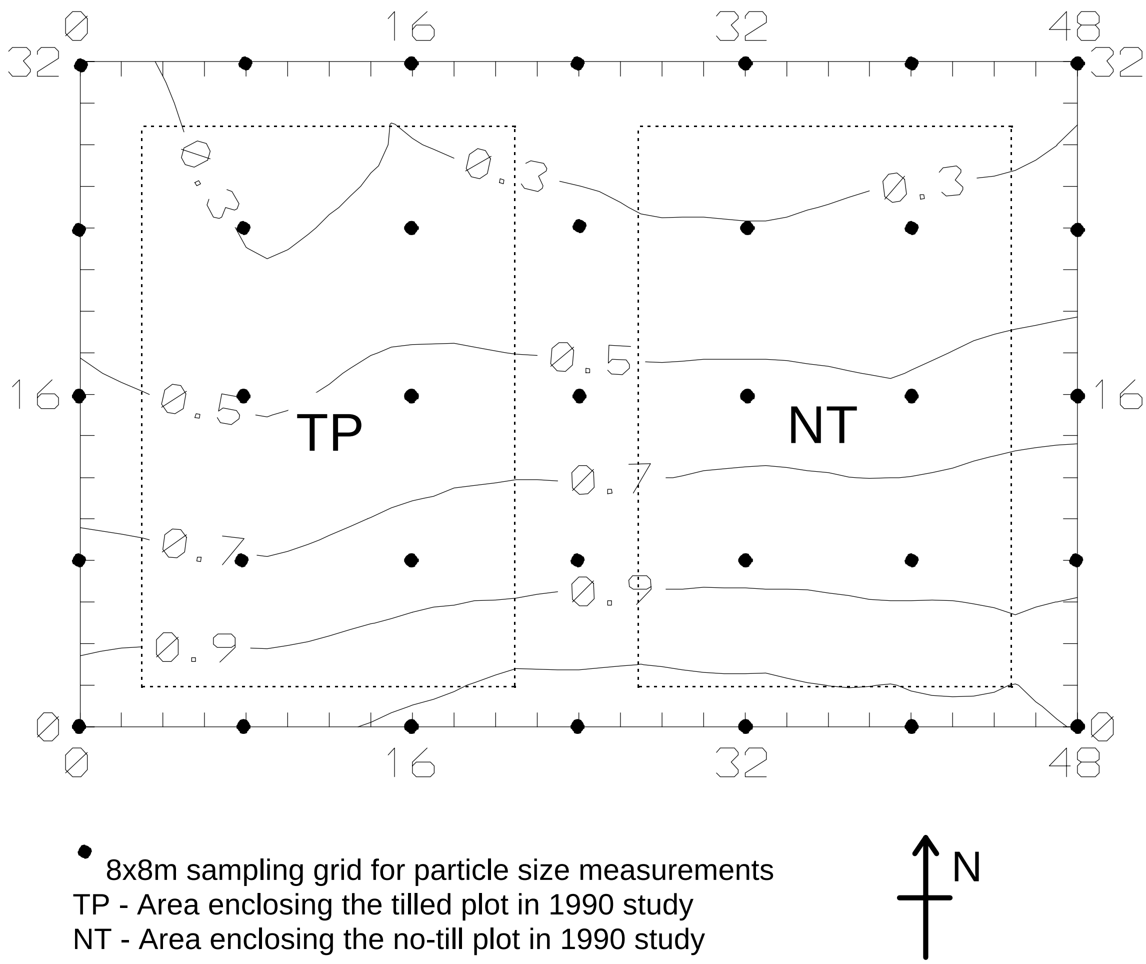


Figure 16. Nomini Creek study area, showing the elevation contours, the sampling grid for the particle size measurements, and the location of the 1990 field study plots.

Table 15. Statistical characteristics of soil properties at the Nomini Creek site, used in the estimation of spatially variable soil parameters in Opus-SF and GLEAMS-SF.

Soil property	Measured data			Order of	Detrended data†		
	Mean	St.dev.	PDF	Trend Surface†	Mean	St.dev.	PDF
Sand Content, %							
Depth 1 (0-0.15 m)	71.6	3.4	Normal	Second[1]	0	2.69	Normal
Depth 2 (0.15-0.3 m)	60.4	4.6	Normal				
Depth 3 (0.3-0.45 m)	57.4	8.6	Normal	First[2]	0	8.16	Normal
Depth 4 (0.45-0.6 m)	68.8	10.3	Normal	Second[3]	0	10.27	Normal
Clay content, %							
Depth 1 (0-0.15 m)	6.9	1.5	Normal	First[4]	0	1.39	Normal
Depth 2 (0.15-0.3 m)	12.3	3.7	Normal	Second[5]	0	3.49	Normal
Depth 3 (0.3-0.45 m)	16.7	4.8	Normal				
Depth 4 (0.45-0.6 m)	12.6	4.2	Normal				
Porosity							
Depth 1 (0-0.15 m)	0.387	0.049	Normal				
Depth 2 (0.15-0.3 m)	0.37	0.035	Normal				
Depth 3 (0.3-0.45 m)	0.369	0.028	Normal				
Depth 4 (0.45-0.6 m)	0.402	0.034	Normal				
Organic matter, %							
Depth 1 (0-0.15 m)	0.938	0.188	Normal				
Depth 2 (0.15-0.3 m)	0.552	0.19	Normal				
Depth 3 (0.3-0.45 m)	0.414	0.18	Normal				
Depth 4 (0.45-0.6 m)	0.304	0.165	Normal				

† Only for properties that exhibited spatial trend

[1]Trend coefficients of Sand(1): β_0=69.267, β_1=0.420, β_2=0.026, β_3=-0.008, β_4=0.003, β_5=-0.008

[2]Trend coefficients of Sand(3): β_0=51.552, β_1=0.049, β_2=0.335

[3]Trend coefficients of Sand(4): β_0=59.305, β_1=-0.026, β_2=1.403, β_3=-0.010, β_4=0.035, β_5=-0.054

[4]Trend coefficients of Clay(1): β_0=6.403, β_1=-0.033, β_2=0.060

[5]Trend coefficients of Clay(2): β_0=12.806, β_1=-0.107, β_2=0.354, β_3=-0.002, β_4=0.010, β_5=-0.014

Table 16. Correlation between soil properties measured at the Nomini Creek site.

(a) Correlation† between sand and clay content in each soil layer

Depth (m)	Sand-Clay
0-0.15	-0.83
0.15-0.3	-0.90
0.3-0.45	-0.74
0.45-0.6	-0.87

† Correlation coefficients were calculated on detrended residuals for variables that exhibited spatial trends.

(b) Correlation between organic matter content in different soil layers

Depth (m)	0-0.15	0.15-0.3	0.3-0.45	0.45-0.6
0-0.15	1.00			
0.15-0.3	0.29	1.00		
0.3-0.45	-0.17	0.15	1.00	
0.45-0.6	0.09	0.34	0.33	0.00

Table 17. Estimates of important soil parameters used in Opus-SF simulation of the Nomini Creek site.

Soil parameter	Mean	St.dev.†
Init. water content (θ_i or THST), mm mm^{-1}	0.228	
Sat. hyd. conductivity (K_s or RC), mm hr^{-1}		
Depth 1 (0-0.15 m)	44.3	32.9
Depth 2 (0.15-0.3 m)	12.9	10.0
Depth 3 (0.3-0.45 m)	10.9	13.4
Depth 4 (0.45-0.6 m)	60.6	64.3
Depth 5 (0-6-0.9 m)	210.0	
Depth 6 (0.9-1.2 m)	210.0	
Air entry pressure (ψ_b or PBUB), mm		
Depth 1 (0-0.15 m)	136.3	39.9
Depth 2 (0.15-0.3 m)	207.3	63.7
Depth 3 (0.3-0.45 m)	239.2	105.6
Depth 4 (0.45-0.6 m)	125.6	61.8
Depth 5 (0-6-0.9 m)	60.7	
Depth 6 (0.9-1.2 m)	57.2	
Pore size index (λ or ALAM)		
Depth 1 (0-0.15 m)	0.453	0.033
Depth 2 (0.15-0.3 m)	0.401	0.040
Depth 3 (0.3-0.45 m)	0.356	0.050
Depth 4 (0.45-0.6 m)	0.390	0.044
Depth 5 (0-6-0.9 m)	0.456	
Depth 6 (0.9-1.2 m)	0.457	
Sat. water content (θ_s or THS), mm mm^{-1}		
Depth 1 (0-0.15 m)	0.368	0.047
Depth 2 (0.15-0.3 m)	0.352	0.033
Depth 3 (0.3-0.45 m)	0.351	0.026
Depth 4 (0.45-0.6 m)	0.382	0.032
Depth 5 (0-6-0.9 m)	0.390	
Depth 6 (0.9-1.2 m)	0.415	
Residual water content (θ_r or B15), mm mm^{-1}		
Depth 1 (0-0.15 m)	0.056	0.005
Depth 2 (0.15-0.3 m)	0.070	0.010
Depth 3 (0.3-0.45 m)	0.080	0.010
Depth 4 (0.45-0.6 m)	0.073	0.010
Depth 5 (0-6-0.9 m)	0.059	
Depth 6 (0.9-1.2 m)	0.053	
Organic carbon content (ORGC), %		
Depth 1 (0-0.15 m)	0.54	0.11
Depth 2 (0.15-0.3 m)	0.32	0.11
Depth 3 (0.3-0.45 m)	0.24	0.10
Depth 4 (0.45-0.6 m)	0.18	0.09
Depth 5 (0-6-0.9 m)	0.14	
Depth 6 (0.9-1.2 m)	0.10	

† Standard deviation is given only for spatially variable parameters

Table 18. Estimates of important pesticide parameters used in Opus-SF simulation of the Nomini Creek site.

Parameter	Atrazine			Metolachlor		
	Mean	**St.dev.†**	**PDF†**	**Mean**	**St.dev.†**	**PDF†**
Solubility in water (PSOLUB), mg L^{-1}	33			530		
Adsorption coefficient (DKOC), $cm^3\ g^{-1}$	100			200		
Washoff fraction (FWASH)	0.5			0.6		
Foliar degradation rate (DKFL), day^{-1}	0.1386			0.1386		
Soil degradation rate (DKSOIL), day^{-1}	0.0116	0.0023	LogNormal	0.0385	0.0077	LogNormal
Plant uptake coefficient (PUPTK)	0.59			0.32		
Application rate (QPEST), kg ha^{-1}	0.98	0.34	LogNormal	1.05	0.49	LogNormal
Bromide‡ application rate, kg ha^{-1}	37.36	10.39	LogNormal			

† Standard deviation and PDF's are given only for spatially variable parameters

‡ Other bromide properties used in the simulation are: PSOLUB = 1000 mg L^{-1}; DKOC = 0 $cm^3\ g^{-1}$; FWASH=0.75; DKFL = DKSOIL = 0 day^{-1}; PUPTK = 0.6.

Table 19. Mean monthly evapotranspiration (ET) and percolation predicted by Opus-SF at the Nomini Creek site, along with ET and percolation predicted by deterministic Opus.

Month-Year	Rainfall (mm)	Runoff (mm)	ET (mm) Opus-SF	ET (mm) Opus	Percolation (mm) Opus-SF	Percolation (mm) Opus
Apr-90†	57.4	0.2	10.7	10.6	45.6	43.7
May-90	295.0	41.0	50.3	50.2	215.8	219.8
Jun-90	47.7	0.0	151.7	148.5	35.9	32.5
Jul-90	87.2	0.4	103.8	100.3	-3.1	-3.0
Aug-90	206.4	13.3	97.7	97.5	-2.0	-1.9
Sep-90	47.9	0.0	101.3	101.2	-0.2	0.5
Total	741.6	54.8	515.4	508.4	291.9	291.7

† April 22-30 only

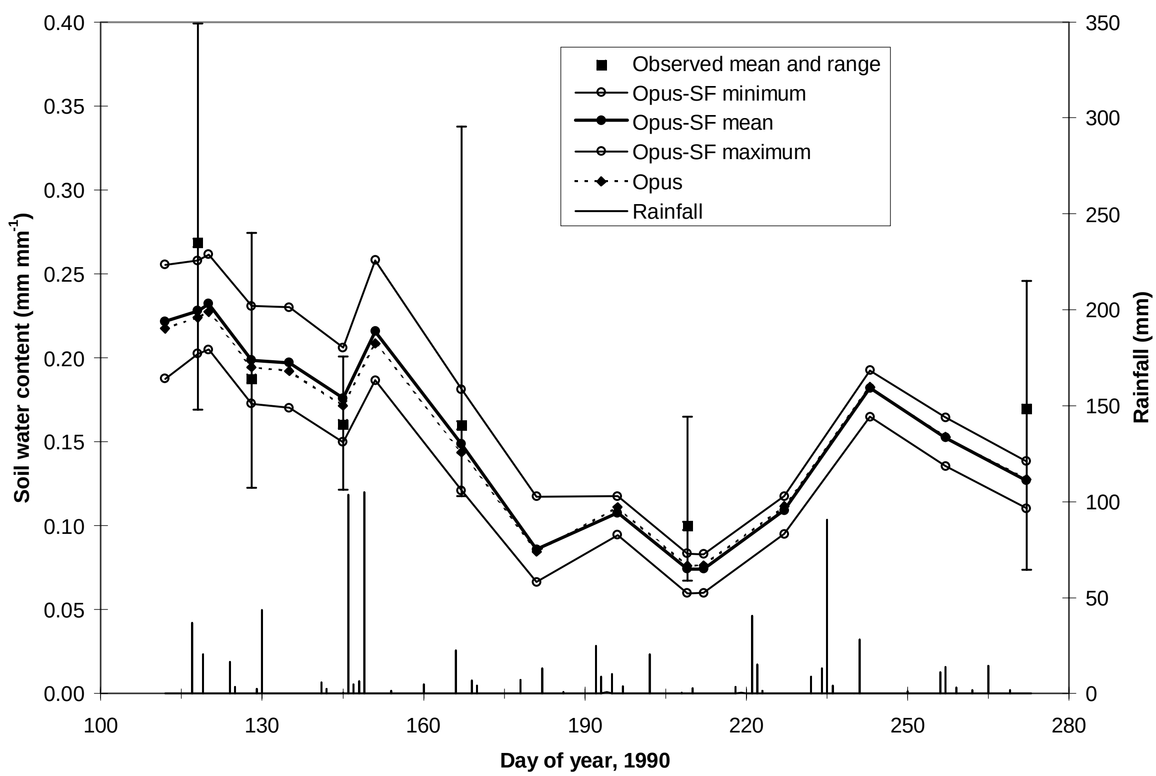


Figure 17. Observed and simulated (Opus-SF) mean and range of depth-averaged soil water content in the root zone (0.9 m) at the Nomini Creek site over the simulation period, along with depth-averaged soil water content predicted by deterministic Opus.

Table 20. Statistical comparison of observed and simulated (Opus-SF) depth-averaged soil water content in the root zone at the Nomini Creek site.

Day of	Observed			Opus-SF			p-value†		Range
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistic‡
118	0.269	0.267	0.059	0.228	0.228	0.008	0-0.01	0.000	35
128	0.187	0.182	0.038	0.199	0.198	0.008	0-0.01	0.011	45
145	0.160	0.161	0.020	0.176	0.176	0.008	0-0.01	0.000	70
167	0.160	0.142	0.050	0.149	0.148	0.009	0.01-0.02	0.246	75
209	0.100	0.096	0.022	0.074	0.074	0.003	0-0.01	0.000	20
272	0.170	0.157	0.045	0.127	0.127	0.004	0-0.01	0.000	10

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

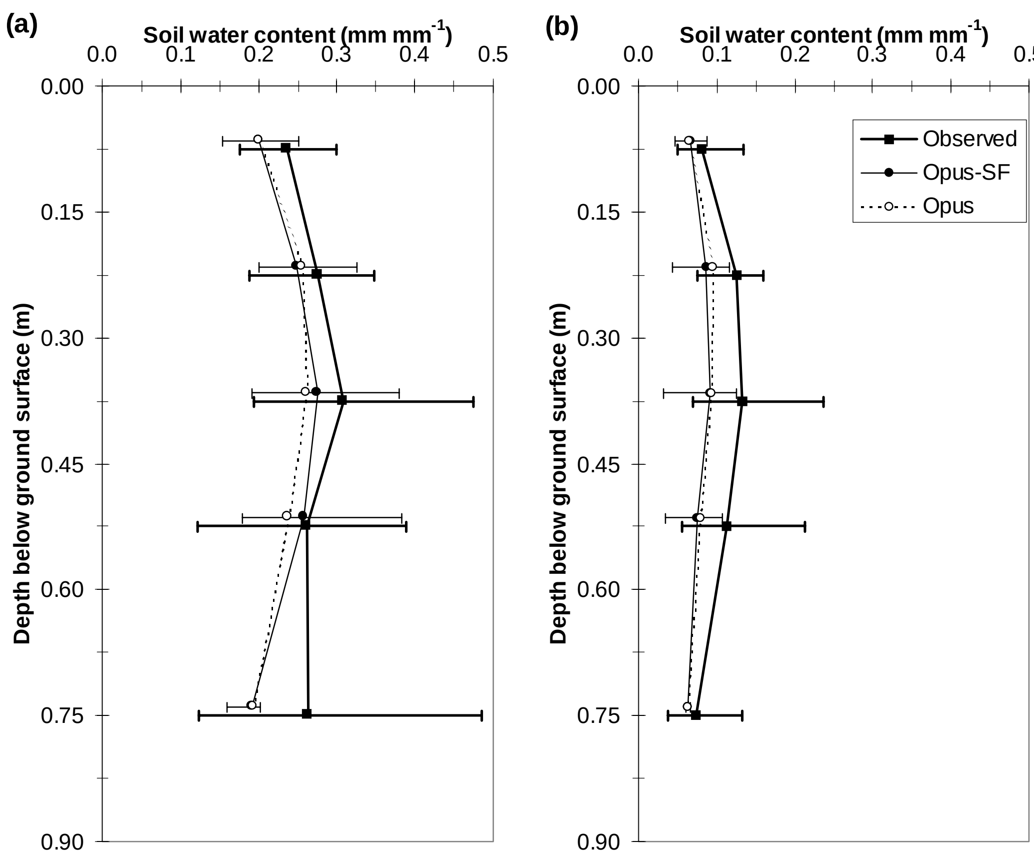


Figure 18. Observed and simulated (Opus-SF) mean and range of soil water content in the root zone at the Nomini Creek site, along with soil water content predicted by deterministic Opus, on: a) day 118 and b) day 209.

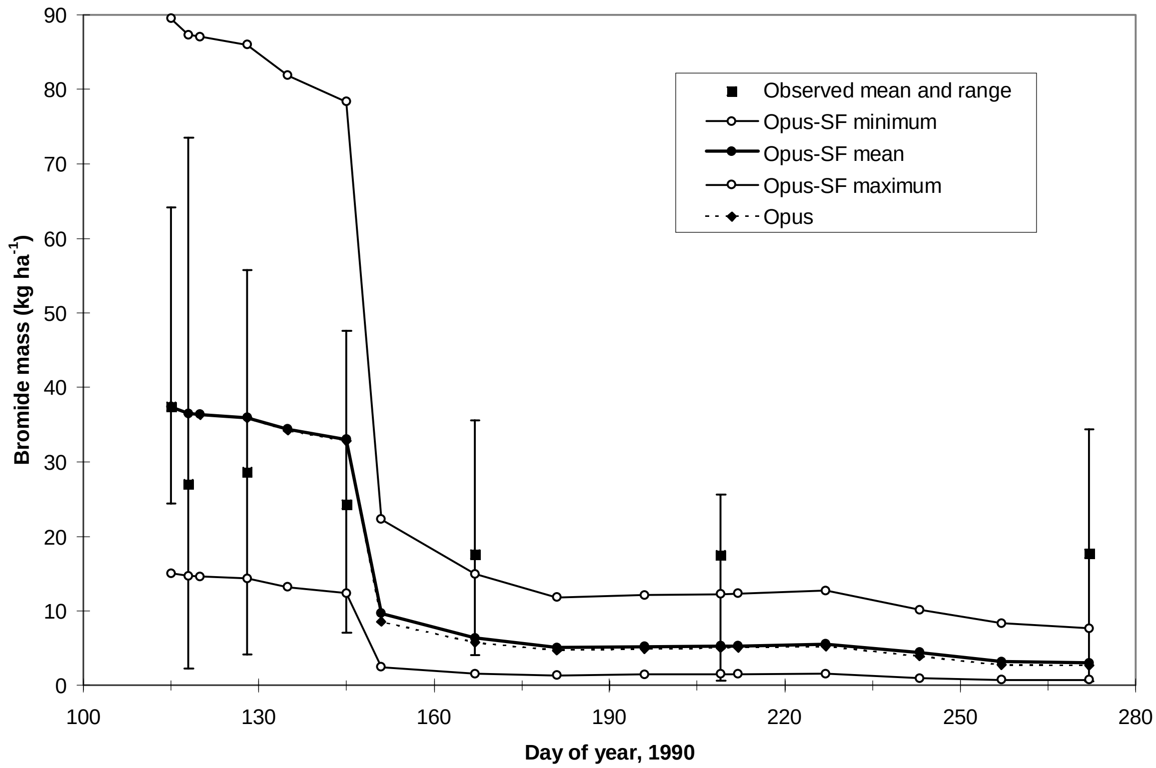


Figure 19. Observed and simulated (Opus-SF) mean and range of total bromide mass in the root zone (0.9 m) at the Nomini Creek site over the simulation period, along with bromide mass predicted by deterministic Opus.

Table 21. Statistical comparison of observed and simulated (Opus-SF) total bromide mass in the root zone at the Nomini Creek site.

Day of	Observed			Opus-SF			p-value†		Range
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistic‡
118	26.99	24.10	16.56	36.47	35.10	10.14	0-0.01	0.001	80
128	28.64	28.14	11.95	35.93	34.59	9.99	0.01-0.02	0.002	95
145	24.28	24.94	10.92	33.01	31.88	9.18	0-0.01	0.000	80
167	17.57	15.91	7.70	6.39	6.11	2.01	0-0.01	0.000	45
209	17.46	18.25	6.32	5.28	5.12	1.57	0-0.01	0.000	5
272	17.70	16.33	9.61	3.00	2.85	0.98	0-0.01	0.000	10

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

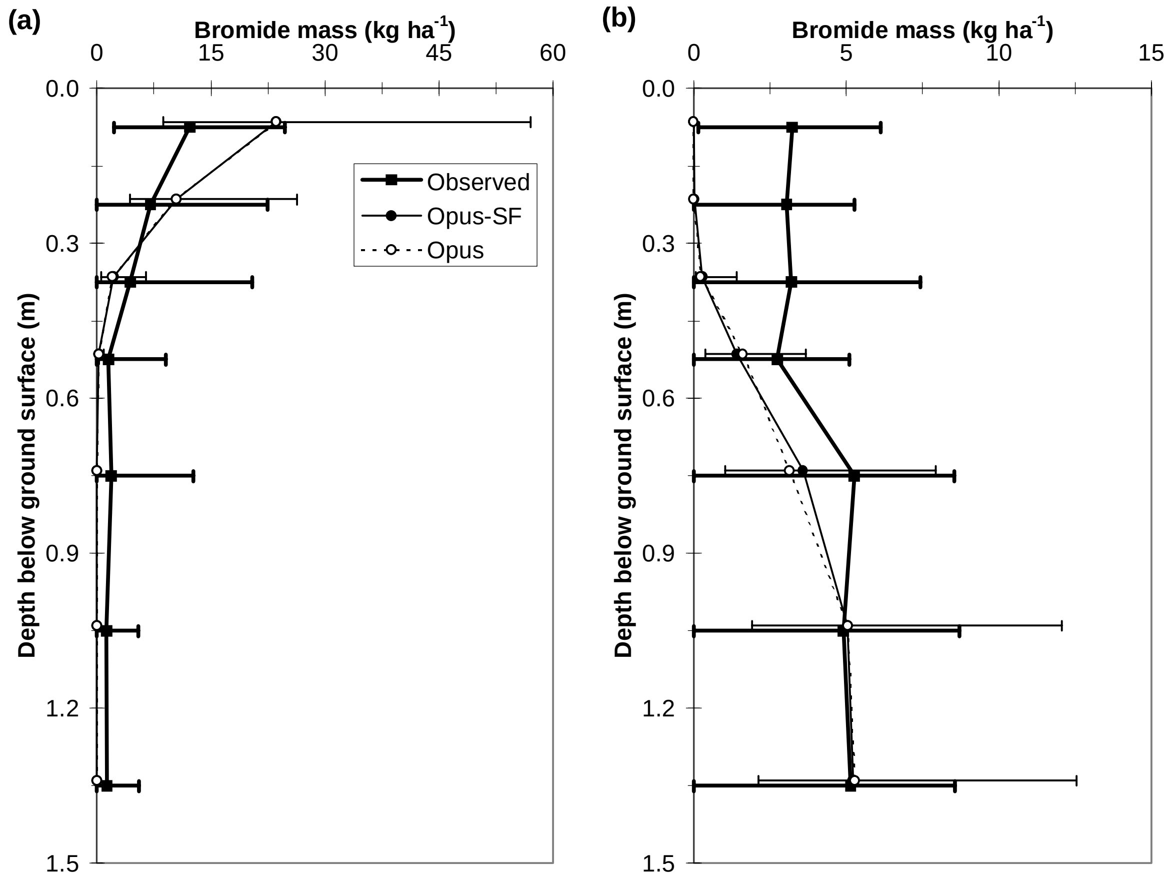


Figure 20. Observed and simulated (Opus-SF) mean and range of bromide mass in the 1.5 m profile at the Nomini Creek site, along with bromide mass predicted by deterministic Opus, on: a) day 118 and b) day 209. (Note difference in scales).

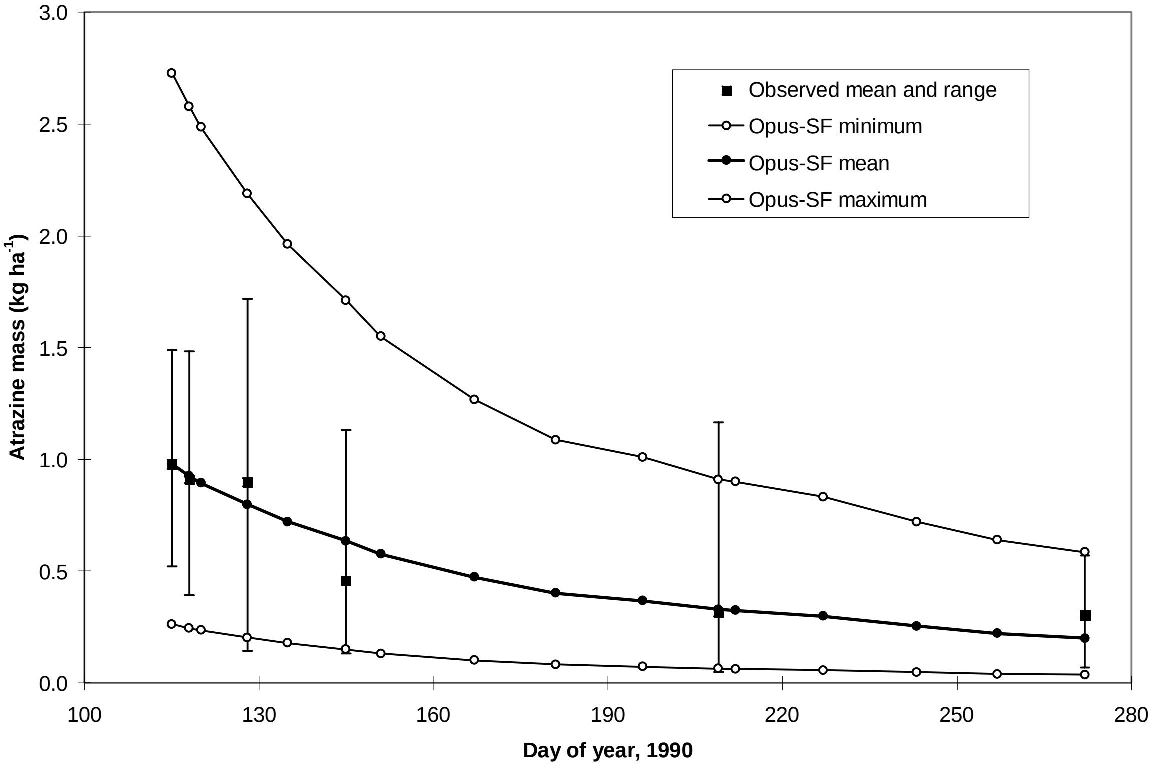


Figure 21. Observed and simulated (Opus-SF) mean and range of total atrazine mass in the root zone (0.9 m) at the Nomini Creek site over the simulation period.

Table 22. Statistical comparison of observed and simulated (Opus-SF) total atrazine mass in the root zone at the Nomini Creek site.

Day of	Observed			Opus-SF			p-value†		Range
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistic‡
118	0.912	0.886	0.347	0.926	0.872	0.322	0.2-1.0	0.908	100
128	0.898	0.883	0.464	0.797	0.752	0.278	0.05-0.1	0.366	95
145	0.458	0.375	0.266	0.635	0.603	0.225	0-0.01	0.000	95
209	0.315	0.227	0.268	0.329	0.308	0.124	0.01-0.02	0.058	85
272	0.304	0.293	0.150	0.200	0.187	0.081	0-0.01	0.002	100

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

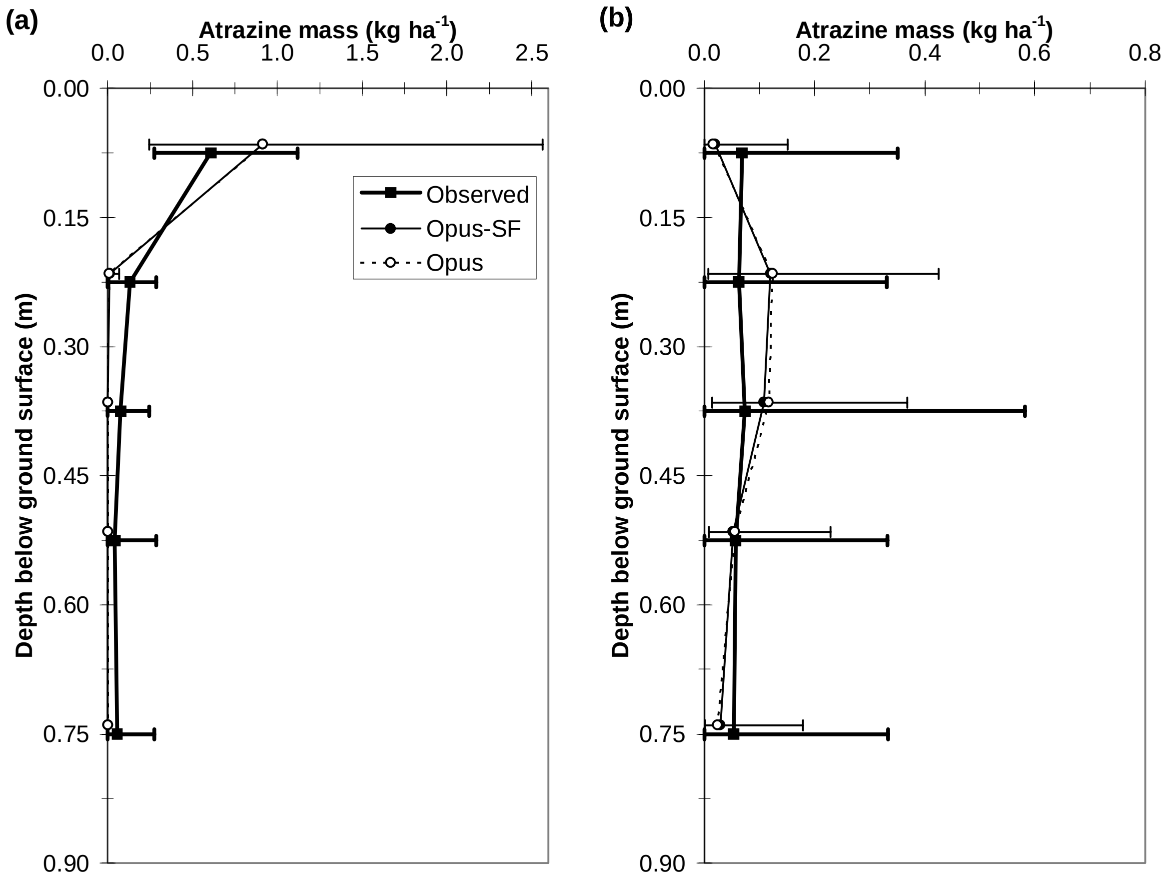


Figure 22. Observed and simulated (Opus-SF) mean and range of atrazine mass in the 1.5 m profile at the Nomini Creek site, along with atrazine mass predicted by deterministic Opus, on: a) day 118 and b) day 209. (Note difference in scales).

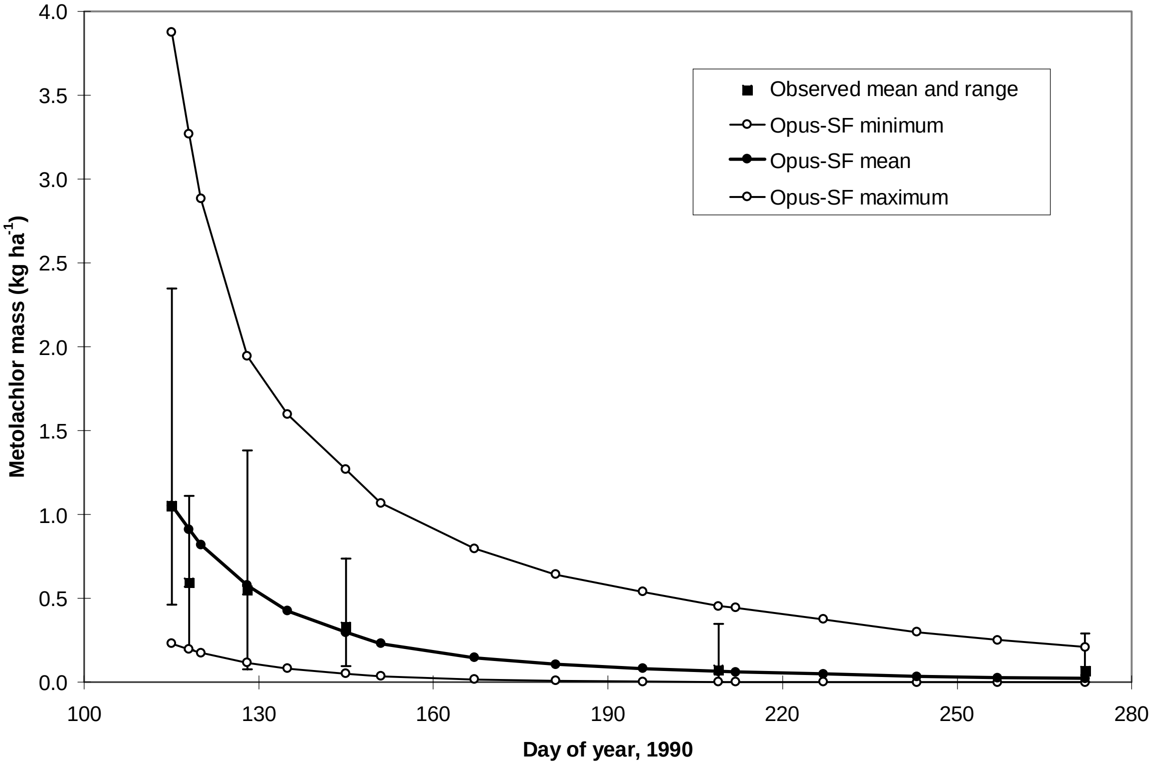


Figure 23. Observed and simulated (Opus-SF) mean and range of metolachlor mass in the root zone (0.9 m) at the Nomini Creek site over the simulation period.

Table 23. Statistical comparison of observed and simulated (Opus-SF) total metolachlor mass in the root zone at the Nomini Creek site.

Day of	Observed			Opus-SF			p-value†		Range
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test	Statistic‡
118	0.594	0.586	0.211	0.911	0.829	0.418	0-0.01	0.000	95
128	0.549	0.505	0.341	0.577	0.518	0.272	0.1-0.2	0.538	95
145	0.333	0.254	0.177	0.298	0.264	0.156	0.2-1.0	0.430	100
209	0.073	0.043	0.081	0.065	0.053	0.048	0.2-1.0	0.609	90
272	0.070	0.063	0.058	0.022	0.015	0.022	0-0.01	0.000	90

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

‡ Percentage of observations within simulated range

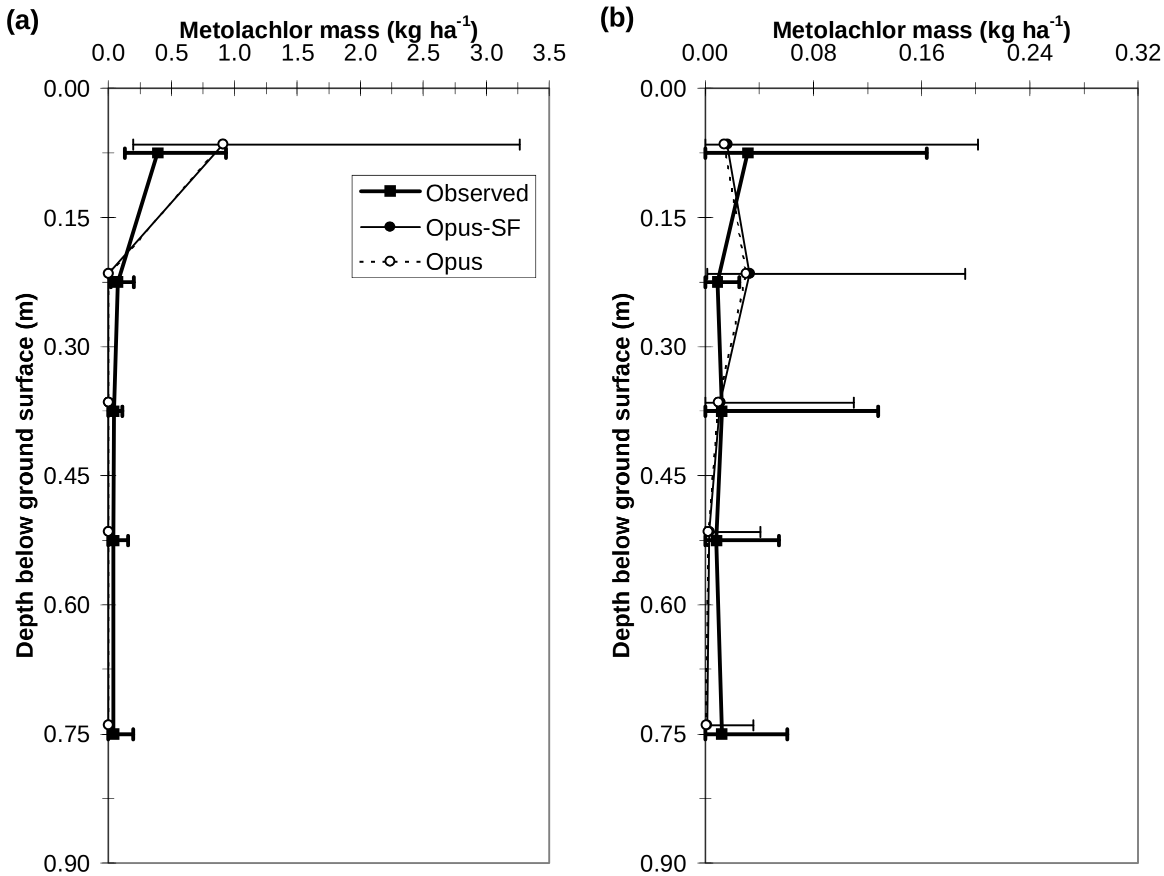


Figure 24. Observed and simulated (Opus-SF) mean and range of total metolachlor mass in the root zone at the Nomini Creek site, along with metolachlor mass predicted by deterministic Opus, on: a) day 118 and b) day 209. (Note difference in scales).

Table 24. Mean monthly evapotranspiration (ET) and percolation predicted by Opus-SF and Opus-MC at the Nomini Creek site.

Month-Year	Rainfall (mm)	Runoff (mm)	ET (mm) GLEAMS-SF	ET (mm) GLEAMS	Percolation (mm) GLEAMS-SF	Percolation (mm) GLEAMS
Apr-90†	57.4	0.2	17.7	17.7	41.1	41.1
May-90	295.0	41.0	59.3	59.3	198.1	198.1
Jun-90	47.7	0.0	66.6	66.6	0.0	0.0
Jul-90	87.2	0.4	127.0	122.0	0.0	0.0
Aug-90	206.4	13.3	104.3	103.8	32.9	35.5
Sep-90	47.9	0.0	93.3	92.7	0.0	0.0
Total	741.6	54.8	468.1	462.0	272.1	274.8

† April 22-30 only

Table 25. Statistical comparison of depth-averaged soil water content in the root zone predicted by Opus-SF and Opus-MC at the Nomini Creek site.

Day of	Opus-SF			Opus-MC			p-value†	
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test
112	0.222	0.222	0.010	0.217	0.217	0.009	0-0.01	0.000
118	0.228	0.228	0.008	0.224	0.224	0.008	0-0.01	0.000
128	0.199	0.198	0.008	0.195	0.195	0.008	0-0.01	0.000
145	0.176	0.176	0.008	0.172	0.172	0.008	0-0.01	0.000
167	0.149	0.148	0.009	0.145	0.145	0.008	0-0.01	0.000
209	0.074	0.074	0.003	0.076	0.076	0.003	0-0.01	0.000
272	0.127	0.127	0.004	0.127	0.127	0.005	0.02-0.05	0.140

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

Table 26. Statistical comparison of total bromide mass in the root zone predicted by Opus-SF and Opus-MC at the Nomini Creek site.

Day of	Opus-SF			Opus-MC			p-value†	
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test
115	37.37	35.97	10.39	37.36	35.09	10.41	0.2-1.0	0.947
118	36.47	35.10	10.14	36.46	35.09	10.16	0.2-1.0	0.954
128	35.93	34.59	9.99	35.91	34.56	10.00	0.2-1.0	0.918
145	33.01	31.88	9.18	32.84	31.62	9.16	0.2-1.0	0.590
167	6.39	6.11	2.01	5.97	5.71	1.87	0-0.01	0.000
209	5.28	5.12	1.57	5.15	4.96	1.53	0.05-0.1	0.036
272	3.00	2.85	0.98	2.80	2.66	0.89	0-0.01	0.000

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

Table 27. Statistical comparison of total atrazine mass in the root zone predicted by Opus-SF and Opus-MC at the Nomini Creek site.

Day of	Opus-SF			Opus-MC			p-value†	
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test
115	0.978	0.923	0.340	0.978	0.923	0.340	0.2-1.0	0.994
118	0.926	0.872	0.322	0.926	0.872	0.322	0.2-1.0	0.999
128	0.797	0.752	0.278	0.797	0.751	0.278	0.2-1.0	0.954
145	0.635	0.603	0.225	0.634	0.600	0.224	0.2-1.0	0.919
167	0.474	0.448	0.173	0.474	0.448	0.172	0.2-1.0	0.984
209	0.329	0.308	0.124	0.334	0.313	0.125	0.2-1.0	0.305
272	0.200	0.187	0.081	0.204	0.189	0.081	0.2-1.0	0.241

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests

Table 28. Statistical comparison of total metolachlor mass in the root zone predicted by Opus-SF and Opus-MC at the Nomini Creek site.

Day of	Opus-SF			Opus-MC			p-value†	
year, 1990	Mean	Median	St.dev.	Mean	Median	St.dev.	KS Test	MW Test
115	1.053	0.957	0.484	1.052	0.956	0.483	0.2-1.0	0.978
118	0.911	0.829	0.418	0.910	0.829	0.417	0.2-1.0	0.958
128	0.577	0.518	0.272	0.574	0.518	0.270	0.2-1.0	0.859
145	0.298	0.264	0.156	0.296	0.265	0.154	0.2-1.0	0.797
167	0.147	0.127	0.089	0.146	0.126	0.088	0.2-1.0	0.908
209	0.065	0.053	0.048	0.065	0.052	0.047	0.2-1.0	0.959
272	0.022	0.015	0.022	0.022	0.015	0.022	0.2-1.0	0.878

† p-values from two sample Kolmogorov-Smirnov (KS) and Mann-Whitney (MW) tests