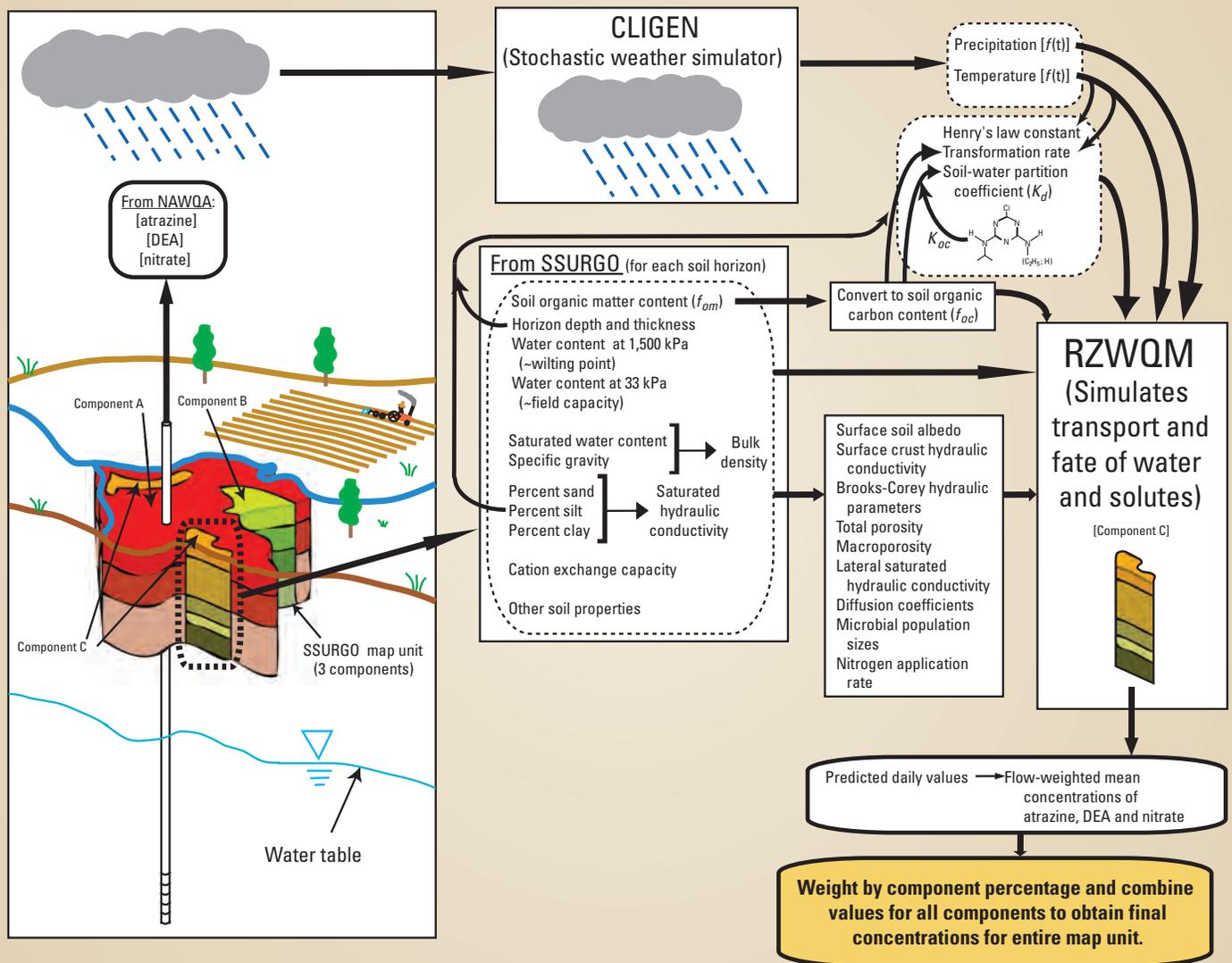


Design and Testing of a Process-Based Groundwater Vulnerability Assessment (P-GWAVA) System for Predicting Concentrations of Agrichemicals in Groundwater Across the United States



Cover: Diagram showing sources of data for several P-GWAVA-RZ (Phase 2) model input parameters related to soil properties, chemical properties, weather, and other site-specific variables. Soil (SSURGO) map-unit graphic provided by Leah Wasser, Pennsylvania State University Geospatial Technology Program, Land Analysis Laboratory (written commun., March 24, 2008). Used with permission.

Design and Testing of a Process-Based Groundwater Vulnerability Assessment (P-GWAVA) System for Predicting Concentrations of Agrichemicals in Groundwater Across the United States

By Jack E. Barbash and Frank D. Voss

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Contents

Abstract.....	1
Introduction.....	3
Previous Assessments of Groundwater Vulnerability	3
Purpose and Scope	4
Study Design.....	4
Design Objectives	4
Study Phases.....	5
Methods.....	6
Study Site Selection and Characteristics	6
Locations of Study Sites Relative to National Water-Quality Assessment Groundwater Networks.....	6
Locations of Study Sites Relative to Spatial Patterns of Agrichemical Use and Corn Cultivation	6
Phase 1	7
Phase 2	7
Statistical Methods.....	11
Sample Collection and Chemical Analysis	11
P-GWAVA System	12
Overall Simulation Approach.....	12
Initial Conditions and Simulation Periods.....	12
Effects of Simulation Approaches on Model Predictions.....	16
Vadose-Zone Models	16
Pesticide Root-Zone Model (Phase 1).....	16
Root-Zone Water-Quality Model (Phase 2).....	17
Processes Simulated and Input Data.....	18
Physical and Chemical Properties of Soils.....	18
Phase 1	19
Phase 2	19
Characteristics and Use of SSURGO Data	19
Reductions in Soil Permeability Caused by Surface Crusts	22
Soil Macroporosity	24
Water Movement Through the Subsurface.....	24
Phase 1	24
Phase 2	28
Weather.....	31
Phase 1	31
Phase 2	33
Assessment Depths and Depths to Water.....	33
Irrigation.....	35
Phase 1	35
Phase 2	37

Contents

Methods

Study Site Selection and Characteristics

Runoff	37
Phase 1	37
Phase 2	38
Evapotranspiration	38
Phase 1	38
Phase 2	38
Timing and Intensity of Agrichemical Applications	38
Atrazine.....	38
Nitrogen Fertilizers	41
Estimating Physical and Chemical Property Values for Atrazine and Deethylatrazine	41
Partitioning and Mass Transfer of Atrazine and Deethylatrazine.....	42
Henry's Law Constant (Phase 2 only)	42
Octanol-Water Partition Coefficient (Phase 2 only).....	42
Soil-Water Partition Coefficients	43
Wash-off Parameters for Crop Foliage and Residue (Phase 2 only).....	44
Mass Transfer Rates (Phase 2 only).....	45
Kinetic Controls on Sorption	45
Solute Exchange Between Micropores and Mesopores.....	46
Atrazine and Deethylatrazine Transformation Rates.....	48
Atrazine and Deethylatrazine Transformation in the Hydrologic System.....	48
Atrazine and Deethylatrazine Disappearance Rates in Soil.....	51
Atrazine Disappearance Rates.....	51
Photochemical Transformations	51
Thermal Transformations in Soil.....	51
Initial Disappearance Rates and Temperature Variations.....	52
Influence of Soil Moisture on Disappearance Rates (Phase 2 only)	55
Deethylatrazine Production from Atrazine Reaction in Soil (Phase 2 only).....	56
Deethylatrazine Disappearance Rate in Soil (Phase 2 only)	56
Atrazine and Deethylatrazine Disappearance Rate Adjustments with Depth	
Below Land Surface	59
Formation, Transport, and Fate of Nitrate	
(Phase 2 only).....	59
Model Formulation and Output.....	61
Soil Column Discretization	61
Phase 1	61
Phase 2	61
Quantifying Solute Concentrations from Model Output.....	61
Accounting for the Potential Effects of Corn and-Soybean Rotations on Agrichemical	
Occurrence.....	62

Contents

P-GWAVA Simulation and Groundwater Sampling Results	63
Phase 1 (P-GWAVA-PR)	64
Soil Column Discretization for Simulations	64
Effect of Spatial Variability of Atrazine Application Intensities on Simulation Results..	66
Effect of Transformation Site (Dissolved versus Sorbed State) on Simulation Results	68
Approaches for Distributing Irrigation	70
Spatial Averaging of Soil Parameter Values	73
Temporal Variability of Atrazine Concentrations and Water Flow.....	78
Modeling Approaches and Simulation Results	78
Modeling Approach for Final P-GWAVA-PR Simulations	78
Water Flow	81
Atrazine Concentrations and Detection Frequencies	81
Geographic Distribution of Model Residuals	84
Statistical Correlations with Site Characteristics	84
Phase 2 (P-GWAVA-RZ)	88
Spatial and Temporal Patterns of Material Transport	88
Water Flow.....	88
Solute Transport.....	90
Solute Distributions Among Chemical Forms and Environmental Media.....	93
Atrazine and Deethylatrazine	93
Nitrogen.....	97
Model Residuals and Water-Table Depths.....	99
Atrazine and Deethylatrazine	99
Nitrate 102	
Agreement Between Simulated and Observed Solute Concentrations	102
Atrazine.....	102
Simulated Atrazine Concentrations Compared with Concentrations	
Measured in Groundwater	102
Simulated Frequencies of Atrazine Detection Compared with Measured	
Values.....	105
Comparison of Predictions from the P-GWAVA-PR and P-GWAVA-RZ	
Simulations	107
Deethylatrazine	111
Comparisons of Atrazine and Deethylatrazine Concentrations Predicted by	
P-GWAVA-RZ with those from Stackelberg Regression Model.....	115
Deethylatrazine Fractions	115
Nitrate 115	
Influence of Corn-and-Soybean Rotations on Model Residuals	121
Solute Detection Classifications	124
Overall Frequencies of Simulated and Measured Solute Detection.....	127

Contents—Continued

P-GWAVA Simulation and Groundwater Sampling Results	
Phase 1 (P-GWAVA-PR)	
Geographic Patterns of Agreement Between Simulated and Measured Frequencies of Detection.....	130
Statistical Correlations with Site Characteristics	133
Suggestions for Future Work	135
Summary and Conclusions.....	135
Acknowledgments	139
References Cited.....	140
Glossary.....	181
Appendix A. Previous Assessments of Groundwater Vulnerability.....	187
Appendix B. Equations Used to Estimate Deethylatrazine Formation Percentage	202
Appendix C. Groundwater Sampling Networks Examined	206

Figures

1. Map showing locations of Phase 1 (P-GWAVA-PR) sites and the distribution of atrazine application intensity across the conterminous United States during 1997	8
2. Map showing locations of Phase 2 (P-GWAVA-RZ) sites and the distribution of atrazine application intensity across the 10 northernmost states in the Corn Belt of the United States during 1997	9
3. Map showing locations of Phase 2 (P-GWAVA-RZ) sites and the distribution of nitrogen fertilizer application across the 10 northernmost states in the Corn Belt of the United States during 2001	10
4. Graphs showing temporal variations in the routine reporting limits used for atrazine, deethylatrazine, and nitrate at the 453 sites examined for Phase 2 of this study and sampled in the 10 northernmost states in the Corn Belt of the United States, 1992–2006.....	13
5. Schematic diagram showing primary features of the P-GWAVA-PR (Phase 1) system used to simulate the transport and fate of atrazine in the vadose zone using the Pesticide Root-Zone Model.....	14
6. Schematic diagram showing primary features of the P-GWAVA-RZ (Phase 2) system used to simulate the transport and fate of atrazine, deethylatrazine, and nitrate in the vadose zone using the Root-Zone Water-Quality Model	15
7. Diagram showing steps used with the P-GWAVA-PR (Phase 1) system to obtain spatially weighted averages of individual soil parameters for each State Soil Geographic database map unit, using soil organic matter as an example.....	20
8. Graph showing variations in soil organic carbon content among sites in the groundwater networks examined in the conterminous United States for Phase 1 of this study, 1992–98.....	21
9. Diagram showing sources of data for several P-GWAVA-RZ (Phase 2) input parameters related to soil properties, chemical properties, weather, and other site-specific variables.....	23

Figures—Continued

10. Flow chart showing procedure used to select the macroporosity value assigned to every soil horizon where soil texture, organic matter and depth data were available in the Soil Survey Geographic database for the sites examined in the 10 northernmost states of the Corn Belt of the United States during Phase 2 of this study25
11. Generalized diagram showing variations in soil water content with depth in the vadose zone26
12. Graph showing comparison between estimates of field capacity (FC) at the P-GWAVA-PR (Phase 1) study sites using the Rawls and Brakensiek (1983) equation (R&B), estimates for the same sites from Rosetta, and the range of values typically measured in soils in the United States27
13. Graph showing comparison between estimates of wilting point (WP) at the P-GWAVA-PR (Phase 1) study sites using the Rawls and Brakensiek (1983) equation (R&B), estimates for the same sites from Rosetta, and the range of values typically measured in soils in the United States.....28
14. Graph showing comparison between groundwater temperatures measured at each of the 1,224 P-GWAVA-PR (Phase 1) study sites examined across the conterminous United States and the average air temperature for May in the same locations from the National Oceanic and Atmospheric Administration (2010)32
15. Map showing average daily air temperature during May from 1971 to 2000 and the P-GWAVA-RZ (Phase 2) study sites in the 10 northernmost states in the Corn Belt of the United States34
16. Boxplot showing average depths to water at the sites examined in the conterminous United States (Phase 1) and in the 10 northernmost states in the Corn Belt (Phase 2) of the United States for this study, relative to the assessment depths used for the P-GWAVA simulations during each study phase.....35
17. Map showing the prevalence of irrigated agricultural areas near each P-GWAVA-PR (Phase 1) study site in the conterminous United States in 199236
18. Boxplot showing variations in atrazine use intensity on agricultural land among sites in the groundwater networks examined in the conterminous United States for Phase 1 of this study, 1992–9840
19. Graphs showing apparent diffusion coefficient for the exchange of atrazine between micropores and mesopores compared with clay content (percent clay), and cation exchange capacity normalized to clay content for 1,657 soil horizons at P-GWAVA-RZ (Phase 2) study sites in the 10 northernmost states of the Corn Belt.....49
20. Diagram showing the reactions producing the atrazine transformation products that have been examined most extensively in the hydrologic system50
21. Schematic diagram showing processes and storage compartments for nitrogen cycling through water, soil, and biota in agricultural systems60
22. Graphs showing effect of model grid discretization in the 10–100 centimeter depth interval on the degree of agreement between atrazine concentrations simulated at an assessment depth of 100 centimeters (1 meter) by the P-GWAVA-PR (Phase 1) model and measured in shallow groundwater at 331 sites in unirrigated agricultural areas in the conterminous United States with average depths to water greater than 1 meter65

Figures—Continued

23. Graph showing effect of spatial variability of atrazine application intensities on model residuals for atrazine concentrations measured in shallow groundwater beneath unirrigated agricultural areas where the average depth to water was greater than 1 meter in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–98.....67
24. Graphs showing effect of the location of simulated atrazine transformation on model residuals for atrazine concentrations in shallow groundwater beneath unirrigated agricultural areas where the average depth to water was greater than 1 meter in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–98.....69
25. Graph showing amounts of atrazine predicted in sorbed and dissolved states in soil at the end of a 5-year P-GWAVA-PR (Phase 1) simulation in an agricultural area (site 2086) in Grant County, Washington, 1991–95.....70
26. Graph showing effect of irrigation simulation approach on model residuals for atrazine concentrations in shallow groundwater beneath agricultural areas where the average depth to water was greater than 1 meter in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–9871
27. Maps showing effect of irrigation simulation approach on P-GWAVA-PR model residuals for frequencies of atrazine detection in groundwater networks with 10 or more sites when irrigation was not simulated at any sites and irrigation was simulated at all sites across the conterminous United States for Phase 1 of this study, 1992–98.....72
28. Graphs and map showing influence of spatial averaging of soil parameter values on atrazine chemographs simulated at a depth of 153 centimeters in the vadose zone by the P-GWAVA-PR (Phase 1) model using spatially averaged State Soil Geographic database values and the original Soil Survey Geographic database values for soil parameters at four agricultural sites in central Washington State, 1986–9574
29. Graph showing influence of spatial averaging of soil parameter values on the extent of agreement between atrazine concentrations predicted at a depth of 153 centimeters in the vadose zone by a set of 10-year simulations using the P-GWAVA-PR model (1986–1995) and atrazine concentrations measured in shallow groundwater at four irrigated agricultural sites in central Washington State, 1992–95.....75
30. Maps showing locations where atrazine concentrations predicted by the P-GWAVA-PR (Phase 1) simulations were compared with atrazine concentrations measured in shallow groundwater at six unirrigated agricultural sites in an agricultural area of Portage County, Wisconsin76
31. Graph showing influence of spatial averaging of soil parameter values on the extent of agreement between atrazine concentrations predicted at a depth of 153 centimeters in the vadose zone by a set of 10-year P-GWAVA-PR simulations (1986–1995) and atrazine concentrations measured in shallow groundwater at six unirrigated agricultural sites in Portage County, Wisconsin, 1992–9577
32. Time series graphs showing temporal variability in measured precipitation, and in the infiltration and atrazine concentrations simulated at an assessment depth of 153 centimeters using the P-GWAVA-PR (Phase 1) model at site 2233 in an unirrigated agricultural area of Portage County, Wisconsin, during the 1986–95 simulation period79

Figures—Continued

33. Boxplots showing influence of different modeling approaches on the P-GWAVA-PR model residuals for atrazine concentrations at all of the Phase 1 study sites in agricultural areas of the conterminous United States, 1992–98.....80
34. Graph showing cumulative distributions of model residuals for atrazine concentrations at Phase 1 study sites for the final set of P-GWAVA-PR simulations in agricultural areas of the conterminous United States, 1992–9881
35. Graph showing mean annual groundwater recharge rates simulated by the P-GWAVA-PR (Phase 1) model with no irrigation, and by the base-flow index method excluding irrigation, at all of the unirrigated agricultural sites in the conterminous United States where the depth to water was known82
36. Graph showing atrazine concentrations simulated in the vadose zone by the P-GWAVA-PR system and concentrations measured in groundwater at Phase 1 sites in the conterminous United States, 1992–98.....83
37. Graphs showing frequencies of atrazine detection simulated at a depth of 1 meter in the vadose zone using the final set of P-GWAVA-PR (Phase 1) simulations and the measured frequencies of atrazine detection in shallow groundwater networks in agricultural areas of the conterminous United States, 1992–98.....85
38. Map showing distribution of P-GWAVA-PR (Phase 1) model residuals for atrazine detection frequencies in 47 groundwater networks in agricultural areas of the conterminous United States, 1992–9886
39. Graph showing cumulative distributions of P-GWAVA-PR model residuals for atrazine concentrations at Phase 1 study sites in agricultural areas of the Corn Belt and western, southeastern, and northeastern regions of the United States.....87
40. Graphs showing temporal patterns of water fluxes estimated for precipitation and irrigation, deep seepage and runoff, and crop transpiration and evaporation at a site in south-central Wisconsin during the P-GWAVA-RZ (Phase 2) simulation period, 1998–2004.....89
41. Table showing vertical variations of soil texture (from Soil Survey Geographic database) and graphs showing vertical variations of simulated soil water content, pressure head, total atrazine mass, total deethylatrazine mass, and nitrate concentration at a site in south-central Wisconsin on the last day of the 7-year P-GWAVA-RZ (Phase 2) simulation period (1998–2004)91
42. Graph showing average annual estimated groundwater recharge rates simulated at the 3-meter assessment depth by the P-GWAVA-RZ (Phase 2) model, and rates estimated from the Base Flow Index method including irrigation withdrawals, in 10 contiguous states in the Corn Belt of the United States92
43. Graphs showing variations in solute concentrations and water flow simulated at the 3-meter assessment depth by the P-GWAVA-RZ (Phase 2) simulations for atrazine concentration, deethylatrazine concentration, atrazine residue yield, nitrate concentration, and deep seepage and runoff at Soil Survey Geographic database site 21840 in south-central Wisconsin during the 7-year simulation period, 1998–2004.....94
44. Pie charts showing distributions of atrazine and deethylatrazine, computed from the P-GWAVA-RZ (Phase 2) simulations, in water, soil, and plants after 7 years of simulated annual atrazine applications at a rate of 2 kilograms of active ingredient per hectare per year to sites in Marquette County, Wisconsin , and Daviess County, Indiana96

Figures—Continued

45. Pie charts showing nitrogen distributions among primary environmental compartments estimated by the P-GWAVA-RZ (Phase 2) simulations before and after 7 years of nitrogen fertilizer applications, estimated inputs and losses of nitrogen, and nitrate concentrations estimated in the vadose zone and measured in shallow groundwater at study sites in Marquette County, Wisconsin and Daviess County, Indiana98
46. Graphs showing relations between P-GWAVA-RZ (Phase 2) model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations and the average depth of the water table at study sites in the 10 northernmost states of the Corn Belt, 1992–2006100
47. Graphs showing cumulative distributions of P-GWAVA-RZ (Phase 2) model residuals for atrazine concentrations at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006103
48. Graph showing atrazine concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006104
49. Graphs showing frequencies of atrazine detection simulated at a depth of 3 meters in the vadose zone using the P-GWAVA-RZ (Phase 2) model and the measured frequencies of atrazine detection in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006106
50. Graph showing cumulative distributions of model residuals for atrazine concentrations simulated by P-GWAVA-PR (Phase 1, 1992–98) and P-GWAVA-RZ (Phase 2, 1992–2006) at 136 study sites where simulations were done with both models and the depth to water was greater than 3 meters in agricultural areas of the 10 northernmost states in the Corn Belt.....108
51. Boxplots showing statistical distributions of model residuals for atrazine concentrations from selected P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) scenarios at agricultural sites in the conterminous United States (Phase 1, 1992–1998) and the 10 northernmost states of the Corn Belt (Phase 2, 1992–2006)110
52. Graph showing average annual precipitation at 338 of the agricultural sites examined during one or both phases of this study in the 10 northernmost states of the Corn Belt, 1990–2007111
53. Graphs showing cumulative distributions of P-GWAVA-RZ (Phase 2) model residuals for deethylatrazine concentration at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006112
54. Graphs showing frequencies of deethylatrazine (DEA) detection simulated at a depth of 3 meters in the vadose zone by the P-GWAVA-RZ (Phase 2) model and the measured frequencies of DEA detection in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006.....113
55. Graph showing deethylatrazine concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006114
56. Graph showing cumulative distributions of P-GWAVA-RZ (Phase 2) model residual for the deethylatrazine fraction at agricultural sites in the 10 northernmost states in the Corn Belt, 1992–2006.....116

Figures—Continued

57. Graph showing deethylatrazine fractions simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and values measured in shallow groundwater at the same locations in agricultural areas of the 10 northernmost states in the Corn Belt, 1992–2006117
58. Graph showing cumulative distributions of P-GWAVA-RZ (Phase 2) model residuals for nitrate concentrations at agricultural sites in the 10 northernmost states in the Corn Belt, 1992–2006118
59. Graph showing nitrate concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006119
60. Graphs showing frequencies of nitrate detection simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and frequencies of nitrate detection measured in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006.....120
61. Graphs showing the P-GWAVA-RZ model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations, 1992–2006, and average annual percentage of corn-and-soybean area in corn cultivation in the surrounding county during 1995–2005 for all Phase 2 sites where the depth to water was greater than the 3-meter assessment depth in the 10 northernmost states of the Corn Belt.....122
62. Graph showing relations between solute detection classifications and different combinations of simulated and measured detections and non-detections for a hypothetical solute125
63. Graphs showing accuracy of solute detection classifications from the Phase 1 (P-GWAVA-PR) simulations for the conterminous United States, 1991–95 and the Phase 2 (P-GWAVA-RZ) simulations for the 10 northernmost states in the Corn Belt, 2000–2004.....126
64. Graphs showing overall frequencies of atrazine, deethylatrazine, and nitrate detection predicted in the vadose zone by the final set of P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) simulations and measured in shallow groundwater in agricultural areas of the conterminous United States (Phase 1) or the 10 northernmost states of the Corn Belt (Phase 2), using a fixed reporting limit for the Phase 1 results and temporally varying reporting limits for the Phase 2 results.....128
65. Graphs showing overall frequencies of atrazine, deethylatrazine, and nitrate detection predicted in the vadose zone by the final set of P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) simulations and measured in shallow groundwater in agricultural areas of the conterminous United States (Phase 1) or the 10 northernmost states of the Corn Belt (Phase 2), using fixed reporting limits for the results from both phases.....129
66. Map showing model residuals for the frequencies of atrazine detection calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006.....130
67. Map showing model residuals for the frequencies of deethylatrazine detection calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006131

Figures—Continued

68. Map showing model residuals for the frequencies of nitrate detection (calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006.....132

Tables

1. Distinguishing features of the two phases of the process-based groundwater vulnerability assessment (P-GWAVA) system study of agrichemicals in groundwater of the conterminous United States.6
2. Principal characteristics of groundwater networks examined by the U.S. Geological Survey National Water-Quality Assessment (NAWQA) program.7
3. Ranges of Brooks-Corey parameter values reported for 11 U.S. Department of Agriculture soil texture classes, and ranges estimated from van Genuchten parameters using Rosetta30
4. Approaches selected to improve agreement between simulated and measured solute concentrations for the final set of P-GWAVA-PR (Phase 1) simulations across the conterminous United States, and for the final set of P-GWAVA-RZ (Phase 2) simulations in the 10 northernmost states of the Corn Belt.....31
5. Effects of model grid discretization in the 10–100 centimeter depth interval on the level of agreement between atrazine concentrations simulated at the 100-centimeter (1 meter) assessment depth in the vadose zone using P-GWAVA-PR (Phase 1) and those measured in shallow groundwater at 331 unirrigated agricultural sites where the average depth to the water table was greater than 1 meter in the conterminous United States, 1992–98.66
6. Effects of 15 modeling approaches on the extent of agreement between atrazine concentrations predicted at the 1-meter assessment depth in the vadose zone by the P-GWAVA-PR (Phase 1) simulations and concentrations measured in shallow groundwater in agricultural areas where the depth to water exceeded 1 meter in the conterminous United States, 1992–98.68
7. Correlations between atrazine concentrations simulated by the P-GWAVA-PR (Phase 1) model at the 1-meter assessment depth in the vadose zone and concentrations measured in shallow groundwater at the same locations in agricultural areas of the conterminous United States, 1992–98.82
8. Correlations between the P-GWAVA-PR (Phase 1) model residuals for atrazine detection frequencies in shallow groundwater in 47 groundwater networks in agricultural areas of the conterminous United States, 1992–98 (1,149 sites), and selected site characteristics.88

Tables—Continued

9.	Correlations between average depths to water and P-GWAVA model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations in agricultural areas of the United States.....	101
10.	Agreement between atrazine, deethylatrazine (DEA), or nitrate concentrations (or DEA fractions) simulated at the 3-meter assessment depth in the vadose zone by the P-GWAVA-RZ (Phase 2) model and the concentrations (or DEA fractions) measured in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006	105
11.	Correlations between simulated and measured frequencies of detection of atrazine, deethylatrazine, and nitrate in shallow groundwater sampling networks with 10 or more sites.	107
12.	Correlations between P-GWAVA-RZ model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations, 1992–2006, and average annual percentages of corn-and-soybean area in corn cultivation in the surrounding county during 1995–2005 for all Phase 2 sites where the depth to water was greater than the 3-meter assessment depth in the 10 northernmost states of the Corn Belt.	121
13.	Correlations between model residuals for the detection frequencies of atrazine, deethylatrazine, and nitrate in shallow groundwater simulated by the P-GWAVA-RZ (Phase 2) model and selected site characteristics in the 10 northernmost states of the Corn Belt, 1992–2006.	134
14.	Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.....	157

Conversion Factors

[Inch/pound to International System of Units]

Multiply	By	To obtain
Area		
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km ²)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Flow rate		
inch per hour (in/h)	0.0254	meter per hour (m/h)
Pressure		
bar	100	kilopascal (kPa)

[International System of Units to inch/pound]

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
hectare (ha)	2.471	acre
hectare (ha)	0.003861	square mile (mi ²)
square kilometer (km ²)	247.1	acre
square kilometer (km ²)	0.3861	square mile (mi ²)
Flow rate		
centimeter per day (cm/d)	0.3937	inch per day (in/d)
centimeter per year (cm/yr)	0.3937	inch per year (in/yr)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
kilopascal (kPa)	0.01	bar
Hydraulic conductivity		
centimeter per hour (cm/h)	0.7874	foot per day (ft/d)
Density		
gram per cubic centimeter (g/cm ³)	62.4220	pound per cubic foot (lb/ft ³)
Activation energy		
kilojoule per mole (kJ/mol)	0.2390	kilocalorie per mole (kcal/mol)
Application rate		
kilogram of active ingredient per hectare (kg a.i./ha)	0.8921	pound of active ingredient per acre (lb a.i./acre)

Conversion Factors

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Temperature in degrees Celsius (°C) may be converted to absolute temperature, in Kelvin (K), as follows:

$$\text{K} = ^{\circ}\text{C} + 273.15.$$

Supplemental Information

Concentrations of chemical constituents in water are given either in micrograms per liter ($\mu\text{g/L}$) or, for nitrate, in milligrams per liter as nitrogen (mg-N/L).

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Abbreviations

ACT	agricultural chemicals team
a.i.	active ingredient
AWC	available water capacity
BFI	base-flow index
CEC	cation-exchange capacity
CF	crust factor
CFC	chlorofluorocarbon (compound)
CI	confidence interval
DEA	deethylatrazine
DTW	depth to water
EPA	U.S. Environmental Protection Agency
eSW	extended Shuttleworth-Wallace (method used to estimate evapotranspiration rate)
ET	evapotranspiration
FC	field capacity
FPS	flow-path study (NAWQA groundwater study component)
FWM	flow-weighted mean
GIS	geographic information system
GWAVA	groundwater vulnerability assessment system

Abbreviations

LUS	land-use study (NAWQA groundwater study component)
NATSGO	National Soil Geographic database (NRCS)
NAWQA	National Water-Quality Assessment (Program)
NCDC	National Climatic Data Center (NOAA)
NLCD	National Land-Cover Database
NOAA	National Oceanic and Atmospheric Administration (U.S. Department of Commerce)
NRCS	Natural Resources Conservation Service (USDA)
NRI	National Resources Inventory (USDA)
OM	organic matter
PAS	principal aquifer study (NAWQA groundwater study component)
PCA	principal components analysis
PET	potential evapotranspiration
P-GWAVA	process-based groundwater vulnerability assessment system
P-GWAVA-PR	process-based groundwater vulnerability assessment system using PRZM to simulate the transport and fate of water and the solute(s) of interest
P-GWAVA-RZ	process-based groundwater vulnerability assessment system using RZWQM to simulate the transport and fate of water and the solute(s) of interest
PM equation	Penman-Monteith equation (used to estimate potential evapotranspiration rate)
PRISM	Parameter-elevation Relationships on Independent Slopes Model
PRZM	Pesticide Root-Zone Model
PTF	pedotransfer function
QMRR	quantitative medium-reactivity relation
QPPR	quantitative property-property relation
QSPR	quantitative structure-property relation
QSRR	quantitative structure-reactivity relation
RCN	runoff curve number
R ²	Pearson coefficient of determination
RZWQM	Root-Zone Water-Quality Model
SQL	Structured Query Language
SSURGO	Soil Survey Geographic database (NRCS)
STATSGO	State Soil Geographic database (NRCS)
SUS	study-unit survey (NAWQA groundwater study component)
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey
v/v	designation for a soil-related parameter expressed as volume of material per unit volume of soil
w/w	designation for a soil-related parameter expressed as weight of material per unit weight of soil

Design and Testing of a Process-Based Groundwater Vulnerability Assessment (P-GWAVA) System for Predicting Concentrations of Agrichemicals in Groundwater Across the United States

By Jack E. Barbash and Frank D. Voss

Abstract

Efforts to assess the likelihood of groundwater contamination from surface-derived compounds have spanned more than three decades. Relatively few of these assessments, however, have involved the use of process-based simulations of contaminant transport and fate in the subsurface, or compared the predictions from such models with measured data—especially over regional to national scales. To address this need, a process-based groundwater vulnerability assessment (P-GWAVA) system was constructed to use transport-and-fate simulations to predict the concentration of any surface-derived compound at a specified depth in the vadose zone anywhere in the conterminous United States. The system was then used to simulate the concentrations of selected agrichemicals in the vadose zone beneath agricultural areas in multiple locations across the conterminous United States. The simulated concentrations were compared with measured concentrations of the compounds detected in shallow groundwater (that is, groundwater drawn from within a depth of 6.3 ± 0.5 meters [mean \pm 95 percent confidence interval] below the water table) in more than 1,400 locations across the United States. The results from these comparisons were used to select the simulation approaches that led to the closest agreement between the simulated and the measured concentrations.

The P-GWAVA system uses computer simulations that account for a broader range of the hydrologic, physical, biological and chemical phenomena known to control the transport and fate of solutes in the subsurface than has been accounted for by any other vulnerability assessment over regional to national scales. Such phenomena include preferential transport and the influences of temperature, soil properties, and depth on the partitioning, transport, and transformation of pesticides in the subsurface. Published methods and detailed soil property data are used to estimate a wide range of model input parameters for each site, including surface albedo, surface crust permeability, soil water content, Brooks-Corey parameters, saturated hydraulic conductivity,

macroporosity and sizes of microbial populations, as well as solute partition coefficients, reaction rates, and meso-micropore diffusion rates. To ensure geographic consistency among the predictions, the only site-specific input data that are used are those that are available for all of the 48 conterminous states.

The investigation was carried out in two phases. For Phase 1, the Pesticide Root-Zone Model (PRZM) was used in the P-GWAVA system (designated as P-GWAVA-PR) to simulate the concentrations of atrazine at an assessment depth of 1 meter in the vadose zone beneath 1,224 agricultural sites across the United States. During Phase 2, the Root-Zone Water-Quality Model (RZWQM) was substituted for PRZM and used in the P-GWAVA system (designated as P-GWAVA-RZ) to simulate the concentrations of atrazine, the atrazine degradate deethylatrazine (DEA), and nitrate at an assessment depth of 3 meters in the vadose zone beneath 453 agricultural sites across the 10 northernmost states of the corn-growing region of the midcontinent (the Corn Belt). Some aspects of the overall modeling approaches were modified to improve the fit between the simulated and measured concentrations. However, because the P-GWAVA system was designed to predict concentrations in millions of locations across the conterminous United States, the final simulations were completed without any site-specific calibration.

For both study phases, significant, positive Spearman rank correlations ($P[\rho]$ less than or equal to $[\leq] 0.0001$) were noted between the atrazine concentrations predicted by the final set of simulations and the concentrations measured in shallow groundwater. The model residuals for the atrazine concentrations (simulated minus measured values) among all sites exhibited 95th percentile values of 0.39 microgram per liter ($\mu\text{g/L}$) for the P-GWAVA-PR simulations and 0.87 $\mu\text{g/L}$ for the P-GWAVA-RZ simulations—values that were an order of magnitude less than the Maximum Contaminant Level of 3 $\mu\text{g/L}$ established by the U.S. Environmental Protection Agency for atrazine. Atrazine concentrations simulated by the P-GWAVA-RZ model generally were in closer agreement with

2 Process-Based Groundwater Vulnerability Assessment System for Agrichemicals in Groundwater in the United States

those measured in groundwater than were the concentrations simulated by the P-GWAVA-PR model, perhaps in part because the P-GWAVA-RZ simulations were carried out over a substantially smaller geographic area and focused on shallower wells. However, the model residuals of atrazine concentrations for the two models showed a weak, negative correlation with one another among the 136 sites in the Corn Belt where simulations were carried out using both models and the depth to water was greater than the larger of the two assessment depths (Spearman $\rho = -0.17$; $P[\rho] = 0.04$). This indicated that different factors were likely responsible for the errors associated with the two models.

As noted for atrazine, the DEA concentrations simulated by the P-GWAVA-RZ model were significantly and positively correlated with the measured values ($P[\rho] \leq 0.0001$; Spearman rank correlation), with the model residuals exhibiting a 95th percentile value of $0.003 \mu\text{g/L}$ among all 453 sites examined. Additionally, the sum of the concentrations of atrazine and DEA simulated in the vadose zone was positively correlated with the sum of the concentrations of the two compounds predicted in shallow groundwater by a 2012 Tobit regression model at 329 of the Phase 2 sites in the Corn Belt ($P[\rho] \leq 0.0001$; Spearman rank correlation). The nitrate concentrations simulated by the P-GWAVA-RZ model, however, were not significantly correlated with the measured values ($P[\rho]$ greater than $[>] 0.05$; Spearman rank correlation). Statistically significant, positive correlations were noted between the simulated and the measured detection frequencies for atrazine ($R^2 = 0.24$; $P = 0.046$) and DEA ($R^2 = 0.56$; $P = 0.0006$) among the 17 Phase 2 groundwater sampling networks with 10 or more wells, but not for atrazine among the 47 such networks examined during Phase 1, nor for nitrate among the Phase 2 networks. The P-GWAVA-PR simulations generated correct predictions with regard to atrazine detections (either true detects or true non-detects) at 50 percent of the 1,224 Phase 1 sites, whereas the P-GWAVA-RZ simulations produced correct predictions for atrazine at 62 percent of the 453 Phase 2 sites. The solute with the highest rate of correct predictions during either of the two study phases was DEA, for which the P-GWAVA-RZ simulations predicted a correct result at 70 percent of the Phase 2 sites. The P-GWAVA-RZ simulations predicted overall frequencies of atrazine and DEA detection (39 percent and 23 percent, respectively) that were within the ranges spanned by the results reported for the two compounds by several previous large-scale studies of pesticide occurrence in shallow groundwater beneath agricultural areas of the Corn Belt.

The model residuals for atrazine, DEA, and nitrate concentrations at individual sites were significantly correlated with the depth of the water table ($P[\rho]$ less than $[<] 0.05$). The positive relations with the depth of the water table noted during both study phases for atrazine (increasing degree of overprediction with increasing water-table depth) and the negative relation noted for DEA during Phase 2 (increasing degree of underprediction with increasing water-table depth) were consistent with previous research indicating that the

extent of conversion of atrazine to DEA in the subsurface—an aerobic process—increases with increasing vadose-zone thickness. Similarly, the negative relation noted for nitrate indicated that the formation of nitrate from the oxidation of the more reduced forms of nitrogen that are applied to the land—also an aerobic process—is likely to occur to a greater extent in locations with deep water tables than in areas where the water table is closer to the land surface.

Model residuals for the concentrations of all three solutes examined during Phase 2 were significantly correlated ($P[\rho] < 0.0004$) with the average percentage of nearby corn-and-soybean area that was in corn cultivation—relative to soybeans—at the individual study sites during the simulation period (2000–2004). A negative correlation for nitrate (greater underprediction with increasing percentage of corn) was consistent with expectation because the simulations assumed that corn was grown at every site during every year of both study phases, that nitrogen fertilizers were applied more heavily to corn than to soybeans, and that nitrate behaved as an essentially conservative solute as it migrated through the well-aerated soils where corn is commonly grown. Although atrazine is not applied to soybeans, a positive correlation (increasing overprediction with increasing percentage of corn) was noted for the herbicide, in contrast with the pattern noted for nitrate. This suggested that in areas where atrazine is applied in multiple years, microbial adaptation (a well-known phenomenon in which the rate of biotransformation of some compounds increases with repeated applications) exerts greater influence over the amount of atrazine that reaches groundwater than the total amount applied. A negative correlation was observed between the model residuals for DEA concentrations and the percentage of nearby land in corn cultivation, consistent with the positive correlation noted for atrazine.

Correlations were examined between the model residuals for the frequencies of detection of all three compounds and various network-averaged variables related to soil properties, climate and, for atrazine and DEA, the intensity of atrazine use. No statistically significant relations with any of the explanatory variables were observed for nitrate ($P > 0.05$; Pearson and Spearman [rank] correlations), but relations with several variables were significant for atrazine and DEA. The patterns of correlation with the soil-related variables indicated that the P-GWAVA-PR (Phase 1) simulations underemphasized the effect of hydraulic conductivity on atrazine transport to the water table, but exaggerated the effect of recharge. By contrast, the patterns of correlation during Phase 2 indicated that the P-GWAVA-RZ (Phase 2) simulations exaggerated the effects of hydraulic conductivity on the transport of atrazine and DEA to the water table. Although a statistically significant, positive correlation was evident between the mean annual air temperature and the model residuals for atrazine detection frequencies derived from the P-GWAVA-PR simulations, no significant correlations were noted between the average temperature in May and the model residuals for atrazine or DEA detection frequencies from the P-GWAVA-RZ

simulations. These observations suggest that the activation energy value used for the rate of atrazine disappearance during Phase 1 may have been too low, but that the higher value specified for atrazine and DEA for the P-GWAVA-RZ simulations adequately accounted for the effect of temperature on the rates of disappearance of both compounds. No significant correlations between the intensity of atrazine use and the model residuals for atrazine detection frequencies were noted during either study phase, and only a weak correlation was noted with the residuals for the frequencies of DEA detection. This indicated that the approaches used to quantify the intensities of atrazine use adequately accounted for the effects of atrazine use on the frequencies of detection of the two solutes during this study, and that factors other than the intensity of atrazine use are likely to be more important in controlling spatial patterns of atrazine and DEA occurrence in groundwater.

Introduction

One of the most persuasive ways to demonstrate an understanding of a particular phenomenon is to simulate its occurrence and consequences with an acceptable degree of accuracy over a sufficiently wide range of circumstances. Thus, one of the main goals of contaminant hydrogeology is to produce accurate predictions of the concentrations of surface-derived solutes in groundwater. In pursuit of this goal, the present study involved developing and testing a process-based groundwater vulnerability assessment (P-GWAVA) system capable of predicting the concentrations of any surface-derived compound in the vadose zone anywhere in the conterminous United States. *Groundwater vulnerability* is defined herein as the likelihood of detecting a particular surface-derived contaminant at a concentration equal to or greater than a given value, such as its reporting limit or a water-quality criterion, in shallow groundwater. *Shallow groundwater*, in turn, is defined as water that is located at a relatively short distance below the water table; for this report, this consisted of water drawn from within a depth of 6.3 ± 0.5 m below the water table. (All confidence intervals [CIs] in this report are expressed as 95 percent CIs for the mean.) This study had four primary objectives:

1. Develop a set of parameter estimation methods and models (the P-GWAVA system) that can predict the concentrations of agrichemicals and their transformation products at a specified depth in the vadose zone beneath any location in the conterminous United States by simulating the most important physical, hydrologic, biological, and chemical phenomena known to control the transport and fate of these compounds in the subsurface. (Throughout this report, the term *subsurface* is used to refer to all regions below the land surface, including the vadose and saturated zones.)
2. To the extent possible, use data with the finest spatial resolution available on a nationwide basis for the model input parameters.
3. Assess the accuracy of the simulated concentrations by comparing them with the concentrations measured in shallow groundwater beneath agricultural areas of the United States, especially the 10 northernmost states of the corn-growing areas of the midcontinent (the *Corn Belt*).
4. Use the results from these comparisons to select the simulation approaches that lead to the closest agreement between the simulated and measured concentrations.

Previous Assessments of Groundwater Vulnerability

Numerous groundwater vulnerability assessments (GWAVAs) have been carried out over the past three decades. An overview of the approaches that have been used to conduct these assessments is presented in [appendix A](#). The assessment of groundwater vulnerability requires that the collective influence of three types of controlling variables be accounted for: (1) anthropogenic factors related to land and chemical management that influence the types and loads of specific contaminants that are released at the land surface (either intentionally or inadvertently) and the timing of those releases; (2) climatic, edaphic, chemical, biological and hydrogeologic factors that control the transport and fate of surface-derived solutes in the subsurface; and (3) chemical properties of the contaminants that influence their distribution, mobility and persistence in the hydrologic system. These three types of variables may exhibit considerable interdependence. For example, the likelihood of detecting a pesticide in groundwater may depend on the timing of its application relative to the timing of subsequent recharge, a linkage that is generally more evident for reactive compounds than for those that are more persistent (Barbash and Resek, 1996). (For this report, a *pesticide* is defined as a chemical that is used to kill or otherwise control unwanted plants, insects, or other organisms.)

Assessments of groundwater vulnerability have typically focused on the manner in which contaminant concentrations are distributed among different compounds, by location, or over time. Whereas some GWAVAs have focused on ranking chemicals according to their detection frequencies or concentrations, most have been directed toward predicting the spatial distributions of occurrence of individual compounds ([appendix A](#)). Although previous research has shown that the likelihood of detecting pesticides in groundwater may vary seasonally (Barbash and Resek, 1996; Silva and others, 2012), most efforts to predict temporal variations in pesticide concentrations beneath the land surface have been confined to

numerical simulations (for example, Sauer and others, 1990; Pollock and others, 2002; Bayless and others, 2008; Webb and others, 2008), rather than statistical models.

Most of the physical, hydrologic, chemical, and biological processes that control the transport and fate of surface-derived contaminants in the subsurface have been well known for at least three decades (Barbash and Resek, 1996). Thus, the primary constraints on the development of GWAVA methods have not come from limitations in the conceptual understanding of the fundamental processes governing the likelihood of groundwater contamination, but from various challenges associated with the implementation and evaluation of these methods (appendix A). In particular, the development of large-scale GWAVA systems has been constrained primarily by limitations in (1) the availability, consistency, and spatial resolution of many of the physical, hydrologic, chemical, and land-use data that most GWAVA systems require; (2) the computing speeds needed to carry out the calculations for these assessments; and (3) the subsurface monitoring data needed to evaluate the accuracy of the predictions.

Previous approaches for predicting the vulnerability of groundwater to contamination from surface-derived solutes over large geographic areas have not explicitly accounted for preferential transport in the subsurface (Barbash and Resek, 1996)—a key process known to exert considerable influence over the rates of water and solute transport through the vadose zone in many hydrogeologic settings. However, as part of a study to assess the accuracy with which water flow and agrichemical concentrations predicted in the subsurface by seven vadose-zone models reproduced measurements beneath two agricultural sites, Nolan and others (2005) included several models that simulated preferential transport.

Purpose and Scope

This investigation was carried out to develop and test a process-based groundwater vulnerability assessment (P-GWAVA) system that uses transport-and-fate simulations in conjunction with national-scale input data to predict the concentrations of surface-derived compounds at a specified depth in the vadose zone anywhere in the conterminous United States. This report describes the approach and procedures used to develop the P-GWAVA system, as well as the results from a study during which the P-GWAVA system was used to simulate the concentrations of selected agrichemicals in the vadose zone beneath agricultural areas at more than 1,400 locations across the conterminous United States. The accuracy of the simulated concentrations was evaluated through comparison with the concentrations of the compounds measured in shallow groundwater in the same locations

during the period from 1992 to 2006. The results from these comparisons were used to select the simulation approaches that led to the closest agreement between the predicted and the measured concentrations.

Study Design

Design Objectives

The design of the P-GWAVA system was guided by four main objectives:

1. Develop the capability to predict the concentration of any surface-derived contaminant for which the rates of release into the environment are known—or to predict the concentrations of any of its transformation products—in the subsurface anywhere in the conterminous United States, by simulating the transport and fate of the compounds within the vadose zone.

Each of two one-dimensional (or *stream-tube* [Jacques and others, 1997]) vadose-zone models were linked to a geographic information system (GIS) to perform the following tasks for any location in the conterminous United States: (1) retrieve all required site-specific input data for that location; (2) generate an appropriate input file for the model; (3) simulate water flow, as well as the transport and fate of the compounds of interest, within the vadose zone; and (4) compute simulated concentrations at a specified depth in the vadose zone for all compounds of interest. The models considered for use in the P-GWAVA system were restricted to those capable of simulating solute transport and fate in the vadose zone because of the critical importance of this region in affecting the likelihood of detecting surface-derived contaminants in shallow groundwater. As with the work of Nolan and others (2005), this study used *cold simulations*, that is, model simulations conducted without calibration. This approach made it feasible to assess the accuracy with which existing process knowledge, models, and input data may be combined to simulate the concentrations of surface-derived contaminants in shallow groundwater at hundreds of locations across large geographic areas. Along with the nitrate metamodeling work of Nolan and others (2012), this investigation represents one of the first instances where the simulation of solute transport and fate in the subsurface has been used to predict the concentrations of agrichemicals in the vadose zone, and the simulated concentrations compared with measured concentrations of the compounds in the underlying groundwater, over large spatial scales (regional to national).

2. Maximize the extent to which the P-GWAVA predictions of solute concentrations account for the major physical, hydrologic, chemical, and biological phenomena known to control the transport and fate of surface-derived contaminants in the subsurface.

Following the approach of Nolan and others (2005), models were considered for use in the P-GWAVA system only if they could simulate a relatively broad range of the physical, hydrologic, chemical, and biological phenomena known to influence the transport and fate of solutes in the subsurface. As a result, the two models used in the P-GWAVA system were among the seven examined by Nolan and others (2005). The use of models that could account for the effects of a wide range of controlling factors and phenomena was consistent with a recommendation made by an advisory group to the U.S. Environmental Protection Agency (EPA) that "... the development of screening protocols should be more consistent, and where possible use common models between screening levels and more sophisticated levels of analysis" (ILSI Risk Science Institute, 1998, p. 7). One potential disadvantage of accounting for so many processes, however, is that uncertainties in the values of the parameters used to quantify these processes may result in non-unique solutions and decrease the accuracy of the resulting predictions.

3. Use existing models, databases, and methods wherever possible—especially those that have undergone the most extensive testing and verification.

Both of the models used to conduct the simulations for this study have a long history of extensive use. In addition, both codes have been employed, and their predictions tested against field or laboratory observations, by numerous studies published in the scientific literature (for example, Jones and others, 1986; Barbash and Resek, 1996; Watts and others, 1999; Jones and Mangels, 2002; Malone and others, 2004a).

4. Use only national-scale, nationally consistent sources of all site-specific input data (for example, soil properties, pesticide use and weather) compiled at the finest spatial scale available.

To maximize the degree of consistency among the predictions made in different locations, all site-specific input data were obtained from sources that were compiled for the entire conterminous United States using nationally uniform methods. If multiple national-scale sources of data were available for a given parameter (for example, soil properties or pesticide use), the source that provided the data at the finest spatial scale was the one used, to ensure that the simulations of water and solute transport and fate were as site-specific as possible.

Study Phases

This study was carried out in two phases (table 1). During Phase 1, the Pesticide Root-Zone Model (PRZM) was used in the P-GWAVA system for the solute transport-and-fate simulations, and the resulting version of the system designated as P-GWAVA-PR. During Phase 2, to account for the influence of several additional processes that were not simulated by PRZM but are known to affect the transport and fate of water and solutes in the subsurface (for example, upward flow, transport through macropores, and exchange between macropores and the soil matrix), PRZM was replaced with the Root-Zone Water-Quality Model (RZWQM), and the resulting version of the system designated as P-GWAVA-RZ. During both study phases, the model simulations were used to predict the subsurface concentrations of atrazine, one of the pesticides detected most frequently in groundwater in the United States (Kolpin and others, 1993; Barbash and Resek, 1996; Gilliom and others, 2006). However, the Phase 2 simulations also focused on nitrate, one of the most commonly detected groundwater contaminants in the Nation (Hallberg, 1989), and deethylatrazine (DEA), the atrazine transformation product that, like its parent compound, has been among the contaminants detected most frequently in groundwater beneath agricultural areas of the United States (Kolpin and others, 1993; Barbash and Resek, 1996; Gilliom and others, 2006).

Atrazine and nitrate also were of interest during this study because the spatial patterns of application of these chemicals in agricultural areas of the United States are known in considerable detail (Ruddy and others, 2006; U.S. Geological Survey, 2014). To facilitate comparisons between the concentrations simulated in the vadose zone and the concentrations measured in groundwater, all of the simulations were done in locations where recently recharged shallow groundwater was sampled for these compounds by the National Water-Quality Assessment (NAWQA) program of the U.S. Geological Survey (Gilliom and others, 1995). (Among the wells examined for this study, the average depth of the top of the open interval below the water table was 6.3 ± 0.5 m.) Because Phase 2 began after Phase 1 was completed, the solute concentrations predicted by the Phase 2 simulations were compared with concentrations measured over a longer time interval than was the case for Phase 1 (table 1). Additional research results and ancillary data became available during the course of this investigation; therefore, different values and, in some cases, different estimation procedures were used for several model input parameters during the two phases of the study.

Table 1. Distinguishing features of the two phases of the process-based groundwater vulnerability assessment (P-GWAVA) system study of agrichemicals in groundwater of the conterminous United States.

[Additional differences between the two study phases with respect to the vadose-zone models used, the modeling approaches, and the sources of input data are shown in [table 14](#) (at back of report) or discussed in the text. **Abbreviations:** STATSGO, State Soil Geographic Database; SSURGO, Soil Survey Geographic Database; m, meter]

Feature	Phase 1 (P-GWAVA-PR)	Phase 2 (P-GWAVA-RZ)
Vadose-zone simulation model used	Pesticide Root-Zone Model (PRZM)	Root-Zone Water-Quality Model (RZWQM).
Solutes examined	Atrazine	Atrazine, deethylatrazine (DEA), nitrate.
Study areas	Selected agricultural areas in the conterminous United States (fig. 1)	Ten northernmost states of the Corn Belt in the midcontinental United States (fig. 2).
Time interval of sampling	1992–1998	1992–2006
Number of sites examined (all in agricultural settings)	1,224	453
Primary source of data on soil properties	STATSGO	SSURGO
Depth range for simulations	Upper 1 m of soil column	Upper 3 m of soil column.
Heterogeneity of simulated soil column	Uniform soil properties (depth- and component-weighted averages)	Variations in soil properties retained among different horizons, often for two or more different soil columns (components) at each site.
Model stabilization period	01-01-86 to 12-31-90	¹ 01-01-98 to 12-31-99
Model simulation period	01-01-91 to 12-31-95	¹ 01-01-00 to 12-31-04

¹Because none of the input data for Phase 2 were keyed to specific dates, the simulation period was arbitrarily selected to encompass a majority of the most recently sampled sites.

Methods

Study Site Selection and Characteristics

Locations of Study Sites Relative to National Water-Quality Assessment Groundwater Networks

This study examined sites from the NAWQA groundwater sampling networks in agricultural areas (one well per site). The groundwater component of the NAWQA program involves the sampling of several types of well networks spanning a wide range of spatial scales ([table 2](#)). Listed in order of increasing spatial scale, these include agricultural chemicals team (ACT) studies, flow path studies (FPS), land-use studies (LUS), study-unit surveys (SUS) and principal aquifer studies (PAS). Phase 1 of this investigation encompassed all the agricultural LUS in the conterminous United States for which atrazine sampling results were available, as well as a single agricultural FPS in northwestern Washington State. Because Phase 2 focused on a smaller geographic region than Phase 1, it also included wells from

the ACT studies and several FPS, to increase the number of sites examined. Additional information about the groundwater networks examined for this study is provided in [appendix C](#).

Locations of Study Sites Relative to Spatial Patterns of Agrichemical Use and Corn Cultivation

Both phases of this investigation focused on agricultural areas because, to date, these land-use settings have the most consistent and systematic data available on pesticide and fertilizer use across the country. Annual, state-level data from the U.S. Department of Agriculture (USDA) on the use of pesticides and fertilizers in agricultural areas across the United States have been available since the early 1990s, although reporting was suspended between 2008 and 2010 (Engelhaupt, 2008; U.S. Government Accountability Office, 2010; National Agricultural Statistics Service, 2011b). Use data have been apportioned for selected years at the county level for fertilizers (Ruddy and others, 2006), and at the sub-county level for pesticides (Thelin and Gianessi, 2000; U.S. Geological Survey, 2014). By contrast, comparatively little information has been reported about the use of pesticides for

Table 2. Principal characteristics of groundwater networks examined by the U.S. Geological Survey National Water-Quality Assessment (NAWQA) program.

[From Gilliom and others, 1995; Squillace and others, 1996; and Lapham and others, 2005. Only sites from the ACT (agricultural chemicals team); FPS (flow path study) and LUS (land-use study) networks were examined for this study. **Abbreviations:** m, meter, km, kilometer; km², square kilometer]

Network type (abbreviation)	Site characteristics	Approximate spatial scale	Examples
Agricultural chemicals team (ACT) study	New monitoring wells (and lysimeters) installed along inferred groundwater flow paths in specific agricultural settings.	10 ² –10 ³ m long; 10 ¹ –10 ² m wide	Steele and others, 2008
Flow path study (FPS)	New monitoring wells installed along inferred groundwater flow paths in an area of a specific type of land use (for example, agriculture or urban).	10 ⁰ –10 ² km long; 10 ¹ –10 ² m wide	Puckett, 2004; Tesoriero and others, 2007
Land-use study (LUS)	New or existing wells sampling recently recharged shallow groundwater in an area of a specific type of land use.	10 ⁰ –10 ⁵ km ²	Bruce and McMahon, 1996; Burow and others, 1998
Study-unit survey (SUS)	Existing domestic and public-supply wells of widely varying depths, in addition to springs, across an extensive area of mixed land use.	10 ² –10 ⁶ km ²	Ferrari and Denis, 1999
Principal aquifer study (PAS)	Existing domestic and public-supply wells screened in, and distributed throughout a single major aquifer (mixed land use).	10 ⁴ –10 ⁶ km ²	Lapham and others, 2005

non-agricultural purposes in the United States. Exceptions to this include data reported for individual counties (for example, Schreder and Dickey, 2005; Thurston County [Washington] Pest and Vegetation Management Advisory Committee, 2011), multi-county areas (Voss and Embrey, 2000) and individual states (for example, Minnesota Department of Agriculture, 2010; Moran, 2010; New Jersey Department of Environmental Protection, 2012). The only consistent data available regarding non-agricultural pesticide use on a national scale have been summarized for the Nation as a whole, rather than for specific locations (for example, Gianessi and Puffer, 1990; Grube and others, 2011). Data on non-agricultural use of fertilizers across the Nation are also sparse, available for approximately one-half of the states, and only on a statewide basis (Ruddy and others, 2006).

Phase 1

During the first phase of this study, the P-GWAVA-PR model was used to simulate the concentrations of atrazine in the vadose zone beneath all agricultural areas where the NAWQA program had measured the concentrations of the herbicide in shallow groundwater. Between 1992 and 1998, the NAWQA program measured the concentrations of atrazine (as well as many other pesticides) in shallow groundwater at 1,224 agricultural sites across the country (table 1). Locations where atrazine concentrations were predicted using the P-GWAVA-PR simulations are shown in figure 1, relative to the distribution of atrazine use in 1997.

Phase 2

During the second phase of this investigation, the P-GWAVA-RZ model was used to simulate the concentrations of atrazine, DEA, and nitrate in the vadose zone beneath agricultural areas where the concentrations of these compounds had been measured in shallow groundwater by the NAWQA program. However, a smaller study area was examined for Phase 2 than for Phase 1, primarily because the input data related to soil properties were considerably more extensive for the P-GWAVA-RZ simulations than for the P-GWAVA-PR simulations, requiring substantially more time to develop the model at each site. The region of interest for Phase 2 encompassed the 10 northernmost states in the Corn Belt of the midcontinent, where corn is a predominant crop. This area was selected because it is the region where atrazine (fig. 2) and nitrogen fertilizer (fig. 3) have been applied most extensively, and where atrazine detection frequencies (Barbash and Resek, 1996; Gilliom and others, 2006) and nitrate concentrations (Nolan and Hitt, 2006) in groundwater are among the highest in the Nation. Additionally, the general weather patterns and agricultural management practices for corn are relatively homogeneous across this region. These considerations were important because of the current sparsity of weather stations and, despite some recent exceptions (for example, Baker, 2011), the limited availability of consistent information (in digital form) on the spatial distributions of different chemical-, water-, crop-, and land-management practices across the country.

8 Process-Based Groundwater Vulnerability Assessment System for Agrichemicals in Groundwater in the United States

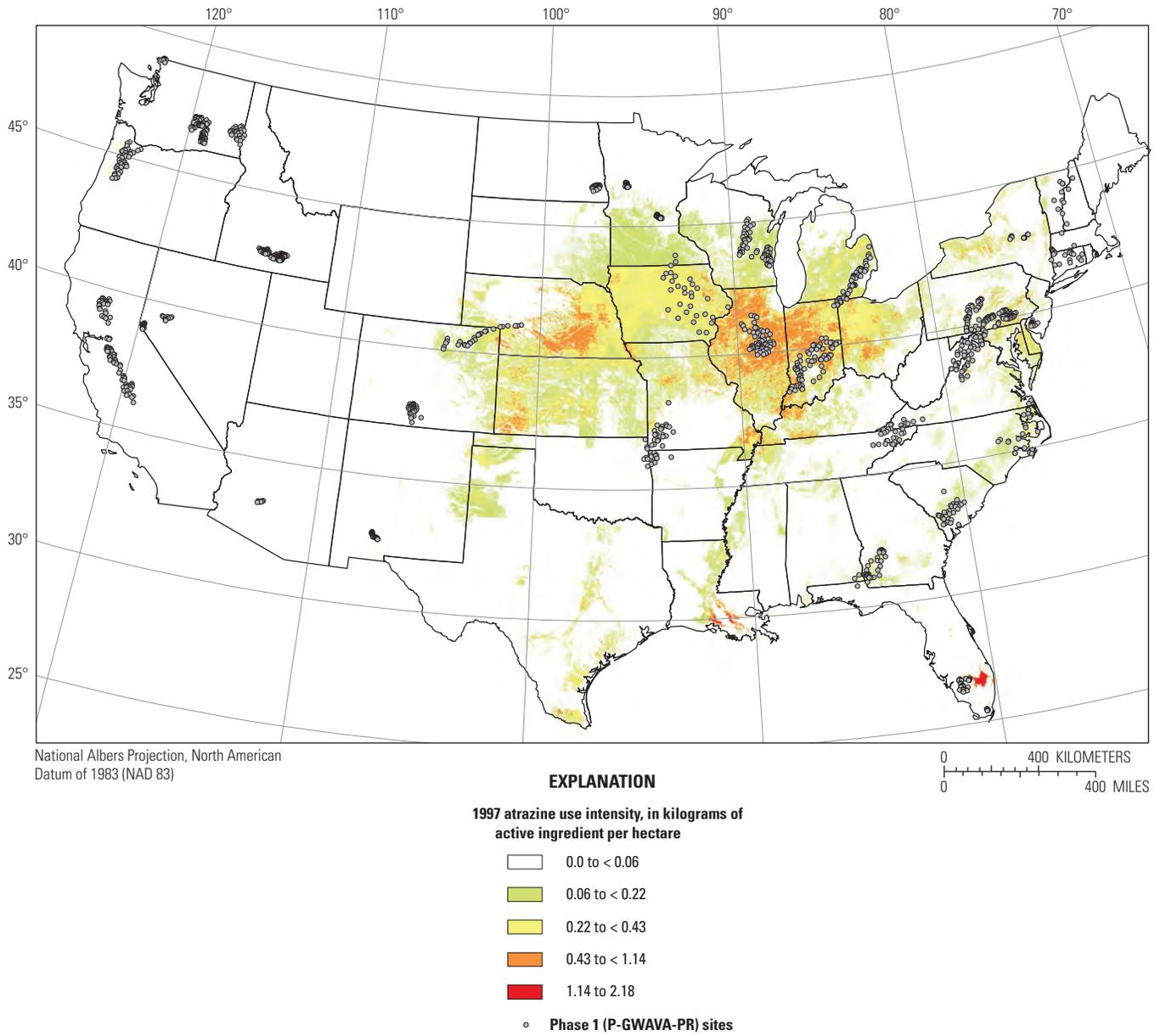


Figure 1. Locations of Phase 1 (P-GWAVA-PR) sites and the distribution of atrazine application intensity across the conterminous United States during 1997. Atrazine use data from U.S. Geological Survey (2014).

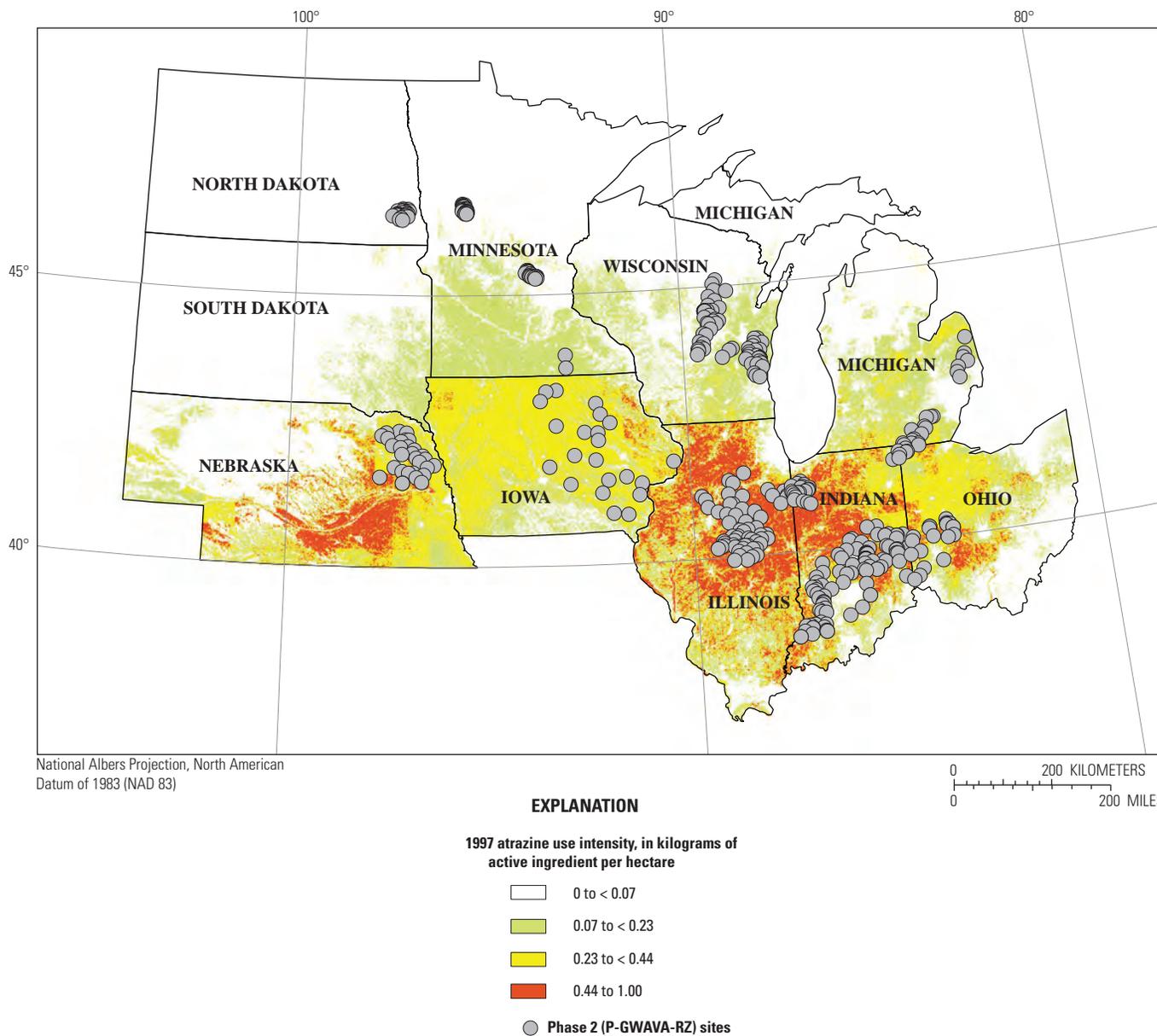


Figure 2. Locations of Phase 2 (P-GWAVA-RZ) sites and the distribution of atrazine application intensity across the 10 northernmost states in the Corn Belt of the United States during 1997. Atrazine use data from U.S. Geological Survey (2014).

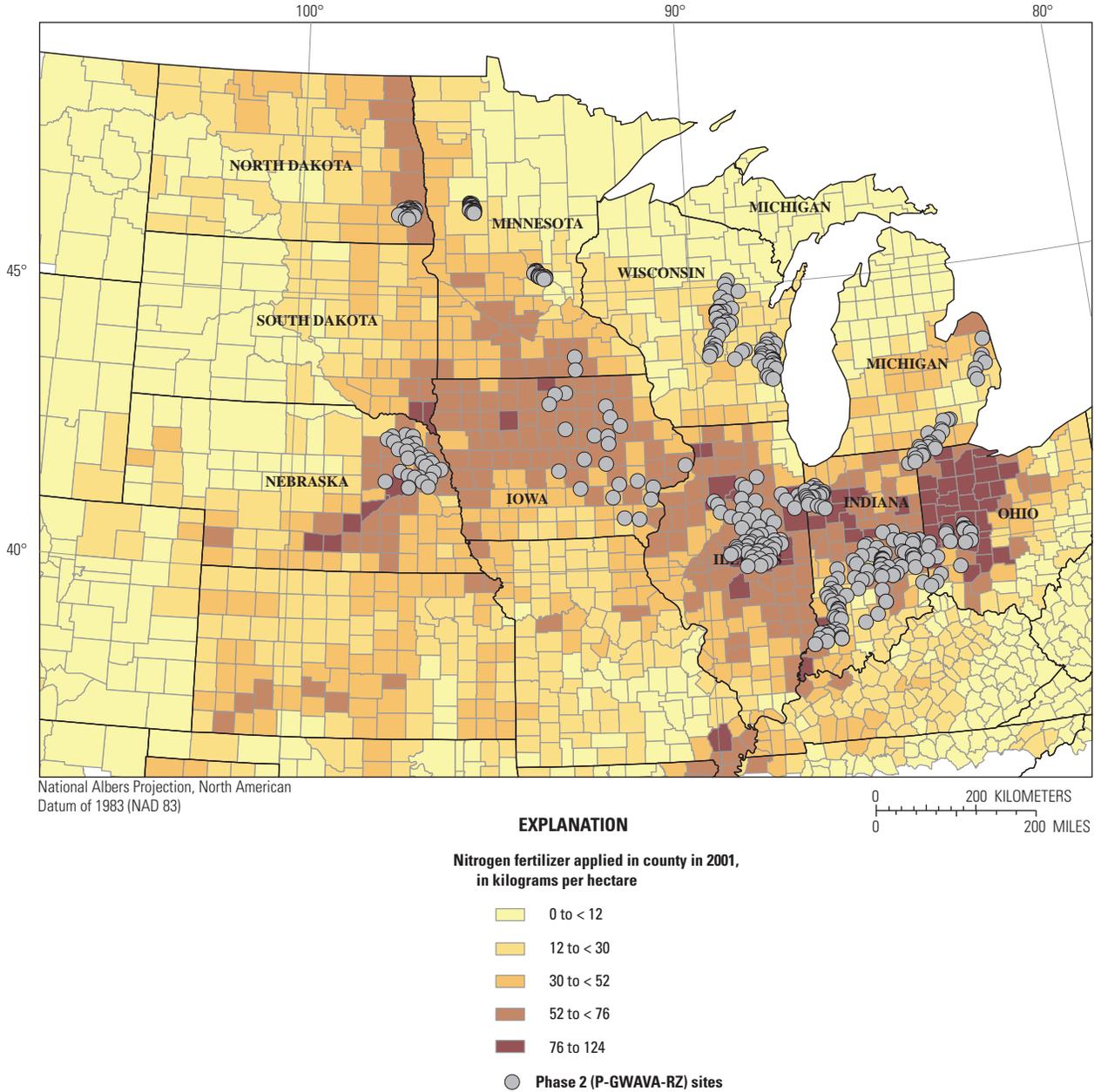


Figure 3. Locations of Phase 2 (P-GWAVA-RZ) sites and the distribution of nitrogen fertilizer application across the 10 northernmost states in the Corn Belt of the United States during 2001. Nitrogen fertilizer use data from Ruddy and others (2006).

Atrazine concentrations were measured in shallow groundwater by the NAWQA program at 7,639 sites in the United States between 1992 and 2006. Among these, 453 sites in the Corn Belt were selected for the Phase 2 simulations (table 1) after it was determined that they were (1) in counties in the Corn Belt where corn occupied 10 percent or more of the county area, (2) not included in NAWQA sampling networks that also encompassed non-Corn Belt sites (all such networks were in southern Nebraska), (3) in locations where

the required soil property data had been digitized, (4) in predominantly agricultural areas where shallow groundwater was sampled, and (5) in areas where RZWQM simulations could be successfully completed. In most cases, the sites where the numerical model repeatedly failed to converge and complete the simulation were sites where low-permeability soil layers were underlain by relatively thick layers with substantially higher permeability.

Statistical Methods

All statistical analyses used commercial software: Excel® (Microsoft, Inc.), DataDesk 6.1 (Data Description, Inc.), TIBCO Spotfire S+ 8.1 (TIBCO Software Inc.), or SYSTAT 13 (Systat Software). A Type-I error rate (α value) of 0.05 was used for all tests of statistical significance. Unless specified otherwise, all of the R^2 values provided in this report refer to parametric relations, that is, Pearson R^2 values. All probability values reported for Spearman rank (non-parametric) correlation coefficients ($P[\rho]$) were those associated with the R^2 values for the correlations between the ranks of the two variables of interest. In most cases, these two variables represented simulated and measured values of analyte concentration or detection frequency.

Sample Collection and Chemical Analysis

The NAWQA program uses nationally consistent procedures for selecting wells and well installation sites (Lapham and others, 1995), sampling water from wells (Koterba and others, 1995), measuring the concentrations of the contaminants of interest (for example, Fishman, 1993; Zaugg and others, 1995), and managing the resulting data (Williamson, 2000). During the study period for this investigation (1992–2006), to maintain a relatively consistent level of effort from one year to the next, the NAWQA program concentrated most of its sampling into a 3-year, high-intensity phase in approximately one-third of the major hydrologic basins (or *study units*) examined across the Nation at any point in time. Longer-term variations in water quality were examined through the use of a rotating cycle in each study unit—3 years of high-intensity sampling activity followed by 6 years of relatively low-intensity sampling (Gilliom and others, 1995).

Temperature, pH, dissolved oxygen concentrations, and other field parameters were measured in water drawn from wells during the NAWQA sampling operations, using the protocols described by Koterba and others (1995). All of the chemical analyses for the solutes of interest were carried out by the USGS National Water-Quality Laboratory in Denver, Colorado. Concentrations of atrazine and DEA were measured using solid-phase extraction followed by capillary-column gas chromatography/mass spectrometry (Zaugg and others, 1995). Nitrate concentrations were determined using cadmium reduction colorimetry (Fishman, 1993). Although this report focuses only on the sampling results for atrazine, DEA, and nitrate in groundwater, the NAWQA program conducts analyses for a broad range of organic and inorganic analytes—of either natural or human origin—in groundwater, surface water, aquatic biota, and stream sediments (Gilliom and others, 1995; Lapham and others, 1995).

Reporting limits and analytical recoveries associated with a given chemical species commonly change over time. Such changes for a given analyte may be associated with periodic modifications in analytical procedures, temporary changes caused by the presence of interfering materials in individual samples, or other transient circumstances. Analytical recoveries for atrazine, computed from data reported by Martin and others (2009), were 100 ± 12 percent during the entire period of study (1992–2006); those for nitrate (computed from data provided by Tedmund Struzeski, U.S. Geological Survey, written commun., July 31, 2009) were 98.9 ± 0.5 percent. Analytical recoveries for DEA during this same period (also computed from data reported by Martin and others, 2009) were 45 ± 24 percent, substantially lower and more highly variable than the mean recoveries for the other two solutes. As a result, the simulated concentrations of DEA and atrazine at each site examined during Phase 2 were corrected for temporal variations in the analytical recoveries of each compound. This procedure was carried out for atrazine as well as for DEA during Phase 2 because ratios computed from the concentrations of both solutes were examined for this part of the study.

Corrections for varying analytical recoveries during Phase 2 were applied using the following formula:

$$C_{i,p,t,c} = C_{i,p} * \left(\frac{R_{i,t}}{100\%} \right) \quad (1)$$

where

- $C_{i,p,t,c}$ is the concentration of compound i , in micrograms per liter, simulated at the site of interest at time t , and corrected for the analytical recovery of the compound on the day the concentration was measured in the sample obtained from that location;
- $C_{i,p}$ is the concentration of compound i , in micrograms per liter, predicted at the site of interest by the P-GWAVA simulations; and
- $R_{i,t}$ is the analytical recovery of compound i (percent) from groundwater spiked with a known amount of the compound on the date (t) that the site was sampled.

These corrections were applied to the simulated concentrations, rather than to the measured values, to avoid the uncertainties associated with applying these adjustments to measured concentrations that were less than the reporting limit.

To correct for temporal changes in analytical sensitivities for each of the three solutes (atrazine, DEA, and nitrate), the reporting limit in use at the time of analysis for each sample collected—referred to as the *routine reporting limit*—was applied to the value of $C_{i,p,t,c}$ predicted by the P-GWAVA simulation for a particular location and time.

This procedure was used to determine if the predicted concentration represented a simulated detection or a simulated non-detection. For any site where one or more of the analytes was not detected, but the reporting limit for the analyte in question was temporarily elevated at the time of analysis because of transient interferences, this *raised reporting limit* was used to determine whether or not the predicted concentration represented a simulated detection. However, because this approach has seldom been used to ascertain analyte detections during previous studies of water quality, overall frequencies of detection also were computed among the recovery-corrected simulated values ($C_{i,p,t,c}$) using the more common method of applying a single, uniform value for each solute. For the present investigation, the value used for this purpose was the highest reporting limit used for each analyte during the sampling period (1992–2006). Temporal variations in the routine reporting limits for atrazine, DEA, and nitrate during this time interval are shown in [figure 4](#).

P-GWAVA System

The P-GWAVA system consists of three main components: (1) a process-based model for simulating the transport and fate of water and solutes in the vadose zone, (2) a database for providing values for all the input parameters used by the vadose-zone model, and (3) translator programs for creating input files and processing model output. The main features of the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) systems are shown in [figures 5](#) and [6](#), respectively. Both P-GWAVA systems use a GIS to process and store spatial data pertaining to individual site characteristics, and a relational database to store and provide tabular data for non-spatial input parameters (for example, pesticide properties, crop properties, and so forth). Data management is accomplished using various Arc® tools in conjunction with a relational database and a series of Structured Query Language (SQL) scripts to generate input files for the transport-and-fate models, and to summarize the simulation results from the model output files.

The primary differences between the P-GWAVA-PR and P-GWAVA-RZ models—other than the vadose-zone models used—were related to some of the specific tools used for storing and processing geographic data (ArcInfo® compared with ArcGIS®, Arc Toolbox®, and ArcSDE®), for operating the relational database (SQL Server 2000 compared with 2005), for creating input files, and for summarizing the results (Visual Basic compared with C#.NET). The P-GWAVA approach ([figs. 5](#) and [6](#)) facilitates the process of re-running the simulations for some or all of the sites as changes are made to input parameter values, data sources, and other model features. As with other multi-media modeling systems (for example, Leavesley and others, 1996), this approach also provides a valuable framework for conducting simulations using other models or simulation techniques.

Overall Simulation Approach

Both PRZM and RZWQM offer the option of entering input parameter values for individual sites using a graphical user interface. However, because the P-GWAVA system is designed to carry out simulations at large numbers of locations (that is, thousands or more), rather than for one site at a time, input parameter values are provided to the models directly from a database ([figs. 5](#) and [6](#)). Because of the large number of sites examined, the site-specific manipulations of individual input parameters that are commonly implemented during small-scale modeling studies (for example, Lorber and Offutt, 1986; Hanson and others, 1999; Nolan and others, 2010) were not used; instead, the P-GWAVA model runs were carried out as cold simulations, an approach that also has been used by other modeling studies (for example, Smith and others, 1991; Nolan and others, 2005).

Time constraints precluded a thorough quantitative analysis of the extent to which the variability in the model input parameters contributed to overall model error during this study. Previous work, however, has established that the pesticide concentrations simulated in the vadose zone by PRZM are particularly sensitive to variations in transformation rates, soil organic matter (OM) content, the organic carbon-water partition coefficient (K_{oc}), bulk density, saturated hydraulic conductivity, and the water contents at field capacity and wilting point (Jones, 1986; Donigian and Carsel, 1987; Carsel and others, 1988a, 1988b; Shaffer and Penner, 1991; Smith and others, 1991; Fontaine and others, 1992; Russell and Jones, 2002; Wolt and others, 2002; Dubus and others, 2003; Boesten, 2004). (*Field capacity* is commonly defined as the water content remaining in the soil after most gravity drainage has ceased; *wilting point* is the water content below which most plants are not able to extract water from the soil.) Agrichemical concentrations simulated in the vadose zone by RZWQM are also especially sensitive to variations in transformation rates, bulk density, hydraulic conductivity, and the water content at field capacity (Jaynes and Miller, 1999; Malone and others, 2004b; Bayless and others, 2008; Nolan and others, 2010), as well as to variations in soil crust conductivity, average macropore radius, soil air-entry value, the Brooks-Corey unsaturated hydraulic conductivity constant (N_2), and lateral saturated conductivity (Kumar and others, 1998; Malone and others, 2004a, 2004b). The results from these previous assessments of the sensitivity of PRZM and RZWQM to variations in input parameter values were also presumed to apply to the predictions of the P-GWAVA-PR and P-GWAVA-RZ models.

Initial Conditions and Simulation Periods

At each site of interest, simulations were done for an initial *stabilization period*, followed by a *simulation period* when the predicted concentrations were computed.

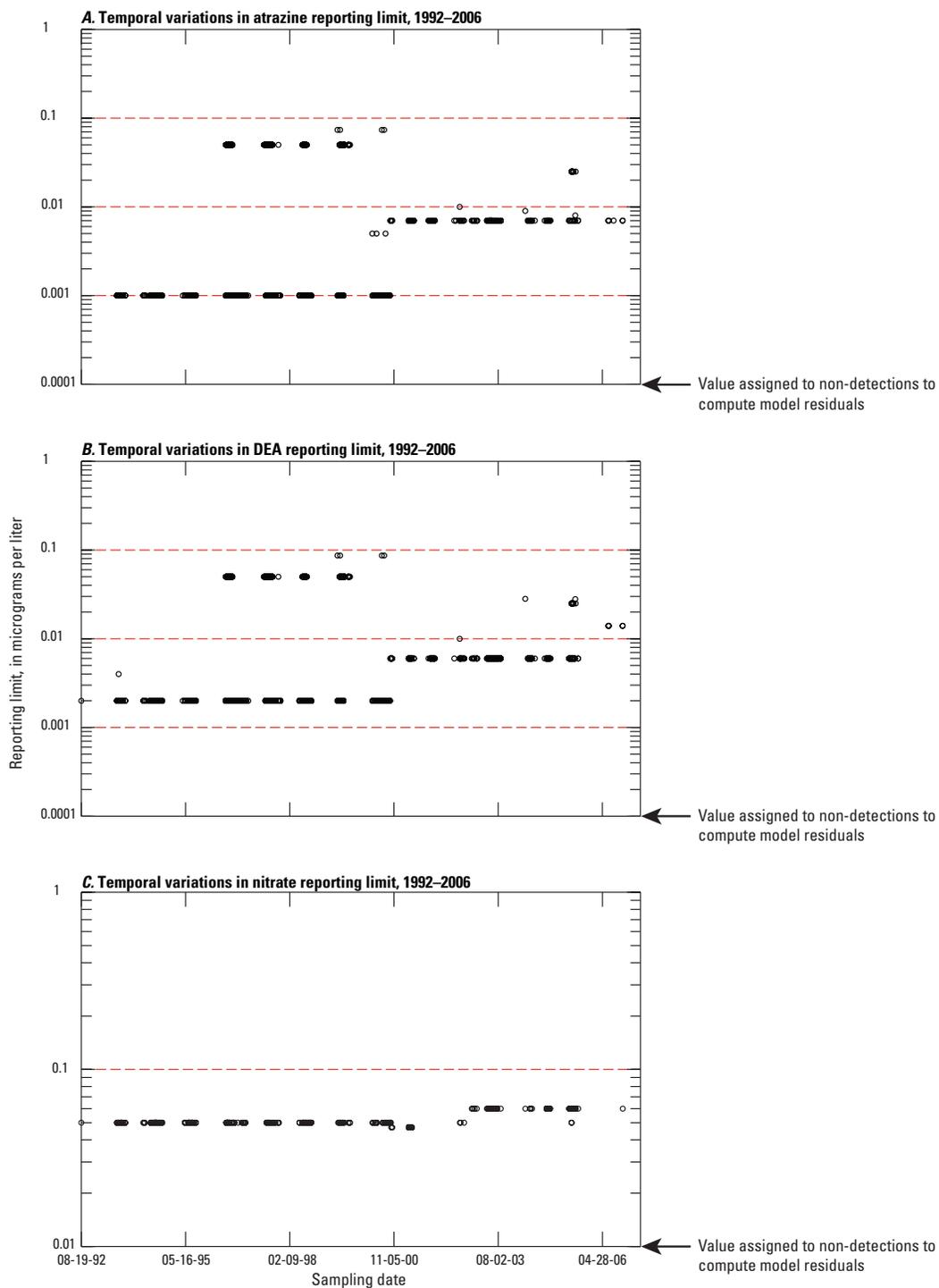


Figure 4. Temporal variations in the routine reporting limits used for (A) atrazine, (B) deethylatrazine (DEA), and (C) nitrate at the 453 sites examined for Phase 2 of this study and sampled in the 10 northernmost states in the Corn Belt of the United States, 1992–2006. Values shown are only for those dates when the chemical analyses of groundwater samples from these sites were done. Locations of sites are shown in [figures 2 and 3](#).

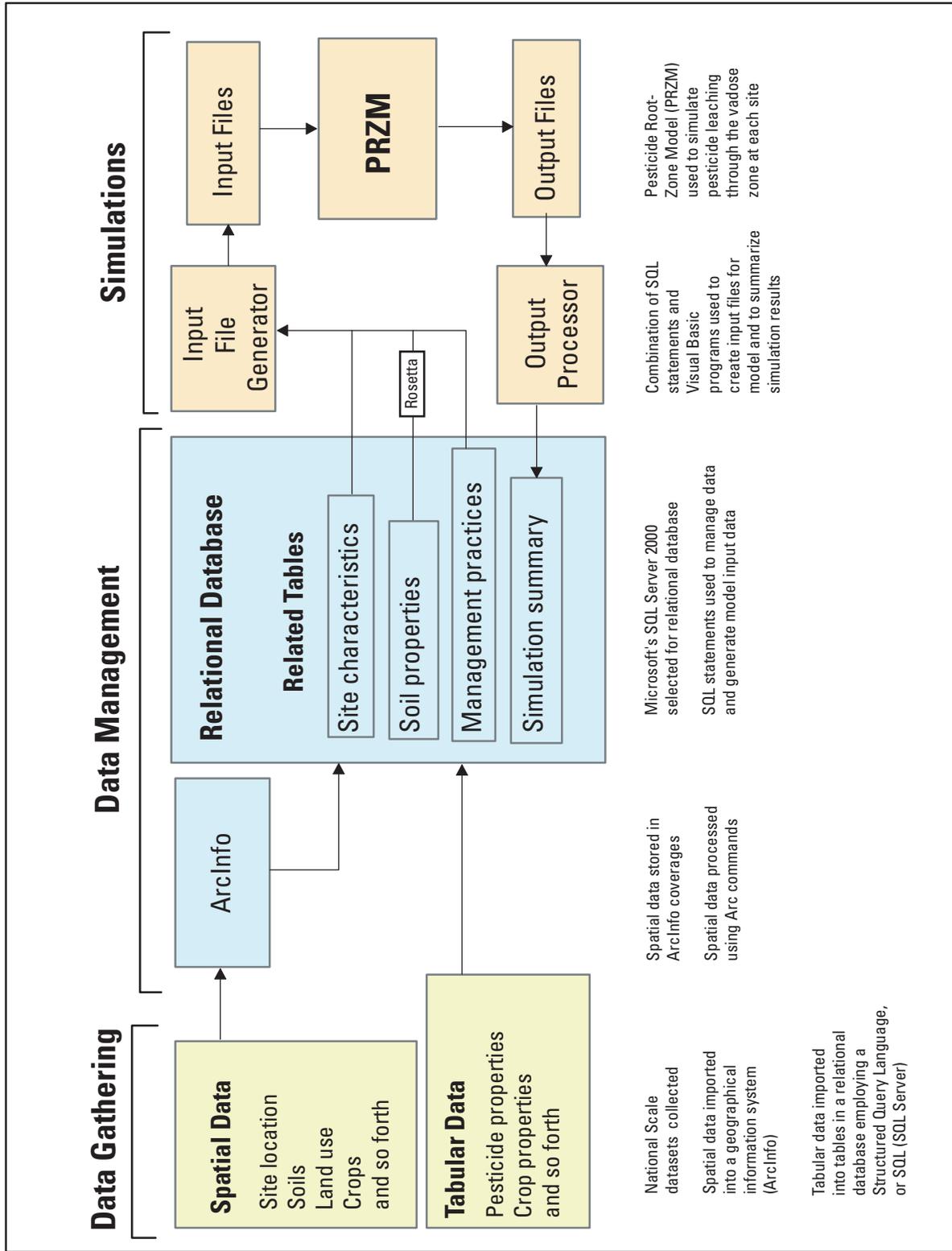


Figure 5. Primary features of the P-GWAVA-PR (Phase 1) system used to simulate the transport and fate of atrazine in the vadose zone using the Pesticide Root-Zone Model (PRZM).

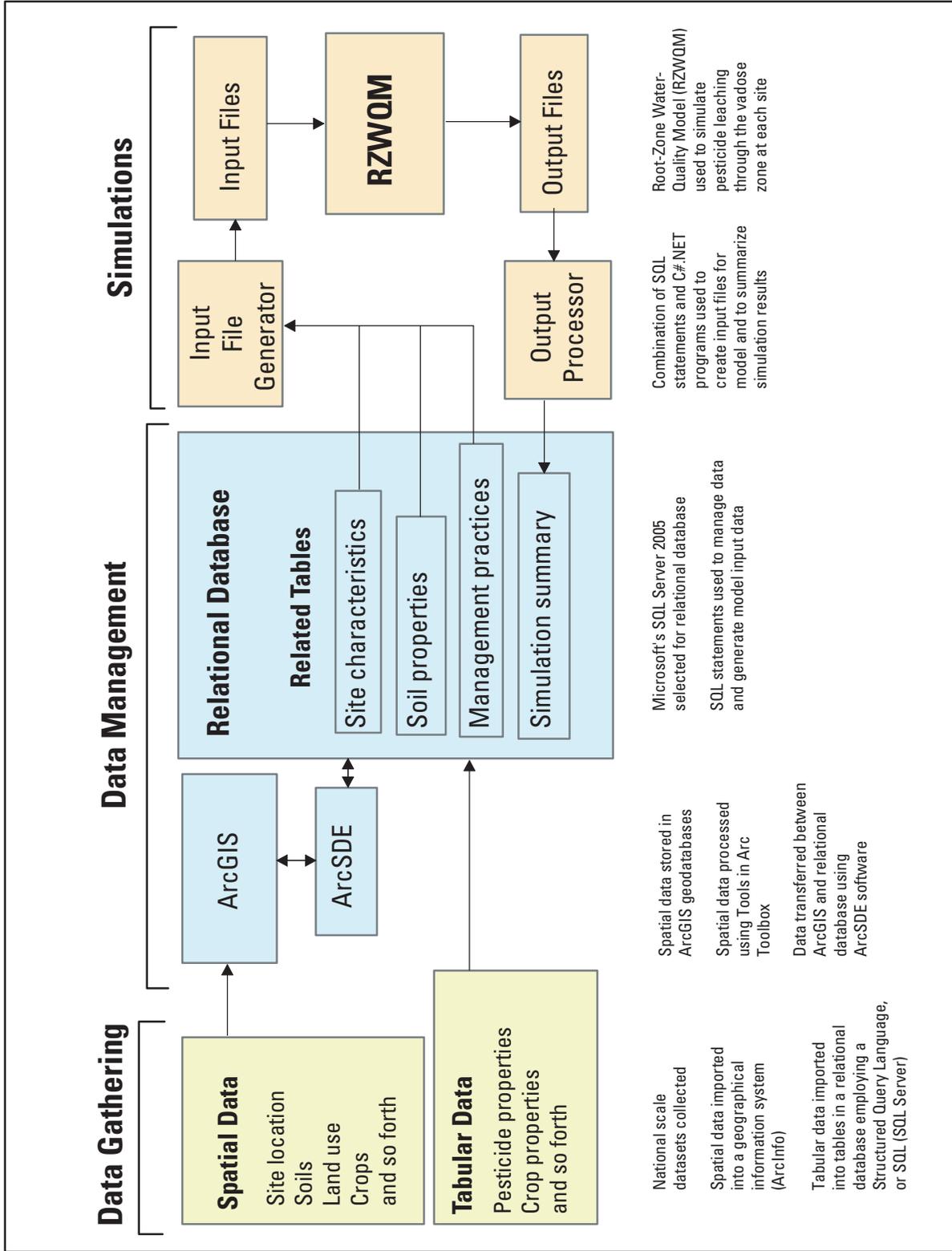


Figure 6. Primary features of the P-GWAVA-RZ (Phase 2) system used to simulate the transport and fate of atrazine, deethylatrazine(DEA), and nitrate in the vadose zone using the Root-Zone Water-Quality Model (RZWQM).

The stabilization period was used to dissipate the transient response to the initial conditions specified at each site. The use of the stabilization period helped to establish distributions of microbial populations, soil OM, nitrogen, and other mutable system characteristics that were more representative at each location of interest than the initial conditions specified uniformly at all the sites for these parameters. Initial conditions that were designated as site-specific values for individual study locations at the beginning of the simulation periods included parameters related to weather and water content (see [table 14](#) at back of report). The initial condition for water content in each soil layer was set to its value at field capacity. Although widely used, field capacity is recognized to be a highly imprecise parameter because some soils may continue to drain for extended periods (Twarakavi and others, 2009). However, the water content at field capacity provided a convenient starting point for water flow and atrazine transformation rates, because data for this parameter are widely available or could be estimated from other data provided by the soil property databases used for this study.

The length of the stabilization period was of particular importance during Phase 2 for establishing the sizes of the five *pools* (types) of soil OM and the three populations of soil microorganisms that RZWQM uses to simulate various microbial and geochemical processes. These processes include the formation and decomposition of organic materials in the soil. The five pools of soil OM simulated by RZWQM include (1) slowly decaying crop residues, (2) rapidly decaying metabolic products from crop decomposition, (3) rapidly metabolized soil OM (*fast* OM), (4) soil OM metabolized at an intermediate rate (*medium* OM), and (5) slowly metabolized soil OM (*slow* OM). The three populations of microorganisms consist of (1) heterotrophic soil decomposers, (2) nitrifiers, and (3) facultative anaerobes (Ahuja and others, 2000).

A 5-year interval was used for the stabilization period during Phase 1, but was shortened to 2 years during Phase 2 ([table 1](#)) to accommodate the substantially longer execution times for the RZWQM model. (Because of the greater complexity of RZWQM relative to PRZM, simulations for Phase 2 took about 30 times longer to complete than for Phase 1.) Although a stabilization period longer than 2 years may have been preferable during Phase 2 to allow sufficient time for the sizes of the slow and medium OM pools to stabilize, the overall execution time of 7 years was consistent with the guidance of Hanson and others (1999), who recommended RZWQM simulation periods of 5 to 7 years to correct for potentially “poor initial estimates” of the sizes of the three microbial populations, the two crop residue pools, and the fast OM pool.

A 5-year interval was used for the simulation period during both study phases. For Phase 1, this interval was from 1991 to 1995, to facilitate comparisons of the model simulation results with water-quality data from the first sampling cycle of NAWQA. For Phase 2, the simulation period was designated as the 5-year interval from 2000 to

2004, to encompass a majority of the most recently sampled sites ([table 1](#)). During the 5-year simulation period for both study phases, recharge and flow-weighted mean solute concentrations were computed at a specific depth within the soil column, referred to herein as the *assessment depth* (see section, “[Quantifying Solute Concentrations from Model Output](#)”).

Effects of Simulation Approaches on Model Predictions

During Phase 1 and Phase 2, multiple simulations were carried out to examine the influence of different modeling approaches on the extent of agreement between the simulated and measured concentrations at individual sites. For Phase 1, these simulations were designed to determine the effects of (1) different grid discretizations; (2) the spatial variability of atrazine applications (areally averaged or spatially uniform); (3) the spatial distribution of simulated irrigation (at all sites, no sites, or sites selected at random in proportion to the amount of nearby land under irrigation); (4) the location(s) of atrazine transformation in the subsurface (in the sorbed state, in the dissolved state, in both, or in neither); and (5) the degree of spatial averaging of soil properties. For Phase 2, these simulation results were used to determine the effects of variations in (1) the spatial variability of atrazine applications (as for Phase 1), (2) the manner in which the initial rates of atrazine and DEA transformation were estimated, (3) the magnitude of the organic carbon-water partition coefficients (K_{oc}) for atrazine and DEA, and (4) the relative sizes of the different soil OM pools.

Vadose-Zone Models

The vadose-zone model comparison study by Nolan and others (2005) examined two types of models that are distinguished by the manner in which they simulate water flow. *Simple models* use a simplified, *tipping-bucket* approach to transfer water downward from each soil layer to the layer below. In contrast, *complex models* simulate water flow through the soil using well-established equations derived from the fundamental principles of fluid flow through porous media. Among the models examined by Nolan and others (2005), one simple model (PRZM) and one complex model (RZWQM) were selected for use in the P-GWAVA system for this investigation.

Pesticide Root-Zone Model (Phase 1)

PRZM is a one-dimensional, single-porosity, dynamic model that uses a finite-difference scheme to simulate the movement of water and the transport and fate of pesticides and nitrogen species, within and immediately below the plant root zone (Carsel and others, 1998). The version of the model used

for this study includes modules for simulating the transport and fate of solutes in the root zone (PRZM) and the underlying vadose zone (VADOFT). The latter was not used because of persistent difficulties that could not be resolved in the time constraints of the project. However, when used alone (without VADOFT) PRZM does not impose any limitation on the maximum depth of simulations (Carsel and others, 1998).

One primary reason PRZM was selected for Phase 1 of this investigation is that this model has been used extensively for small-scale field studies (Pennell and others, 1990; Barbash and Resek, 1996; Jones and Mangels, 2002), thereby satisfying the design objective of using existing, widely tested tools and techniques as much as possible for this study. Although pesticide concentrations simulated in the subsurface by the model have recently been compared with those measured in groundwater by several previous monitoring studies (Baris and others, 2012), the use of PRZM for large-scale GWAVAs, as opposed to its use for small-scale field studies, appears to have been relatively limited to date (National Research Council, 1993; U.S. Environmental Protection Agency, 1993; Corwin and others, 1997; Miller, 2010). PRZM also is among the process-based simulation models that have been used most extensively by pesticide manufacturers and regulatory agencies in the United States and Europe to estimate the concentrations of pesticides, or the likelihood of their detection, in the root zone (for example, Forum for Co-ordination of Pesticide Fate Models and their Use, 2000, 2004; Jones and Mangels, 2002; Morgan, 1999, 2002; U.S. Environmental Protection Agency, 2001).

Another reason PRZM was selected for this study was that it accounts for many of the primary physical, hydrological, chemical, and biological phenomena known to influence the transport and fate of surface-derived solutes in the subsurface. PRZM was also selected because of its inclusion in the vadose-zone model comparison study conducted by Nolan and others (2005). Additionally, Carsel and others (1998) determined that the concentration history predicted by the model for a hypothetical pesticide showed close agreement with an analytical solution for the advection-dispersion equation.

Many versions of PRZM have been produced. Several variations of the model that were available at the beginning of this study were considered but not used (for example, FOCUS PRZM, Visual PRZM), either because they were still under development at the time, or because they appeared to lack the flexibility required for this investigation. The most recent summary of the primary features of PRZM available during Phase 1 was provided in the users' manual for PRZM3.12 by Carsel and others (1998); unless noted otherwise, all descriptions of the characteristics and data requirements of PRZM used for the present study were taken from Carsel and others (1998). Jones and Mangels (2002) provided a summary of results from many of the investigations that have compared the predictions from PRZM simulations with field observations, and a comprehensive summary of some

of the limitations of the model that have been identified by other studies. The PRZM versions used by the investigations whose results were summarized by Jones and Mangels (2002) varied among the studies examined. The version used for the simulations during this study was PRZM3.12F (referred to herein as PRZM), obtained from Mark Cheplick, Waterborne Environmental, Inc. (written commun., July 2003).

Root-Zone Water-Quality Model (Phase 2)

Created by the U.S. Department of Agriculture (USDA), RZWQM is a one-dimensional, finite-difference, dual-porosity model that simulates a wide variety of physical, hydrologic, chemical, and biological processes known to control the transport of water, heat, and dissolved solutes—and the fate of solutes and their transformation products—in the vadose zone (Ahuja and others, 2000). The model is also specifically designed to simulate the effects of different agronomic practices on crop growth, and the transport and fate of water and solutes above and beneath the land surface, over time intervals as long as 100 years. The RZWQM2 Science Model, version 2.2 (downloaded on February 9, 2012) was used for this study, with additional guidance provided by the users' manual from Bartling and others (2011). For the sake of brevity, the abbreviation RZWQM will be used herein to refer to this version of the model.

RZWQM was selected primarily because of results from the model comparison study by Nolan and others (2005). For that investigation, Nolan and others (2005) examined the main features of 20 published models that simulate the transport and fate of surface-derived solutes within the vadose zone. Using a set of screening criteria related to documentation quality, ease of use, availability, range of processes simulated and other characteristics, seven of the models were selected to carry out a set of cold simulations to simulate (1) water flow, the transport and fate of atrazine, and the production and fate of DEA and two other atrazine transformation products in the vadose zone at a field site in the White River Basin, Indiana; and (2) the transport of water and dissolved bromide in the vadose zone at a second field site in Merced, California.

Nolan and others (2005) evaluated all seven models to determine the accuracy with which they predicted the field observations in the vadose zone at the two study locations. Among the atrazine *chemographs* (that is, plots showing variations in concentration in a given environmental medium over time) produced by each of the seven models for the Indiana site, the chemograph generated by RZWQM exhibited the closest agreement with the field data. Nolan and others (2005) attributed this observation to the fact that RZWQM was the only one of the seven models that simulates macropore flow, which had been known from previous research (Bayless, 2001) to occur at this site. The RZWQM simulations also provided predictions that substantially agreed with field observations regarding the evolution of matrix

potentials and DEA concentrations over time at the Indiana site, as well as the variations of moisture, matric potential, and bromide concentrations with depth in the vadose zone at the California site (Nolan and others, 2005). Additionally, Nachabe and Ahuja (1996) have shown that the partial piston displacement routine used by RZWQM to simulate dispersion produces chemographs that are in close agreement with an analytical solution to the convection-dispersion equation.

Many of the processes and factors that RZWQM has been designed to simulate, but that commonly are not accounted for by other vadose-zone models, are known to exert discernible effects on the transport and fate of water and solutes in the subsurface. These include a variety of agricultural management techniques, preferential transport through macropores, the exchange of water and solutes between regions of mobile and immobile water, the production and fate of agrichemical transformation products, the upward transport of solutes in response to evapotranspiration (ET), and the influence of soil depth (presumed to represent a proxy for microbial activity), temperature, and soil moisture on agrichemical transformation rates. Given the emphasis on accounting for as much current understanding as possible regarding the processes and factors that influence agrichemical transport and fate in the subsurface, these features were of considerable interest to the current study. Summaries of the features of RZWQM—as well as critiques of some of its limitations—have been provided in several publications (for example, Malone and others, 2001a, 2004a; Nolan and others, 2005; Bayless and others, 2008).

Processes Simulated and Input Data

Both of the vadose-zone models used for this study (PRZM and RZWQM) can account for the influence of many different processes and factors on the transport and fate of water and solutes in the root zone. As a result, many decisions were required in relation to the methods used to select or, in several cases, estimate values for model input parameters. Processes and factors that were simulated during each of the two phases of this investigation are listed in table 14, which also provides brief descriptions of the approaches used by the models to simulate many of the processes of interest. Sources of model input parameter values or, when such data were not readily available, brief descriptions of the methods used to estimate these values also are listed. Although most of the entries in table 14 are intended to be self-explanatory, additional clarification is provided below, where necessary.

Physical and Chemical Properties of Soils

Most of the quantitative information used to characterize the physical, hydraulic, and chemical properties of soils for this study was obtained from databases maintained by the

USDA Natural Resources Conservation Service (NRCS; Natural Resources Conservation Service, 2011a). The NRCS provides these data for millions of irregularly shaped areas, or *map units*, for most of the United States. (The map units are irregularly shaped because their outlines are determined by the spatial distributions of the soil type[s] they contain, rather than by political boundaries.) The data are provided at three spatial scales: Major Land Resource Areas (for the National Soil Geographic database, or NATSGO), individual States (for the State Soil Geographic database, or STATSGO), and individual soil units from the NRCS county soil surveys (for the Soil Survey Geographic database, or SSURGO). The STATSGO data represent a spatial aggregation of the SSURGO data, and data in the NATSGO database are derived from the National Resources Inventory (NRI; U.S. Department of Agriculture, 1991). By design, the spatial resolutions of the three databases differ considerably, exhibiting minimum sizes for their respective map units of several thousands of square miles for NATSGO (Natural Resources Conservation Service, 2006), approximately 2,500 acres for STATSGO, and 1–10 acres for SSURGO (Natural Resources Conservation Service, 2009).

All STATSGO data for the conterminous United States were available in digital form at the beginning of Phase 1, whereas most SSURGO data were not. For this reason, the soils data for the P-GWAVA-PR simulations were obtained from the STATSGO database. By the beginning of Phase 2 of this study, however, the SSURGO data had been digitized to a sufficient extent across the country to encompass all of the Phase 2 study sites (Natural Resources Conservation Service, 2014). Consequently, SSURGO data were used to characterize soil properties for the P-GWAVA-RZ simulations.

In addition to the variations in the magnitudes of soil parameters among soil map units, the STATSGO and SSURGO databases account for at least three other types of variation for many of the parameters that they include (Natural Resources Conservation Service, 2013). First, the individual map units are comprised of one or more *components*—that is, individual soil sequences that may vary with respect to the properties, vertical locations, and number of soil horizons that they contain. The databases do not report the specific locations of individual components in a given map unit, but instead provide an estimate of the percentage of the total map-unit area that each component occupies (*compct*). A second type of variation accounted for by the STATSGO and SSURGO data is the range of values spanned by many individual soil variables. For each of these parameters, three values are provided: a high value, a representative (intermediate) value, and a low value (for example, *ksat_h*, *ksat_r*, and *ksat_l*, respectively, for saturated hydraulic conductivity). Third, for some individual soil horizons that are stratified or that contain more than one soil texture, STATSGO and SSURGO provide more than one texture designation, but with no indication of the relative prevalence of the different soil textures within the horizon of interest.

Phase 1

PRZM simulates variations in soil properties with depth by representing the soil column as a series of layers with different physical, chemical, and biological characteristics. For computational purposes, each layer is subdivided into one or more separate grid cells. However, because of time constraints that precluded the acquisition and use of data on variations in soil properties with depth at each site, during Phase 1 the soil column at each location was represented as having uniform properties throughout its length. For each STATSGO map unit of interest, a single value for each soil parameter was obtained by computing spatially weighted averages in the vertical and horizontal dimensions.

The process of calculating a spatially weighted average for a given soil parameter is shown in [figure 7](#), using the example of computing an estimate of soil OM content for an idealized, hypothetical STATSGO map unit. The use of spatial averaging to obtain a single value for a given soil property for the entire soil column throughout an entire STATSGO map unit, although deemed necessary during Phase 1, resulted in the loss of a considerable amount of detail regarding the spatial variations of each parameter of interest. However, [figure 8](#) indicates that the spatially averaged values of soil organic carbon content, for example, still showed considerable variability among groundwater networks and, in some cases, among sites in a given network.

The STATSGO database provides information on soil properties to a depth of 152.4 cm, or to shallower depths where bedrock or other types of restrictive horizons are detected (Juracek and Wolock, 2002). However, because actual variations in soil properties with depth were not accounted for during Phase 1, the P-GWAVA-PR simulations were carried out only to an assessment depth of 1 m ([table 1](#)). This assessment depth was selected to correspond with the midrange among the rooting depths for corn (Carsel and others, 1998), to accommodate the specified model discretization (see section, “[Soil Column Discretization for Simulations](#)”), and because approximately 90 percent of corn roots typically are detected in the upper 1 m of the soil (North Dakota State University, 1997).

To examine the potential effects of the spatial averaging of soil parameters on the accuracy of the predictions of the P-GWAVA-PR modeling system, pairs of PRZM simulations were carried out at selected sites using soil parameter values derived from either STATSGO (with one parameter value for the entire soil column) or SSURGO (with different values for a given parameter among different horizons within the soil column). At each site, the atrazine concentrations simulated by the two approaches were compared with the concentration measured in shallow groundwater at that location, and with one another. These comparisons were carried out in two

agricultural locations representing different environmental settings—four sites in an irrigated, arid region in eastern Washington (Grant County) and six sites in an unirrigated, humid area in eastern Wisconsin (Portage County)—to examine the extent to which any differences between the concentrations simulated using the two approaches might have been affected by the environmental setting.

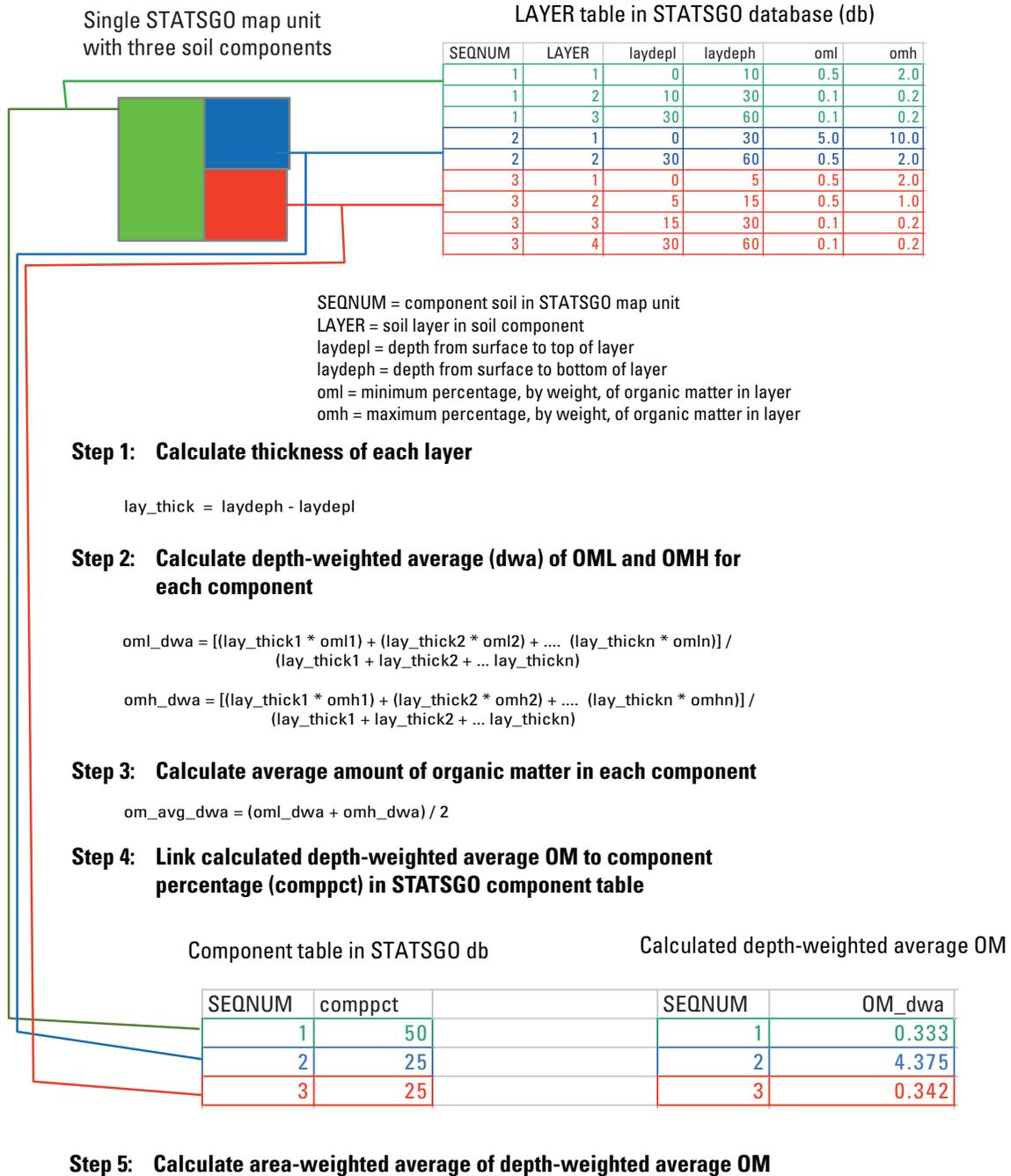
Phase 2

By the time Phase 2 of this study began, nearly all the SSURGO data were available in digital form for the United States (Natural Resources Conservation Service, 2014). As a result, soil properties could be characterized at the most detailed spatial scale possible in both the vertical and horizontal dimensions throughout the Phase 2 study area, eliminating the need for the spatial averaging used for Phase 1. Thus, by using the SSURGO data, the P-GWAVA-RZ simulations took full account of the known spatial variability in the soil properties of the Corn Belt.

Characteristics and Use of SSURGO Data

The number, dimensions, and properties of individual soil horizons typically vary from one SSURGO component to the next, even in the same SSURGO map unit. Depending on the site in question, data on soil properties were available in the SSURGO database for between one and eight soil horizons for the SSURGO components examined during Phase 2. In every case where data for the low, representative (intermediate), and high values were all provided for a given parameter, the representative value was used. For soil horizons where the database provided more than one texture designation but no indication of the relative prevalence of the different textures, the soil texture was determined independently from the weight percentages of three grain-size fractions (percent sand, percent silt and percent clay) using a subroutine embedded in RZWQM that determines soil texture from a standard soil triangle (Brady, 1990).

Although SSURGO provided data on soil OM content (expressed as a mass-based percentage) for the uppermost horizon in all of the SSURGO components examined during Phase 2, values for soil OM content were missing for one or more of the deeper horizons in about 20 components. In these cases, soil OM values for the deeper soil horizons were estimated by scaling the value for the uppermost horizon according to the average soil OM for the relative depth of the horizon of interest among all SSURGO components for which soil OM data were provided for that horizon. Because no components with missing data on the soil OM content had more than four horizons, this procedure was used for between one and three soil horizons beneath the uppermost horizon.



Step 5: Calculate area-weighted average of depth-weighted average OM

$OM_awa = [(compct1 * OM_dwa1) + (compct2 * OM_dwa2) + \dots (compctn * OM_dwan)] / 100$

Result: Organic matter for STATSGO map unit = 1.3 percent by weight

Figure 7. Steps used with the P-GWAVA-PR (Phase 1) system to obtain spatially weighted averages of individual soil parameters (in both the vertical and horizontal dimensions) for each State Soil Geographic database (STATSGO) map unit, using soil organic matter (OM) as an example.

More specifically, the estimated soil OM content in the Nth horizon beneath the land surface for component i ($\%om_{i,N}$) was computed using the following equation:

$$\%om_{i,N} = \%om_{i,1} * \left(\frac{\%om_{N,avg}}{\%om_{1,avg}} \right) \quad (2)$$

where

$\%om_{i,1}$ is the soil OM content in the uppermost horizon of SSURGO component i (obtained from SSURGO);

$\%om_{N,avg}$ is the average soil OM content in the Nth horizon beneath the land surface ($N = 2, 3,$ or 4) among all SSURGO components examined in the Phase 2 study area for which the values were reported to be less than 20 percent. (Soil OM contents equal to or greater than 20 percent were considered anomalous for the agricultural areas examined, and were thus disregarded.) Values of $\%om_{N,avg}$ were 1.1 percent for $N = 2$, 0.53 percent for $N = 3$, and 0.375 percent for $N = 4$; and

$\%om_{1,avg}$ is the average soil OM content in the uppermost horizon among all SSURGO components examined in the Phase 2 study area (3.12 percent).

To account for the effects of variations in soil properties among different soil components in the map unit where a given site was located, a separate P-GWAVA-RZ simulation was done for every component that occupied 10 percent or more of the map unit area, and for which a minimum set of soil parameter data were provided in the SSURGO database. This minimum set of soil parameters consisted of percent sand and percent silt, which were required to estimate the Brooks-Corey parameters (table 14). (The Brooks-Corey parameters are used to construct simplified versions of the relations between matric suction and either hydraulic conductivity or water content for a given soil.) The simulated concentrations for the individual components were combined into a single value for each map unit, in proportion to the fractions of the map unit that the components occupied (see section, “Quantifying Solute Concentrations from Model Output”). Because many of the well sites of interest were in areas with relatively homogeneous environmental characteristics (table 2), many of the sites were co-located in individual map units, with some SSURGO map units containing as many as 14 study sites within their boundaries.

For several soil-related RZWQM input variables, parameter values were obtained directly from the SSURGO database (for example, depths and thicknesses of individual soil horizons, percent sand, percent silt, percent clay, soil OM content and wilting point). However, for several other parameters, one or more intermediate steps were required to obtain the necessary input values (fig. 9, table 14). Examples of these procedures included the use of SSURGO data to estimate partition coefficients, diffusion rates, transformation rates, nitrogen fertilizer application rates, and soil hydraulic properties (table 14).

In many areas, information on soil properties provided by the SSURGO database extended beyond the typical depth of 153 cm, reaching nearly 300 cm in some locations. For this reason, an assessment depth of 3 m was used for all P-GWAVA-RZ simulations. To avoid truncating any of the soils data, the soil columns for the Phase 2 simulations were constructed to reach a depth of 3 m at all sites of interest. For locations where the SSURGO data for an individual component did not reach this depth, the thickness of the bottom soil layer was increased so that the overall length of the simulated soil column for that component reached the assessment depth of 3 m.

Reductions in Soil Permeability Caused by Surface Crusts

Rainfall has long been known to cause the formation of crusts on the surfaces of both undisturbed and anthropogenically modified soils, resulting in substantial decreases in soil permeability. Several decades of research have established that the formation and thickness of surface crusts are affected by a broad range of factors, including soil texture, aggregate stability, soil OM content and land-use practices (Rawls and others, 1990). RZWQM accounts for the influence of surface crusts on soil permeability by allowing the user to specify whether or not a surface crust is present and, if so, to specify its hydraulic conductivity (K_{cr}). Because tillage is known to promote their formation, surface crusts were assumed to be present at all sites where the P-GWAVA-RZ simulations were carried out. Values of K_{cr} were estimated using a set of pedotransfer functions devised for this purpose by Rawls and others (1990). *Pedotransfer functions* (PTFs) are statistical relations that estimate the value of a particular soil parameter from other properties of the soil.

Using measured rates of infiltration through recently tilled soils that either received or were protected from simulated rainfall in cropland and rangeland areas of 24 states, Rawls and others (1990) produced a series of PTFs for predicting the extent to which the surface crusts formed by rainfall led to decreased infiltration rates.

These reductions were quantified in terms of a *crust factor* (CF), which represents the ratio between the hydraulic conductivity of soil subjected to rainfall (K_{cr}) and that of soil protected from rainfall (K_{sat}). Rawls and others (1990) used the following equation to estimate CF values:

$$CF \equiv \frac{K_{cr}}{K_{sat}} = \frac{SC}{\left(1 + \frac{\Psi_i}{L}\right)} \quad (3)$$

where

- SC is the dimensionless reduction factor for subcrust conductivity (which corrects for partial saturation of the subcrust soil);
- Ψ_i is the steady-state capillary potential at the crust-subcrust interface, in centimeters; and
- L is the wetted depth, in centimeters.

Although Rawls and others (1990) provided CF values that were calculated from measured data for 20 agricultural locations, their data encompassed only 9 of the 12 texture classes in the USDA soil triangle (Natural Resources Conservation Service, 2011b). However, Rawls and others (1990) did list values of Ψ_i and SC for 11 of the soil texture classes. These values were used in conjunction with equation 3 to estimate a CF value for each of the 11 texture classes for the P-GWAVA-RZ simulations. The CF value for the remaining texture class (silt) was estimated using two additional PTFs, also provided by Rawls and others (1990), that expressed SC as a function of sand content and Ψ_i as a function of SC . For these calculations, silt was presumed to contain 8 percent sand and 6 percent clay. The CF values obtained using equation 3 were all computed using a wetted depth (L) of 5 cm, because this value provided the closest match between the predicted and measured CF values for each of the nine soil texture classes for which Rawls and others (1990) provided measured values. For the present study, the CF values produced using this approach (table 14) were multiplied by the value of K_{sat} provided by SSURGO for the surface soil layer to obtain a value of K_{cr} for every soil component included in the P-GWAVA-RZ simulations.

Soil Macroporosity

Several parameters are used by RZWQM to characterize the physical and hydraulic properties of macropores (table 14). However, because field measurements have been relatively sparse, values for most of these parameters have been estimated through model calibration (for example, Ahuja and others, 1995; Kumar and others, 1998; Malone and others, 2003, 2004a, 2004b). One exception has been macroporosity. As part of an effort to obtain values for several input parameters for solute transport-and-fate simulations using the MACRO model, Jarvis and others (2007b) devised

a classification system that provides estimates of soil macroporosity as a function of soil texture, soil OM content, depth below land surface, and extent of tillage. This system was adapted into a flow chart (fig. 10) that was used to assign a macroporosity value (n_m , expressed as a fraction of total soil volume) for each soil horizon in the Phase 2 study area for which SSURGO soil texture, soil OM and depth data were available.

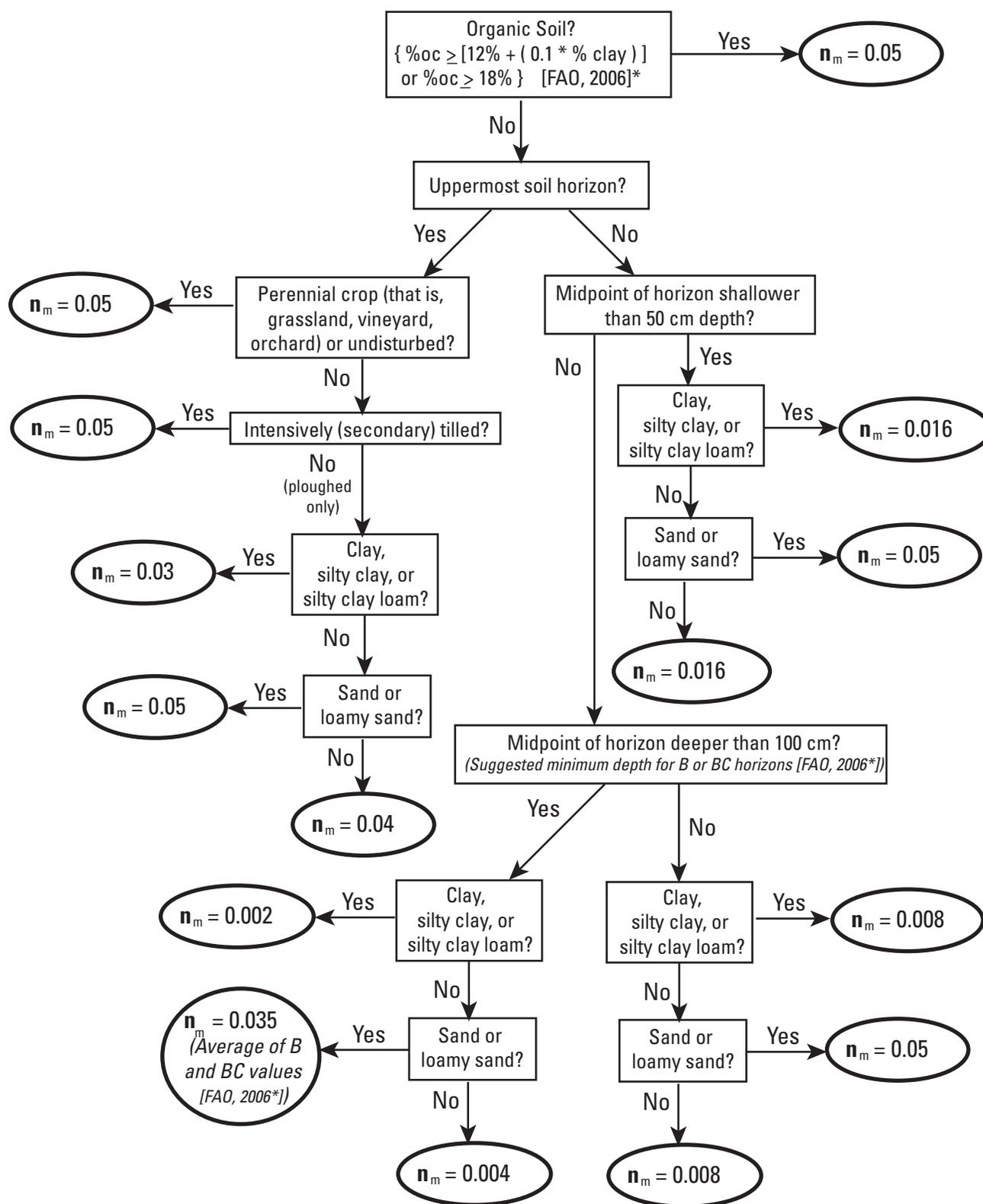
Water Movement Through the Subsurface

One of the primary differences between PRZM and RZWQM is the way they simulate the flow of water through the vadose zone. The tipping-bucket algorithm used by PRZM conveys water downward through the soil profile by allowing water to collect in individual depth increments until a particular threshold is exceeded (the bucket “tips”) and the water is allowed to flow to the next layer below. By contrast, RZWQM uses established equations to simulate the flow of water in two primary flow domains: (1) the soil matrix (which contains both mesopores and micropores), and (2) the soil macropores. *Micropores* are voids within the soil matrix that are sufficiently small that any water they contain is considered stagnant, or *immobile water*, and solute movement occurs primarily through diffusion. *Macropores* are root channels, worm burrows, cracks or other conduits in the soil in which the aqueous phase is predominantly *mobile water*, and through which water and solutes move primarily by advection. *Mesopores* are voids within the soil that are intermediate in size between micropores and macropores, and through which water and solutes move at intermediate rates, by both advection and diffusion.

Phase 1

Two primary water-retention variables are used by PRZM as reference points for characterizing water flow through the soil profile (fig. 11), field capacity and wilting point (Carsel and others, 1998). From an operational standpoint, field capacity is commonly defined as the water content at a matric suction of 33 kPa, designated herein as θ_{33} . The wilting point is often operationally defined as the water content at a matric suction of 1,500 kPa, or θ_{1500} (Carsel and others, 1998; Saxton and Rawls, 2006).

The tipping-bucket algorithm used by PRZM to simulate water flow through the subsurface allows water to collect in a given grid cell until the water content exceeds the field capacity for the soil in which it is located. Once the water content in the grid cell exceeds field capacity, the water is allowed to drain to the underlying grid cell until the water content in the overlying grid cell drops to field capacity. Water uptake by crops, which only occurs within the active root zone, is allowed to take place in a given grid cell only if the water content is greater than the wilting point for that soil.



*Food and Agriculture Organization of the United Nations (2006)

Figure 10. Procedure used to select the macroporosity value (n_m , expressed as a fraction of total soil volume) assigned to every soil horizon where soil texture, organic matter and depth data were available in the Soil Survey Geographic database (SSURGO) for the sites examined in the 10 northernmost states of the Corn Belt of the United States during Phase 2 of this study. Flow chart adapted from classification scheme of Jarvis and others (2007b).

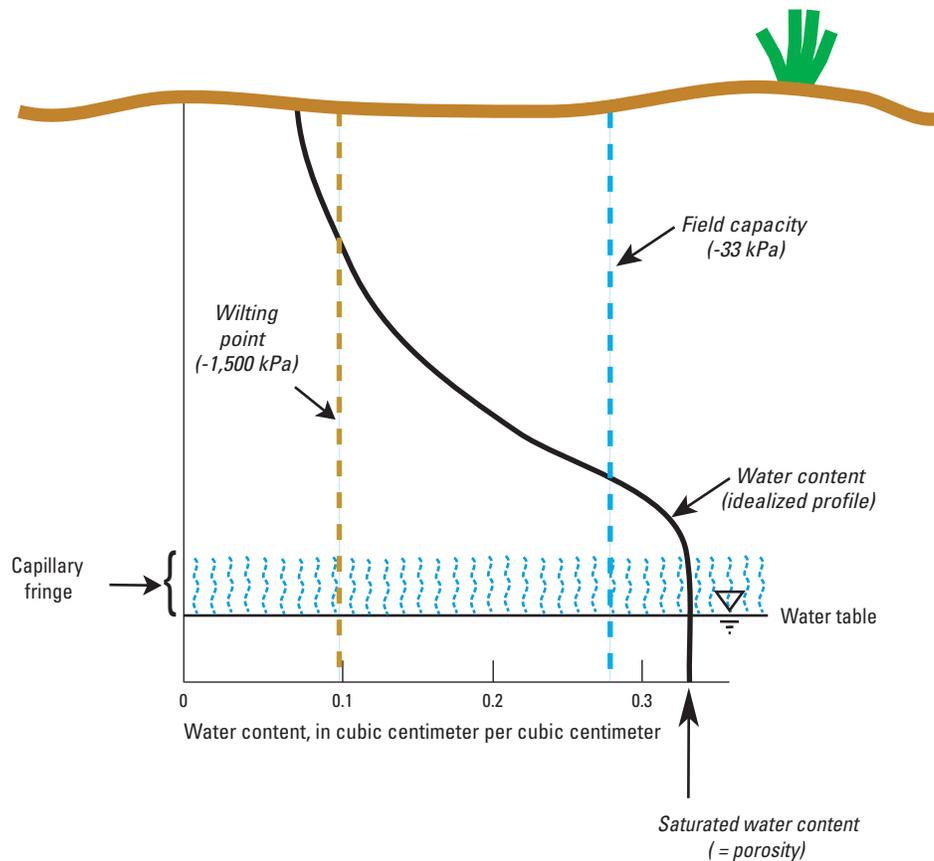


Figure 11. Variations in soil water content with depth in the vadose zone. Approximate values shown for field capacity and wilting point are within ranges reported by Rawls and others (1982) for a loam soil. (kPa, kilopascal.)

These *drainage rules* are invoked to redistribute water through the soil column on a daily basis. The merits and drawbacks of this simplified approach to simulating the movement of water through a soil profile were discussed by Carsel and others (1998).

PRZM offers three internal methods for estimating field capacity and wilting point for each soil of interest, using data and procedures from the USDA (Rawls and Brakensiek, 1983): (1) computation from percentages of sand and clay, organic-matter content, and bulk density using a regression-based PTF; (2) selection on the basis of the percentages of sand and clay; or (3) selection on the basis of soil texture class. Instead of using these procedures, however, field capacity and wilting point were estimated during Phase 1

using the computer program Rosetta (Schaap and others, 2001), which uses neural networks, rather than regression equations, to estimate soil hydraulic parameters from other soil properties. Like PRZM, Rosetta offers the flexibility of estimating water-retention property values using a hierarchy of sets of input parameters, depending on the available data. For Phase 1, field capacity and wilting point were estimated at each site using the PTF in Rosetta that uses percentages of sand, silt and clay, and bulk density, as input parameters.

The use of Rosetta instead of the internal PRZM methods to estimate field capacity and wilting point at the Phase 1 sites was motivated by two primary considerations. First, whereas the methods internal to PRZM for estimating soil hydraulic parameters (Carsel and others, 1998) use

data from 5,760 measurements on 640 samples (Rawls and Brakensiek, 1983), the water-retention parameter estimates provided by Rosetta are derived from a substantially more extensive database of at least 20,574 measurements on at least 2,134 samples (Schaap and others, 2001). Second, comparisons between the estimates obtained from Rosetta and those computed using the Rawls and Brakensiek (1983) equations for field capacity and wilting point for all sites of interest (figs. 12 and 13, respectively) indicated that a higher proportion of the values obtained using Rosetta were within the ranges measured in most soils for these two parameters (Dunne and Leopold, 1978) than was the case for the estimates obtained using the Rawls and Brakensiek (1983) equations. Values of parameters estimated by the Rawls and Brakensiek (1983) equations nearly always exceeded the corresponding values estimated by Rosetta (figs. 12 and 13)

Rosetta was not able to compute field capacity or wilting point for three of the Phase 1 sites with especially high amounts of OM, that is, soil with mass-based organic-carbon fractions (f_{oc}) exceeding 0.3 (30 percent by weight [w/w]). This may have been because the bulk densities of the soils in question were less than 0.5 g/cm^3 , the minimum value for which Rosetta is able to compute water-retention parameters. To address this problem, values of field capacity and wilting point were taken directly from moisture retention curves provided by Marcel Schaap (University of Arizona, written commun., September 2003) for a peat soil from Poland that exhibited a bulk density similar to the organic-rich soils of interest. Water retention data generally are rare for such organic-rich soils.

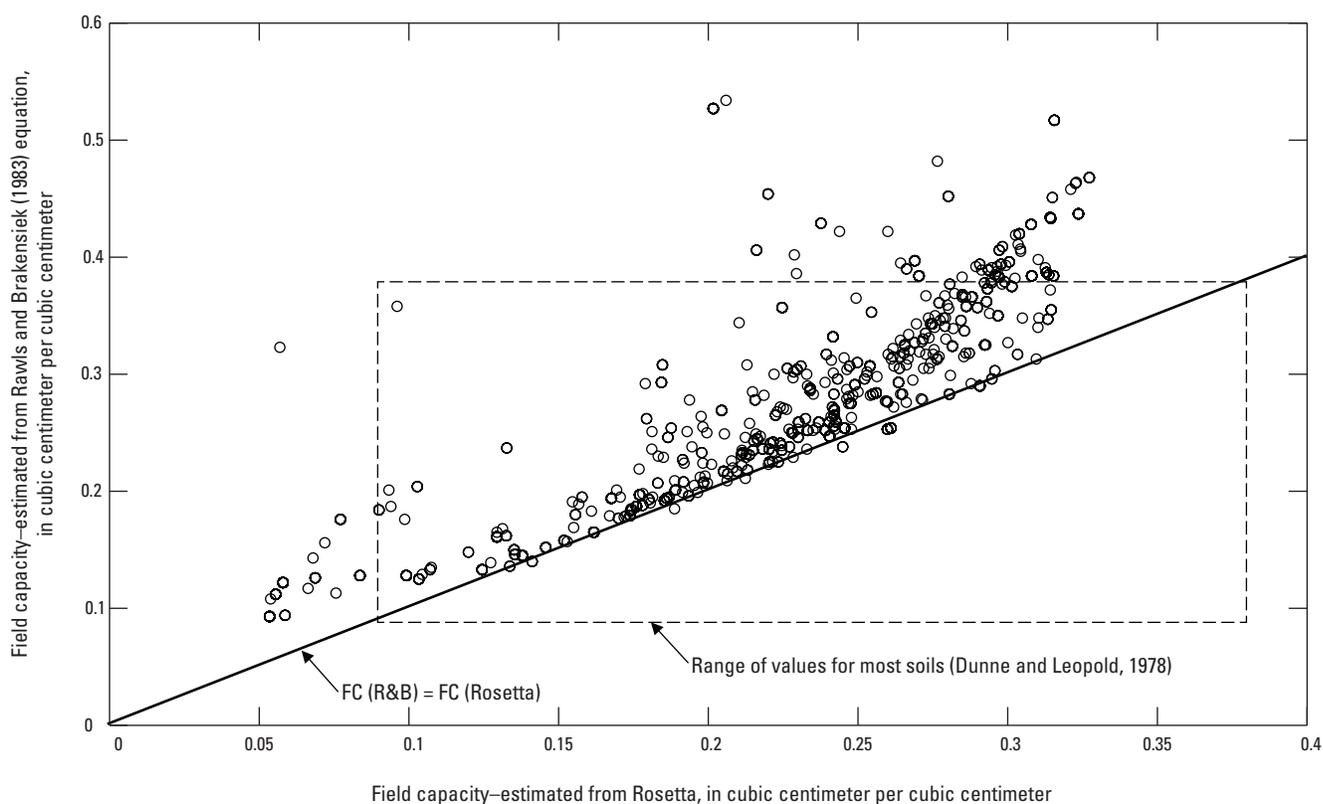


Figure 12. Comparison between estimates of field capacity (FC) at the P-GWAVA-PR (Phase 1) study sites using the Rawls and Brakensiek (1983) equation (R&B), estimates for the same sites from Rosetta, and the range of values typically measured in soils in the United States.

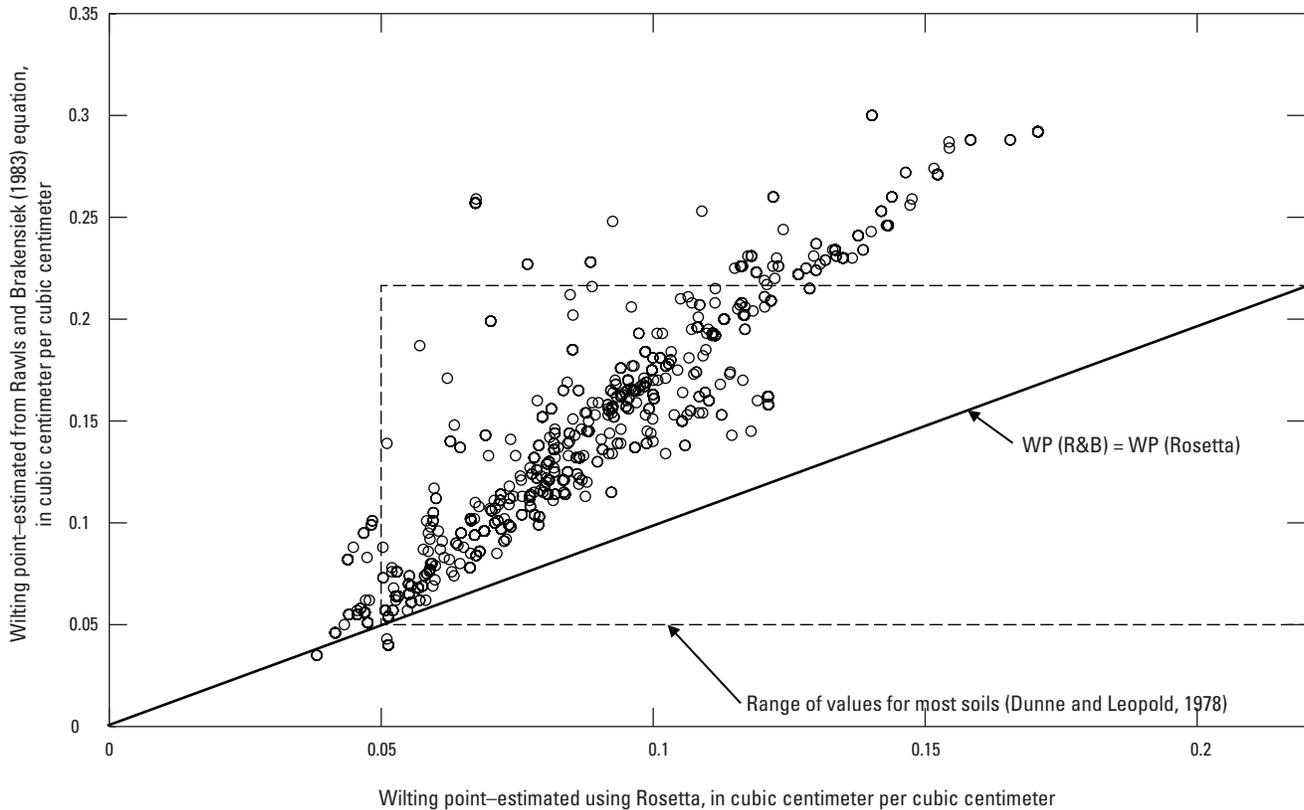


Figure 13. Comparison between estimates of wilting point (WP) at the P-GWAVA-PR (Phase 1) study sites using the Rawls and Brakensiek (1983) equation (R&B), estimates for the same sites from Rosetta, and the range of values typically measured in soils in the United States.

Phase 2

RZWQM simulates the movement of water and dissolved solutes within two distinct but interconnected flow domains in the vadose zone: the soil matrix and macropores. The void space in the soil matrix, in turn, is comprised of micropores and mesopores. The macropores, which are represented as either cylindrical channels (created by worms, plant roots, invertebrates, and other organisms) or planar cracks are also divided into two domains; vertical, continuous channels through which soil water migrates rapidly, and lateral, *dead-end pores* through which water and solutes may move from the continuous pores into the soil matrix. According to the default configuration of the model (which was used to characterize several macropore properties for this study), all the macropores in the uppermost horizon at each site consist of cylindrical channels that connect with planar cracks at greater depths beneath the land surface. The cylindrical channels are presumed to be open (that is, they have a nonzero radius) only in the uppermost soil horizon at each site, whereas the planar cracks are presumed to be open only in the horizons located at greater depths. Water and solutes moving through macropores,

therefore, are presumed to enter through cylindrical channels at the land surface, and flow into the planar cracks to which the cylindrical channels are connected at greater depths. Flow through the vertical macropores occurs only if the rate of water deposition on the land surface (from either precipitation or irrigation) exceeds the rate of infiltration, causing the excess water to pond and flow downward into the macropores or off site as runoff (Ahuja and others, 2000).

Once infiltration begins in response to a recharge event, RZWQM allows water to flow into both the micropores and the mesopores in the soil matrix, to the extent warranted by the infiltration rate. Soil water in the micropores is considered to be immobile, whereas the water in the mesopores, considered to represent mobile water, flows in response to the prevailing hydraulic gradient. Advection of soil water in the macropores occurs in the continuous vertical channels, but not in the dead-end macropores. Modes of preferential transport other than macropore flow, such as finger flow or funnel flow (for example, Kung, 1990; Ju and Kung, 1993; Jarvis and Dubus, 2006; Chapwanya and Stockie, 2010; DiCarlo and others, 2011; Perkins and others, 2011) are not simulated.

Although hydrodynamic dispersion generally is assumed to be caused by variations in pore-water velocities and migration path lengths in the subsurface (Freeze and Cherry, 1979; Amoozegar-Fard and others, 1982; Gelhar and others, 1992), RZWQM does not simulate it in this manner. Instead, the movement of water and solutes through the mesopores is simulated as a two-stage piston-flow process designed to mimic both miscible displacement and hydrodynamic dispersion. The exchange of dissolved solutes between micropores and mesopores takes place through molecular diffusion. Exchange of water and solutes between the macropores (either continuous or dead-end) and the soil matrix occurs through the macropore walls (Ahuja and others, 2000).

RZWQM uses equations derived from fundamental hydraulic principles to simulate the flow of water through the subsurface (Ahuja and others, 2000; Malone and others, 2003, 2004a). Infiltration from the land surface into the soil matrix, and the movement of water from macropores into the soil matrix, are described using different forms of the Green-Ampt equation. Flow in macropores, when it occurs, is simulated using Poiseuille's law (Ahuja and others, 2000). Between infiltration events, the ongoing movement of water in the mesopores (a process sometimes referred to as *redistribution*) is simulated using the Richards equation—the unsaturated version of the Darcy equation that accounts for the fact that both water content (fig. 11) and hydraulic conductivity in the vadose zone vary with pressure head (Freeze and Cherry, 1979).

RZWQM uses the Brooks-Corey model to quantify the *characteristic curves* for the soils of interest—that is, the functional relations between matric suction (τ , where $\tau = |h|$ and h is the soil water pressure head, in centimeters), water content ($\theta(\tau)$, cm^3/cm^3) and hydraulic conductivity ($K(\tau)$, cm/hr) in the vadose zone (Ahuja and others, 2000; Malone and others, 2003). The Brooks-Corey model uses the following equations to describe the $K(\tau)$ function:

$$K(\tau) = K_{sat} \quad \text{for } 0 \leq \tau \leq \tau_{bK} \quad (4a)$$

$$K(\tau) = C_2 * \tau^{N_2} \quad \text{for } \tau > \tau_{bK} \quad (4b)$$

where

- K_{sat} is the saturated hydraulic conductivity, in centimeters per hour;
- τ_{bK} is the air-entry value, or bubbling suction, in centimeters, for the hydraulic conductivity relation ($K(\tau)$ curve);
- C_2 is the coefficient for the $\tau > \tau_{bK}$ segment of the $K(\tau)$ curve; and
- N_2 is the unsaturated hydraulic conductivity constant (Malone and others, 2004b), calculated from the dimensionless poresize distribution index, λ (Schaap and others,

2004), using the following relation (Malone and others, 2003; Ma and others, 2009; Agricultural Research Service, 2010):

$$N_2 = 2 + (3 * \lambda) \quad (5)$$

The coefficient associated with λ in equation 5 has been adjusted during other studies to improve the agreement between simulated and observed soil water contents (Robert Malone, U.S. Department of Agriculture, written commun., November 2011). For example, Malone and others (2004b) used the following version of this relation:

$$N_2 = 2 + \lambda \quad (6)$$

For the present study, however, equation 5 was used to compute N_2 from λ because it is the relation that the RZWQM documentation recommends for this purpose (Agricultural Research Service, 2010). Rearranging equation 4b, and combining it with equation 4a at $\tau = \tau_{bK}$, the coefficient C_2 may be computed as follows:

$$C_2 = K_{sat} * (\tau_{bK}^{-N_2}) \quad (7)$$

As with the hydraulic conductivity form of the characteristic curve (equations 4a and 4b), the Brooks-Corey version of the water-content curve ($\theta(\tau)$) is also a function of λ . Additionally, the Brooks-Corey water-content curve is a function of the bubbling suction, τ_b , the soil water content at saturation, θ_s , and the *residual water content*, θ_r (Ahuja and others, 2000; Schaap and others, 2004). The residual water content is essentially a fitting parameter (McCuen and others, 1981; Saxton and others, 1986), but its physical meaning is often inferred to be the “irreducible” water content of a soil at infinite suction, when no more water can be extracted (Marcel Schaap, University of Arizona, written commun., May 2007). The texture-class-average data reported by Rawls and others (1982) indicate that θ_{1500} —a parameter that is often used as an estimate of the wilting point (table 14)—provides a reasonable approximation of θ_r in coarse soils (sand, loamy sand, and sandy loam). However, data reported by Rawls and others (1982) indicate that θ_{1500} may exceed θ_r by a factor of between 2 and 9 in medium to fine soils. Consequently, for each soil horizon examined during the P-GWAVA-RZ simulations, the water-content characteristic curve was constructed using the texture-based θ_r values obtained by RZWQM from Rawls and others (1982), rather than the θ_{1500} values.

Although SSURGO provides values of K_{sat} for nearly all of the soil horizons examined, in some cases the values given are identical across multiple soil textures—a pattern that is inconsistent with empirical observation (for example, see Rawls and others, 1982). As a result, values of K_{sat} were estimated from the SSURGO-derived weight percentages

of sand and clay using the PTF that was devised for this purpose by Saxton and others (1986), and adapted by Nelson (2012) into an online program. This approach resulted in K_{sat} distributions that were considerably smoother among adjacent soil horizons than distributions obtained directly from the SSURGO K_{sat} data.

When measured values of K_{sat} , τ_{bK} and λ are not available, RZWQM offers three estimation options (Bartling and others, 2011). These options involve using either (1) soil texture alone (using the texture-based PTFs of Rawls and others [1982]); (2) soil texture, θ_{33} and θ_{1500} (Ma and others, 2009); or (3) soil texture and θ_{33} (Williams and Ahuja, 1992). Depending on the data available from SSURGO, the P-GWAVA-RZ simulations used one of these methods to estimate τ_{bK} and λ for each soil horizon. In most cases, the third option was used because values of θ_{33} were available from SSURGO for nearly all the soil horizons examined.

As an alternative to using the texture class-averaged values reported by Rawls and others (1982), the Brooks-Corey parameters also may be computed from variables in the van Genuchten equation that are estimated from soil texture data using Rosetta (Schaap and others, 2004). In table 3, the ranges of values for the Brooks-Corey parameters τ_b (or τ_{bK}), N_2 and C_2 computed from the van Genuchten parameters for 11 of the USDA soil texture classes (using Rosetta) are compared with the values reported for the same texture classes by Rawls and others (1982). Although in some cases $\tau_{bK} = \tau_b$

(Ahuja and others, 2000), neither Rawls and others (1982) nor Schaap (2011) made explicit distinctions between τ_{bK} (the value for the hydraulic conductivity relation) and τ_b (the value for the water-content relation). Consequently, the same values of N_2 and C_2 were presumed to apply for either the hydraulic conductivity relation or the water-content relation for a given soil. For τ_b (or τ_{bK}) and N_2 , the ranges of values obtained using the two methods exhibit a considerable degree of overlap (table 3). However, in the case of C_2 (computed from K_{sat} , τ_{bK} and N_2 using equation 7), the values generated using Rosetta were, in some cases, between one and nine orders of magnitude larger than those provided by Rawls and others (1982).

Thus, whereas the estimates of soil water content at field capacity and wilting point obtained from Rosetta were suitable for the P-GWAVA-PR simulations during Phase 1 (figs. 12 and 13, respectively), this was not the case for the Rosetta-derived values of the Brooks-Corey parameters during Phase 2. As a result, the Rosetta-derived values of the Brooks-Corey parameters were not used for the P-GWAVA-RZ simulations. Instead, the Brooks-Corey parameter values reported for individual texture classes by Rawls and others (1982), which are generated internally by RZWQM and have been used extensively by other studies in the past, were used to produce the soil characteristic curves for the Phase 2 simulations (table 4).

Table 3. Ranges of Brooks-Corey parameter values reported for 11 U.S. Department of Agriculture soil texture classes, and ranges estimated from van Genuchten parameters using Rosetta.

[Although Schaap (2011) provided van Genuchten parameter values for all 12 texture classes in the U.S. Department of Agriculture (USDA) soil texture triangle (Natural Resources Conservation Service, 2011b), the texture classes included in this analysis were limited to the 11 classes that were examined by Rawls and others (1982)—that is, all of the USDA classes except silt. **Abbreviations:** cm, centimeter; cm/h, centimeter per hour; >, greater than]

Brooks-Corey parameter	Range among texture classes reported by Rawls and others (1982)	Range among texture classes estimated from van Genuchten parameters using Rosetta (Schaap, 2011)
Air-entry value ¹ (τ_b or τ_{bK}) (cm)	7.26–37.30	28.38–197.70
Exponent for $\tau > \tau_{bK}$ segment of $K(\tau)$ curve (N_2)	2.38–3.78	2.62–8.53
Coefficient ² for $\tau > \tau_{bK}$ segment of $K(\tau)$ curve (C_2) (cm/h)	346–37,421	3,520–6.65×10 ¹³

¹Although in some cases $\tau_{bK} = \tau_b$ (Ahuja and others, 2000), no distinctions were made by either Rawls and others (1982) or Schaap (2011) between τ_{bK} (value for hydraulic conductivity relation) and τ_b (value for water-content relation). In the absence of additional data, however, the same values were presumed to apply for both parameters.

²Computed from τ_b and N_2 using equation 7, that is

$$C_2 = K_{sat} * (\tau_{bK}^{-N_2})$$

where

- K_{sat} is the saturated hydraulic conductivity of the soil (centimeters per hour);
- τ_{bK} is the air-entry value (centimeters); and
- N_2 is the dimensionless unsaturated hydraulic conductivity constant (Malone and others, 2004b).

Table 4. Approaches selected to improve agreement between simulated and measured solute concentrations for the final set of P-GWAVA-PR (Phase 1) simulations across the conterminous United States, and for the final set of P-GWAVA-RZ (Phase 2) simulations in the 10 northernmost states of the Corn Belt.

[See text and [table 14](#) for details. Other distinguishing features of the approaches used for the two study phases are listed in [table 1](#). **Abbreviations:** cm, centimeter; DEA, deethylatrazine; K_{oc} , organic carbon-water partition coefficient; kg a.i./ha, kilograms of active ingredient per hectare; °C, degrees Celsius]

Parameter, process, or feature	Approach for each model	
	P-GWAVA-PR	P-GWAVA-RZ
Height(s) of grid cells for simulations	0–9.9 cm interval: 0.1 cm 10–100 cm interval: 30 cm	1 cm (entire soil column)
Spatial heterogeneity of atrazine application	Areally averaged	Spatially uniform (2 kg a.i./ha)
Irrigation	Simulated at sites selected at random within each groundwater sampling network in proportion to percentage of nearby land in irrigation	Simulated at all sites
Method used to estimate or obtain values for selected soil hydraulic parameters [parameters of interest shown in brackets]	Rosetta database (Schaap and others, 2001) [Water contents at field capacity and wilting point]	Pedotransfer functions from Rawls and others (1982) [Brooks-Corey parameters]
Relative sizes of pools of soil organic matter (fast/medium/slow)	Not applicable (not used by model)	Original values (percent): 2 / 18 / 80 Final values (percent): 10 / 20 / 70
K_{oc}	Literature value (atrazine)	Reduced to 25 percent of their original literature values (atrazine and DEA)
Rate of atrazine disappearance in soil at 25 °C	Literature value	Original approach: Estimated using updated Fenner-Borsuk relation (eq. B3) Final approach: Literature value
Site(s) of atrazine transformation in soil	Dissolved and sorbed states	Not applicable (rate specified for whole soils only)

Weather

The meteorological data used for the P-GWAVA simulations were obtained at different time scales for different purposes. Most of the temperature-dependent processes that are simulated internally by PRZM or RZWQM use daily values. However, for several temperature-sensitive parameters that were computed externally, values were calculated using the average air temperature for May (T_{May}), the month when atrazine and nitrate were assumed to have been applied every year at each site. This assumption was required because location-specific data on the timing of agricultural applications and other agricultural management practices were not available on a nationwide basis at the time of this study. The temperature-sensitive parameters of interest included the initial rates of atrazine transformation (for both study phases), the rate of DEA transformation, and the Henry's law constant (Phase 2 only). During Phase 1, daily values of precipitation were used. Hourly precipitation data were required during

Phase 2, in order to simulate preferential flow. For all other meteorological parameters quantified using data acquired from other sources for this study, either daily or monthly values were used ([table 14](#)).

Phase 1

Daily values of soil temperature are used by PRZM for estimating the rates of volatilization and transformation of nitrogen species, as well as the rate of evapotranspiration (ET). However, because the transport and fate of nitrogen species were not examined during Phase 1 and an external method was used to estimate ET, no built-in temperature-dependent functions in PRZM were used during the Phase 1 simulations. Nevertheless, soil temperature data were still required for the external calculations used to estimate potential evapotranspiration (PET) and to account for the effect of temperature on atrazine transformation rates.

Nationwide coverages of precipitation, wind speed, and temperature data were obtained from the National Climatic Data Center (NCDC) of the National Oceanic and Atmospheric Administration (NOAA) during Phase 1 (table 14). Daily values of minimum and maximum temperature (T_{min} and T_{max} , respectively), as well as precipitation, were acquired from 11,240 weather stations across the Nation. However, complete records for all three parameters during 1986–95 were available for only 4,953 of these stations. Of these, 331 stations were close to one or more of the 1,224 Phase 1 study sites of interest. After removing weather stations with errors that could not be corrected, 327 stations were used to obtain daily values of T_{min} , T_{max} , and precipitation. Nationwide wind speed data for 1986–95, required for the ET computations, were available only as monthly averages, and were more sparsely distributed than the temperature and precipitation data. As a result, the irregularly shaped grid cells used in GIS to couple individual sites with their nearest weather station—referred to as *Thiessen polygons*—were much larger for the wind speed data than for the temperature or precipitation data.

The temperature of shallow groundwater was measured during the NAWQA sampling operations at all the sites examined for this study. However, in adherence to the design

objective to use only sources of input data that provided parameter values on a nationwide basis, the results from the NAWQA temperature measurements were not used for any model simulations during either phase of this study. PRZM includes a subroutine for simulating temporal variations in soil temperature from heat-flux calculations, but it was not used because site-specific data for several of the parameters that it requires (for example, values for the heat capacity, thermal conductivity, and thermal diffusivity of the soil) were not available on a national scale. Consequently, daily values of air temperature from the National Climatic Data Center (2002b) were used during Phase 1 to estimate ET at each site. T_{May} was used to adjust the rate of atrazine transformation to account for spatial variations in temperature at the time of application. Annual average values of T_{May} , obtained from the Parameter-elevation Relationships on Independent Slopes Model (PRISM) Climate Group (2009), were moderately well correlated with the groundwater temperatures measured at the 1,224 study sites for Phase 1 ($R^2 = 0.39$ [$P \leq 0.0001$]; Spearman $\rho = 0.62$ [$P(\rho) \leq 0.0001$]; $N = 1,800$ measurements) (fig. 14). As a result, the T_{May} data were considered to be adequate proxies for groundwater temperature for the P-GWAVA-PR simulations.

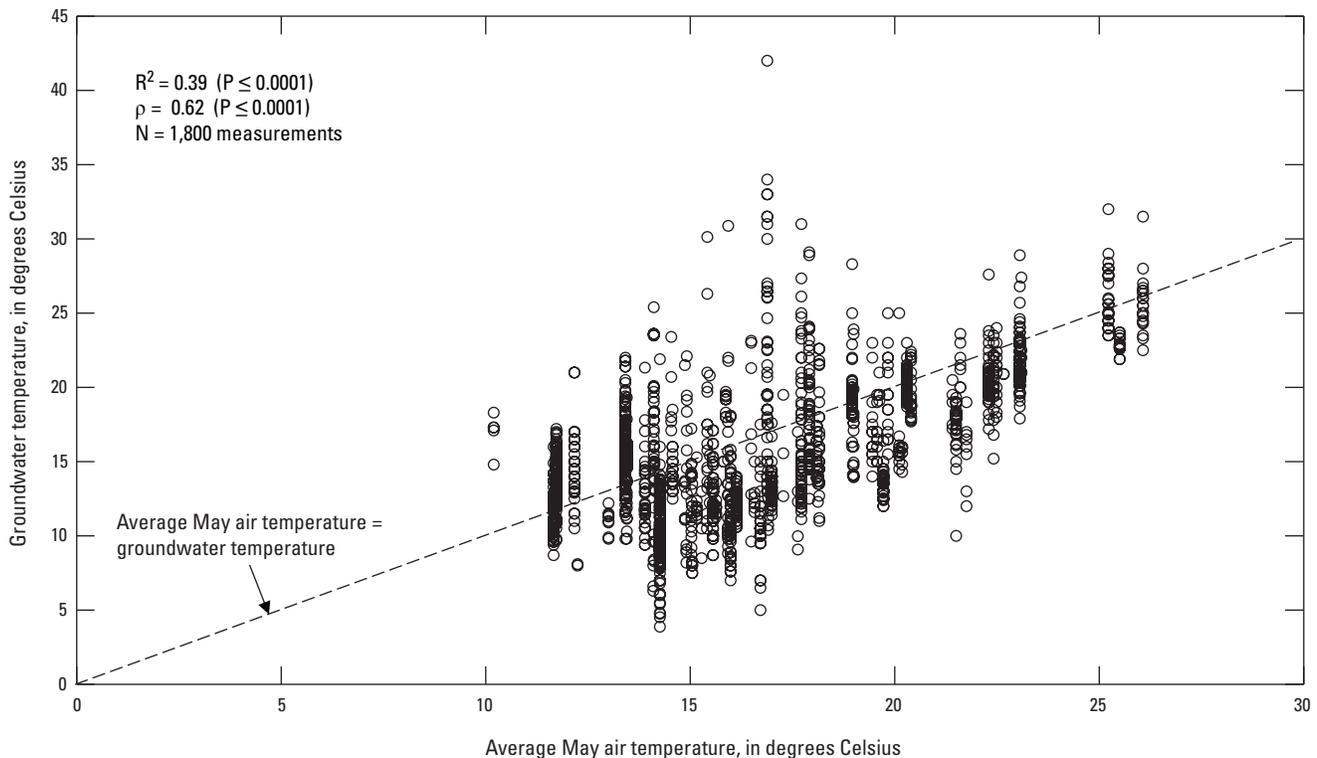


Figure 14. Comparison between groundwater temperatures measured at each of the 1,224 P-GWAVA-PR (Phase 1) study sites examined across the conterminous United States and the average air temperature for May in the same locations from the National Oceanic and Atmospheric Administration (2010). The number of measurements (1,800) exceeds the number of sites (1,224) because multiple measurements were made in some locations. Locations of study sites are shown in figure 1.

Phase 2

The simulation of weather by RZWQM involves the use of daily values for most of the meteorological parameters of interest (table 14). However, to generate macropore flow, hourly data from storms must be provided. Hourly data from storms were not available at a national scale after 1990 (Burns and others, 2007). Consequently, a program embedded in RZWQM known as *Cligen* (Agricultural Research Service, 2009) was used to simulate weather at all of the study sites during Phase 2 (fig. 9). The specific version of the weather simulator used was Cligen90, denoted as “Cligen” herein. Cligen applies probabilistic methods, guided by the statistical properties of historical data gathered between 1949 and 1996 (Agricultural Research Service, 2009), to generate simulated storms on an hourly basis. Similar methods are used to provide daily values for maximum and minimum temperature, wind speed, solar radiation, and relative humidity (table 14). Because Cligen generates these parameter values stochastically from historical data, rather than providing actual historical measurements, the specific years of the Phase 2 simulations were essentially arbitrary. Consequently, all the P-GWAVA-RZ simulations (including those carried out for the initial stabilization period) were nominally carried out for the time interval from 1998 through the end of 2004, to accommodate most of the recent samples against which its predictions were to be compared (table 1). (No samples were collected at any sites in 2005 and samples were collected at only four sites in 2006.) Burns and others (2007) provide a valuable discussion of the relative merits and limitations of using Cligen and other weather simulators, rather than measured data, to simulate weather for solute transport-and-fate simulations.

The data required for the Phase 2 weather simulations were assembled by reconstructing the 1-degree grid used by Cligen (that is, a grid for which each cell has a width in the east-west direction of 1 degree of longitude and a width in the north-south direction of 1 degree of latitude), selecting one Cligen weather station in each grid cell from a list of such stations provided by RZWQM, and using the weather data from that station for all of the Phase 2 sites in that cell. For 109 of the 453 Phase 2 sites, the nearest Cligen weather station that provided complete data for all of the parameters of interest was in the same cell. For these sites, the average distance to the weather station of interest was 25 mi. For most of the remaining sites, the climate data were obtained from the nearest Cligen station outside of the cell that provided complete data for all of the parameters of interest. Four of the Phase 2 sites were in Cligen cells without any weather stations. In these cases, the nearest station outside of the cell that provided complete data for all parameters of interest was used. As a result, no Phase 2 simulation site was located more than 85 mi from the weather station from which its meteorological data were obtained.

As with PRZM, RZWQM accounts for the influence of temperature on various physical, chemical, and biological processes. For RZWQM, these include heat flux through the soil, ET, crop development, solute transformation, ammonia

volatilization, air-water partitioning of oxygen, and the growth and death of microorganisms. RZWQM assumes that the temperature at the soil surface is equal to the air temperature (Ahuja and others, 2000). The temperature used for calculating the initial values for the Henry’s law constants and transformation rates for atrazine and DEA at each site during Phase 2 was the average air temperature in May (T_{May}) because atrazine and nitrogen fertilizers were all assumed to have been applied at the end of May each year in each study location (table 14). At each site, T_{May} (fig. 15) was calculated as the arithmetic average of the daily minimum and daily maximum air temperatures for the month of May during 1971 to 2000, using data from the PRISM climate mapping system (PRISM Climate Group, 2009). This parameter was used, rather than the temperature provided by Cligen on the assigned planting date of May 30, to avoid the variability introduced by the stochastic routines used by Cligen for estimating parameter values.

Assessment Depths and Depths to Water

Although efforts have been made to estimate the depth of the water table beneath the land surface across the United States (Fan and others, 2007, 2013), there are many areas around the Nation where the depth to groundwater has not been measured. Consequently, given the design objective of using only national-scale data as inputs to the P-GWAVA simulations, the selection of the assessment depths for the simulations was guided by (1) the depths to which the required soils data were available and (2) the maximum rooting depth of corn plants, rather than by the depth of the water table. The assessment depths used for this study were 1 and 3 m for the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) simulations, respectively (table 1).

The distributions of depths to water for the sites examined during the two phases of this study are shown in figure 16. For each site, the depth to water (DTW) value used to construct figure 16 was the arithmetic average among all the measurements made at the site of interest. The numbers of water depth measurements varied widely among locations, ranging from 1 to 983 measurements per site, and spanning periods ranging from 5 days to 49 years (data not shown). Results from a statistical analysis of these data using the non-parametric Mann-Whitney test (Helsel and Hirsch, 1992) indicated that the median DTW among the study sites examined for Phase 2 differed significantly from the median DTW for the sites examined for Phase 1 ($P \leq 0.0001$). The data shown in figure 16 also indicate that at many of the study sites examined, the average depth of the water table beneath the land surface was shallower than the assessment depth. The analysis of the results from this study therefore included an examination of the extent to which the agreement between the recharge rates, solute concentrations, and detection frequencies predicted by the P-GWAVA simulations and their measured values may have been related to the depth of the water table.

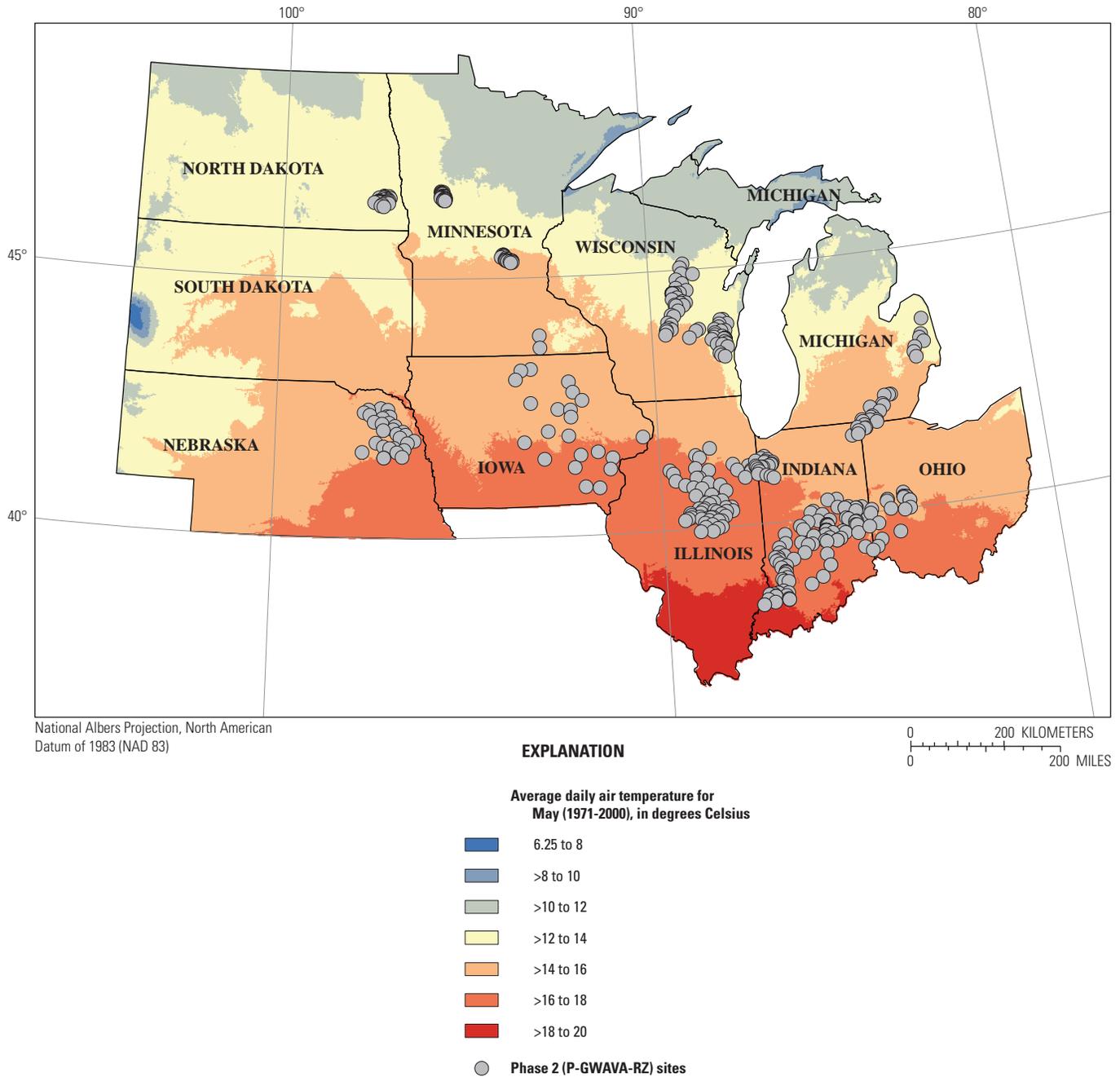


Figure 15. Average daily air temperature during May (T_{May}) from 1971 to 2000 and the P-GWAVA-RZ (Phase 2) study sites in the 10 northernmost states in the Corn Belt of the United States. Temperature values were computed as the arithmetic average of the maximum and minimum air temperature in May at each site, using data from the PRISM Climate Group (2009).

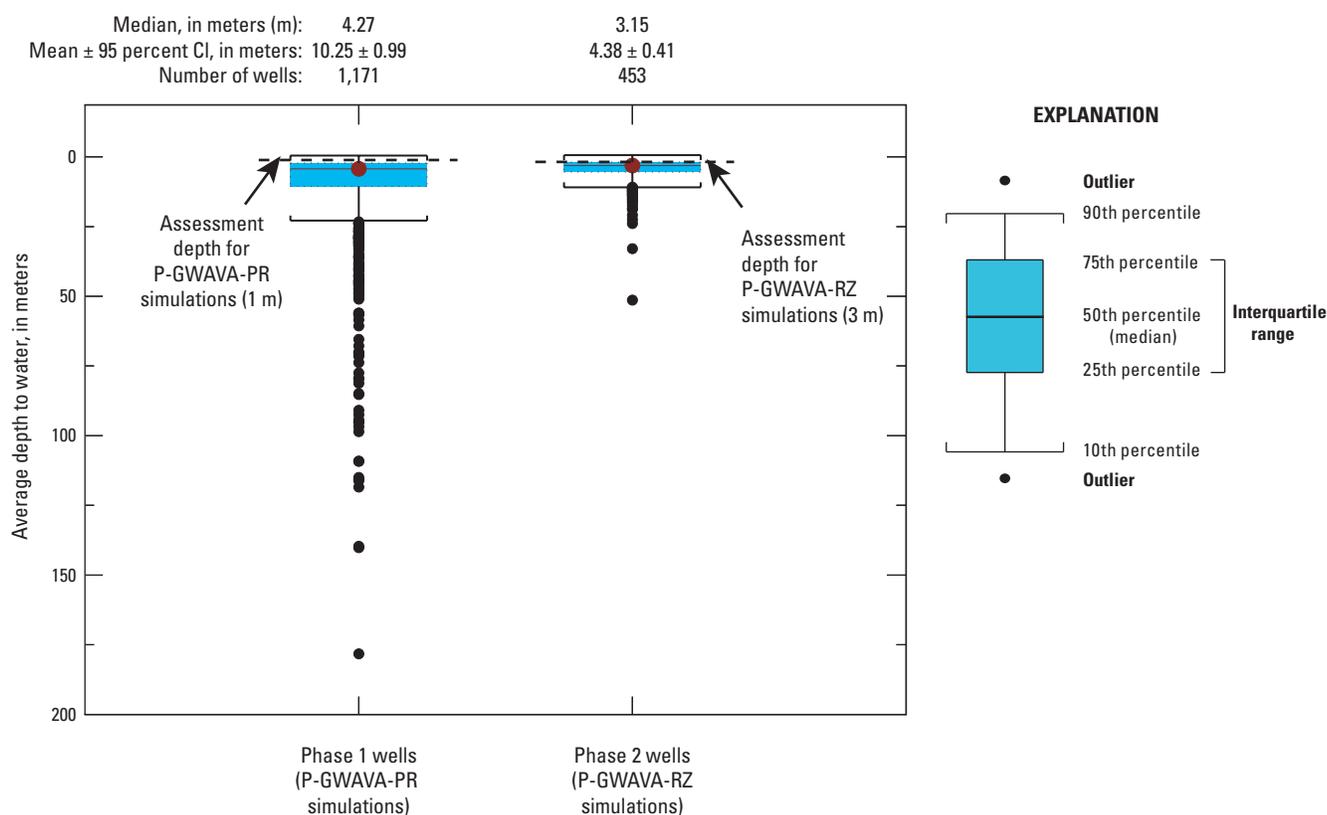


Figure 16. Average depths to water (DTW) at the sites examined in the conterminous United States (Phase 1) and in the 10 northernmost states in the Corn Belt (Phase 2) of the United States for this study, relative to the assessment depths used for the P-GWAVA simulations during each study phase. The number of Phase 1 wells shown is less than the total of 1,224 (table 1) because DTW data were not available for some sites. (CI, confidence interval.)

Irrigation

Phase 1

PRZM includes an option (Carsel and others, 1998) to simulate the automatic application of irrigation water whenever the soil water content drops below a user-specified threshold, defined as the sum of the wilting point and a specified fraction of the *available water capacity* (AWC, calculated as the water content at field capacity minus the water content at the wilting point). When the water content within a given layer drops below this threshold, irrigation is applied at a specified rate until the water content exceeds the threshold value. For the P-GWAVA-PR simulations, a threshold equal to 40 percent of AWC was used (table 14). Initially, an irrigation rate of 1.0 in/hr was used for all sites, a value that was close to the midrange given by Carsel and others (1998) for sprinkler irrigation of a variety of soil types. However, because PRZM applies irrigation only in 1-day increments, use of this rate often led to the generation of excessive runoff, a circumstance not likely for most settings where irrigation is used. Consequently, the rate for all irrigated sites was decreased to 0.1 in/hr, resulting in substantially less runoff than when an irrigation rate of 1.0 in/hr was used.

Because irrigation is not applied uniformly across the Nation, information on the prevalence of nearby irrigation was collected at most of the study sites (Lapham and others, 1995; Koterba, 1998) at the time of sampling (1992–2006). However, to adhere to the design objective of using only sources of input data that are available nationwide, these data were not used to determine which sites were irrigated during Phase 1. Instead, data from the NRI (Natural Resources Conservation Service, 2004) were combined with data from the EPA National Land-Cover Database, or NLCD (U.S. Environmental Protection Agency, 2007) to ascertain the prevalence of irrigation near each of the Phase 1 sites. For each location, data from the NRI (aggregated to the county level, rather than by NRI map unit) and NLCD were used to obtain an estimate of f_i , the fraction of the surrounding agricultural land that was presumed to be irrigated (Naomi Nakagaki, U.S. Geological Survey, written commun., July 2003). This parameter was then used to estimate the likelihood with which each site may have been irrigated at the time of sampling—and thus to determine whether irrigation would be applied during the P-GWAVA-PR simulation for that location.

For each study site, a value of f_i was computed using the following equation:

$$f_I = \frac{f_{I,1992}}{f_{ag}} \quad (8)$$

grains, or left fallow), estimated from the NLCD data (U.S. Environmental Protection Agency, 2007).

where

$f_{I,1992}$ is the fraction of the surrounding area irrigated in 1992, based on NRI data (Natural Resources Conservation Service, 2004); and
 f_{ag} is the fraction of agricultural land in the county (that is, farmland planted in row crops, orchards, vineyards, pasture, hay or small

Because of uncertainties in the NRI and (or) NLCD data, the estimates of f_I obtained from equation 8 sometimes exceeded unity. In such cases, f_I was adjusted to unity, assuming that only agricultural irrigation was recorded by the NRI. Underestimates of f_I , however, were less obvious, and therefore could be neither detected nor corrected. The resulting distribution of the prevalence of irrigation in agricultural areas near each of the Phase 1 study sites across the Nation is shown in figure 17.

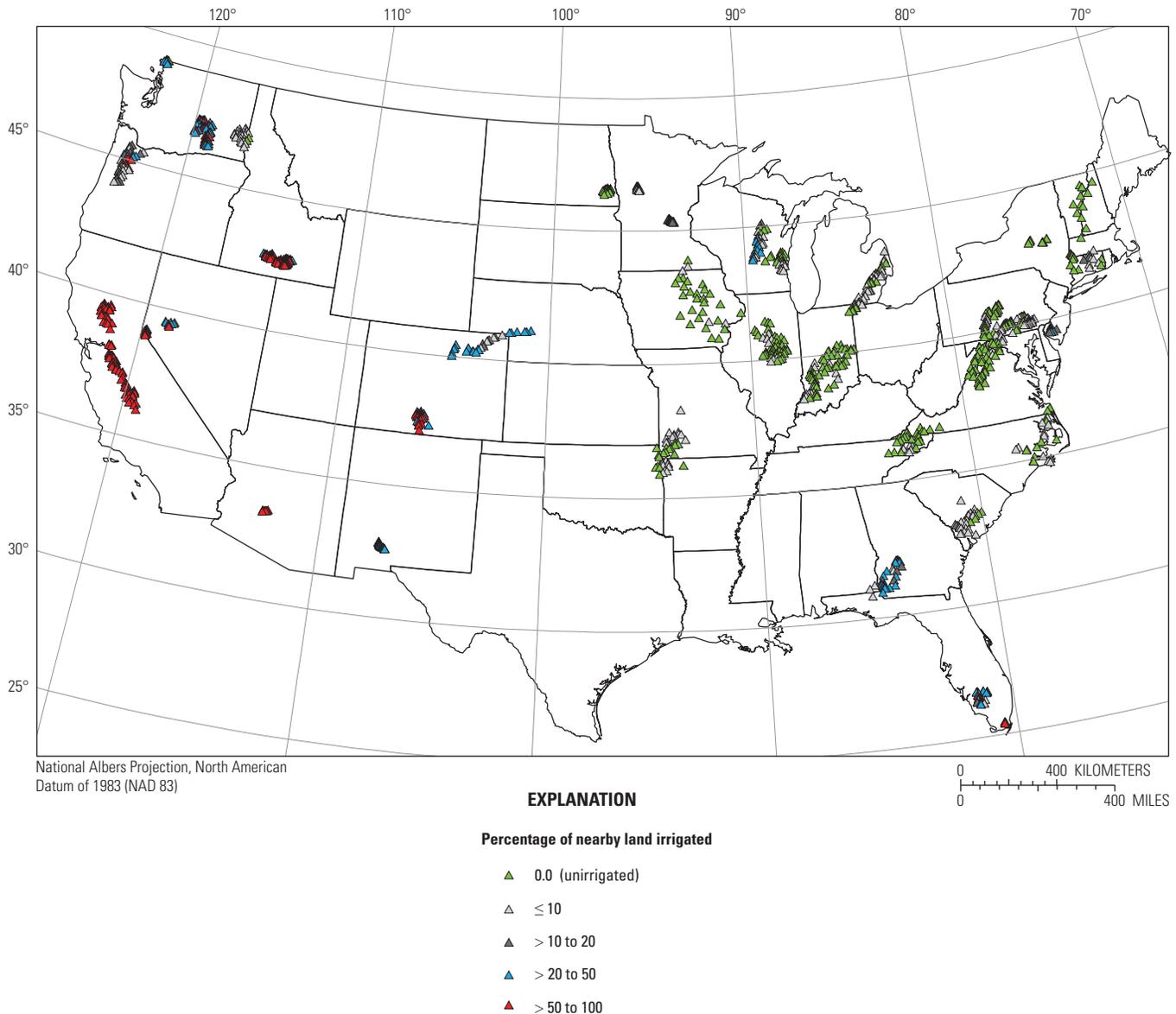


Figure 17. Prevalence of irrigated agricultural areas near each P-GWAVA-PR (Phase 1) study site in the conterminous United States in 1992. Computed from data from the Natural Resources Conservation Service (2004) and National Land Cover Dataset (U.S. Environmental Protection Agency, 2007) using equation 8.

To account for the effects of irrigation in comparing the atrazine concentrations simulated by the P-GWAVA-PR model with the concentrations measured in shallow groundwater, two sets of simulations were carried out at each site—one set that simulated irrigation for all components of interest and one that did not simulate irrigation for any of the components. One of the two sets of simulations was selected for the site by generating a random number between 1 and 100 (using a Microsoft Excel® spreadsheet), dividing by 100, and comparing the result to the f_i value computed for that site with equation 8. If the resulting fraction was less than or equal to the f_i value for the site, the results from the simulations that included irrigation were used; otherwise, the results from the simulations without irrigation were used.

Phase 2

RZWQM simulates irrigation using one of four application methods: sprinkler, furrow, flood, or drip. The model applies irrigation water either at fixed time intervals on specific dates or in response to specified degrees of soil-water depletion in the root zone (Ahuja and others, 2000; Agricultural Research Service, 2010; Bartling and others, 2011). The P-GWAVA-RZ simulations used furrow irrigation, applied in response to particular soil-moisture thresholds for initiating and ending irrigation (rather than on a specific date or according to a fixed schedule) over the course of the 100-day growing season. To avoid applying excessive amounts of water, a 3-day minimum time interval between successive irrigation events was specified. Additional details on the approach used to simulate irrigation with the P-GWAVA-RZ model are provided in table 14.

Runoff

Phase 1

PRZM simulates runoff flux (Q_{sw}) using the curve number equation originally introduced by the Soil Conservation Service (SCS, now known as the NRCS), and modified to the following form by Carsel and others (1998):

$$Q_{sw} = \frac{(P + SM - [0.2 * S])^2}{(P + SM + [0.8 * S])} \quad (9)$$

where

- Q_{sw} is the runoff flux, in centimeters per day;
- P is precipitation, in centimeters per day;
- SM is snowmelt, in centimeters per day; and
- S is the watershed retention parameter, in centimeters per day.

Snowmelt (SM) is estimated using the following equation:

$$SM = C_M * T$$

where

- C_M is the degree-day snowmelt factor, in centimeters per degree Celsius per day; and
- T is temperature, in degrees Celsius.

The watershed retention parameter (S) is estimated in the following manner:

$$S = (1,000/RCN) - 10$$

where

- RCN is the SCS (NRCS) runoff curve number, in days per centimeter.

The degree-day snowmelt factor (C_M) was approximated using the average value of this parameter provided by Carsel and others (1998) for open areas of the United States. The RCN value used by these equations is a function of the *soil hydrologic group* and the surface condition of the soil. The NRCS classifies soils into four soil hydrologic groups that vary in permeability from the well-drained sands and gravels of group A to the poorly drained, clay soils of group D. Group D soils also may exhibit high swelling potential and (or) be underlain by impervious layers (Natural Resources Conservation Service, 2007b). For the P-GWAVA-PR simulations, three surface conditions were used at different times of year: *fallow* prior to crop planting, *cropping* during crop growth, and *post-harvest* (that is, with a residue cover). However, following the suggestion of Carsel and others (1998) for corn grown without conservation tillage—and in the absence of consistent, nationwide data on the spatial distribution of conservation tillage practices at the time—the RCN values for the cropping and post-harvest stages of corn cultivation were presumed to be identical.

The data associated with each STATSGO map unit provide percentages of each hydrologic group present, rather than a single hydrologic group. Consequently, a stochastic procedure was used to select a set of RCN values randomly at each site of interest. The percentage of each of the four soil hydrologic groups present within a 500-m radius of each site was determined (David Wolock, U.S. Geological Survey, written commun., March 2000) and a random-number generator was used to select a single hydrologic group for each site, the likelihood of selecting a given hydrologic group being proportional to its percentage within the 500 m radius surrounding the site. For example, a hydrologic group occupying 40 percent of the 500-m circle surrounding a given site had a 40 percent chance of being assigned to that site. Data from Carsel and others (1998) were then used to select a set of RCN values for the site (that is, one value for fallow conditions and a second value for cropping/post-harvest conditions) on the basis of its assigned hydrologic group.

Phase 2

During Phase 2, runoff was generated by RZWQM whenever the rate of water delivery from precipitation and (or) irrigation exceeded the rate of infiltration. RZWQM computes the rate of runoff as the difference between the rate of water delivery to the land surface (from precipitation and [or] irrigation) and the rate of infiltration (Ahuja and others, 2000).

Evapotranspiration

Phase 1

PRZM computes the rate of ET from estimates of PET which, in turn, are obtained either from measured pan evaporation data or, if such information is not available, from an empirical formula introduced by Hamon (1961). Pan evaporation data were not available on a nationwide basis for the Phase 1 simulation period (1986–95). However, the Penman-Monteith (PM) procedure (Allen and others, 1998) was selected to estimate PET, rather than the Hamon method embedded in PRZM, for several reasons.

First, in keeping with the P-GWAVA design objectives, the PM equation was preferred because it accounts for a broader range of processes and factors known to affect PET than do most other methods that have been proposed for estimating this parameter. In particular, whereas the Hamon equation estimates PET from saturated water vapor density (that is, absolute humidity) and the duration of daily sunshine (Hamon, 1961), the PM method uses temperature, solar radiation, humidity, wind speed, surface albedo, leaf conductance, canopy radiation extinction, canopy height, and leaf area data to estimate PET (Vörösmarty and others, 1998). Despite the relatively large number of variables for which data are required with the PM method, national-scale data sources or estimation procedures were available for all of its parameters.

A second reason that PET rates predicted by the PM method were used for the P-GWAVA-PR simulations was that they have been found to be in close agreement with values measured in lysimeters beneath alfalfa and a variety of grasses in 11 locations across the United States, Denmark, Zaire, and Australia (Allen and others, 1989). Although Vörösmarty and others (1998) observed closer agreement with the results from global-scale water-balance calculations for the Hamon method than for the PM method, the agreement reported by Allen and others (1989) between PM-based estimates of ET and those obtained from direct, field-scale measurements was deemed to be more important for the purpose of simulating water movement in the vadose zone beneath specific locations for the P-GWAVA project. Additionally, the PM method has been recommended by the United Nations Food and Agriculture Organization (Allen and others, 1998) and the American Society of Civil Engineers (Ahuja and others, 2000) for estimating ET.

Phase 2

The method used by RZWQM to estimate PET during Phase 2, the extended Shuttleworth-Wallace, or eSW model (table 14), represents a further refinement of the PM approach, broadening the scope of the method in at least three major ways. First, although the PM method simulates the crop canopy as a single, uniform layer (a “single big leaf”), the eSW model estimates changes in ET as the area of soil covered by the crop canopy increases over time during the growing season. Second, whereas the PM method designates the land surface as the sole source or sink for heat, the eSW model simulates heat fluxes separately for the crop canopy and the soil surface. Finally, the eSW model simulates the effect of crop residue on heat and water fluxes at the soil surface, a factor not accounted for by the PM approach (Ahuja and others, 2000).

Timing and Intensity of Agrichemical Applications

Information regarding the precise timing of agrichemical applications was not available on a nationwide basis at the time of this study. Consequently, atrazine (during both study phases) and nitrogen (during Phase 2) were assumed to have been applied annually at every site, following spring planting.

Atrazine

Results from previous studies have indicated that the likelihood of detecting pesticides in groundwater is positively related to the intensity of their use (Barbash and Resek, 1996; Kolpin and others, 1998, 2000; Barbash and others, 1999, 2001; Stackelberg and others, 2006, 2012; Åkesson and others, 2013). Consequently, the spatial variability of atrazine concentrations in shallow groundwater may be affected by the spatial variability (if any) of atrazine applications at the land surface. The spatial variations in the intensities of atrazine application (figs. 1 and 2) reflect variations in the rate of atrazine application among different crops and counties, as well as variations in the percentage of each crop to which atrazine is applied in different counties. (*Use intensity* and *application intensity* refer to areally averaged rates of atrazine delivery to the land surface, to distinguish them from actual application rates, which are rarely known.) During some years, however, the actual rates of atrazine application to individual fields may be similar to that recommended on the product label, and thus more spatially uniform than the use intensities shown in figures 1 and 2. Groundwater flow in most hydrogeologic settings (other than areas with particularly large subsurface conduits, such as karst terranes, lava tubes, or highly fractured rock) tends to be more laminar than surface-water flow, and therefore less well mixed. Consequently, small-scale spatial variations in pesticide concentrations caused by spatial variations in application intensity are likely to persist over longer distances along subsurface flow paths than in surface water.

To investigate the potential effects of the spatial variability of atrazine applications on the geographic patterns of agreement between the simulated and measured concentrations of the herbicide in groundwater, two approaches for quantifying the rates of atrazine input at the land surface were examined during each phase of this study. One approach involved using areally averaged, site-specific estimates of atrazine use intensity for each site of interest (figs. 1 and 2); a second approach involved the use of a single, uniform application rate in all locations.

The areally averaged intensities of atrazine use were estimated in each location using a parameter that could be computed for any agricultural setting in the United States, namely, the ratio of the estimated amount of the herbicide that was applied for agricultural purposes in the county where the site was located to the estimated area of agricultural land in the county. These site-specific estimates of use intensity were calculated at each study site of interest using procedures introduced by Thelin and Gianessi (2000). For every county in which one or more of the sites were located, the intensity of atrazine use was estimated using the following formula:

$$U_{atr,i} = \frac{\sum_{j=1}^N (AppRate)_{i,j} * (CropArea)_{i,j} * [(%AcresTreated)_{i,j} / 100]}{(TotalAgriculturalLand)_i} \quad (10)$$

where

- $U_{atr,i}$ is the atrazine use intensity in county i , in kilograms of active ingredient per hectare;
- N is the total number of major crops to which atrazine was applied in the state between 1995 and 1998 (Gianessi and Marcelli, 2000), including (in descending order of use intensity) corn, sorghum, summer fallow land, sugar cane, sweet corn, sod, other hay, and seed crops, but excluding any greenhouse, ornamental plant, or post-harvest applications;
- $(AppRate)_{i,j}$ is the average annual rate of atrazine application per unit area of crop j , in kilograms of active ingredient per hectare, between 1995 and 1998 in the state where county i is located (Gianessi and Marcelli, 2000);
- $(CropArea)_{i,j}$ is the total area of crop j harvested in county i , in hectares, computed from the 1997 Census of Agriculture (U.S. Department of Agriculture, 1999);
- $(%AcresTreated)_{i,j}$ is the average percentage of acres planted in crop j to which atrazine was applied between 1995 and 1998 in the state where county i is located (Gianessi and Marcelli, 2000); and
- $(TotalAgriculturalLand)_i$ is the total area of agricultural land mapped in county i , in hectares, derived from the 30-meter resolution 1992 National Land Cover Database (Vogelmann and others, 2001) enhanced by Nakagaki and others (2007), and including land classified as row crops, small grains, fallow land, pasture/hay, and orchards/vineyards/other.

The *active ingredient* (a.i.) is a chemical included in a commercial pesticide formulation to kill or otherwise control the target organism (for example, atrazine). Pesticide application rates are typically expressed in terms of the amount of active ingredient applied per unit area, rather than the amount of product applied per unit area, because commercial pesticide products typically contain other ingredients, known as *adjuvants* (often referred to as “inert ingredients”), that are added to improve the effectiveness of the active ingredient. Another reason for expressing application rates in this manner is that commercial pesticide products often contain more than one active ingredient.

Equation 10 was used to compute the atrazine use intensities in agricultural settings for the Phase 1 and Phase 2 study areas (figs. 1 and 2, respectively). Variations in atrazine use intensity were substantial among the locations examined across the country (fig. 18). Although data on atrazine use intensities have been compiled for circular areas of 500-m radius surrounding each of the sites examined for this study (for example, Stackelberg and others, 2012), the county-based values computed with equation 10 were used instead, in accord with the design objective of focusing solely on input data that were available for all locations throughout the conterminous United States.

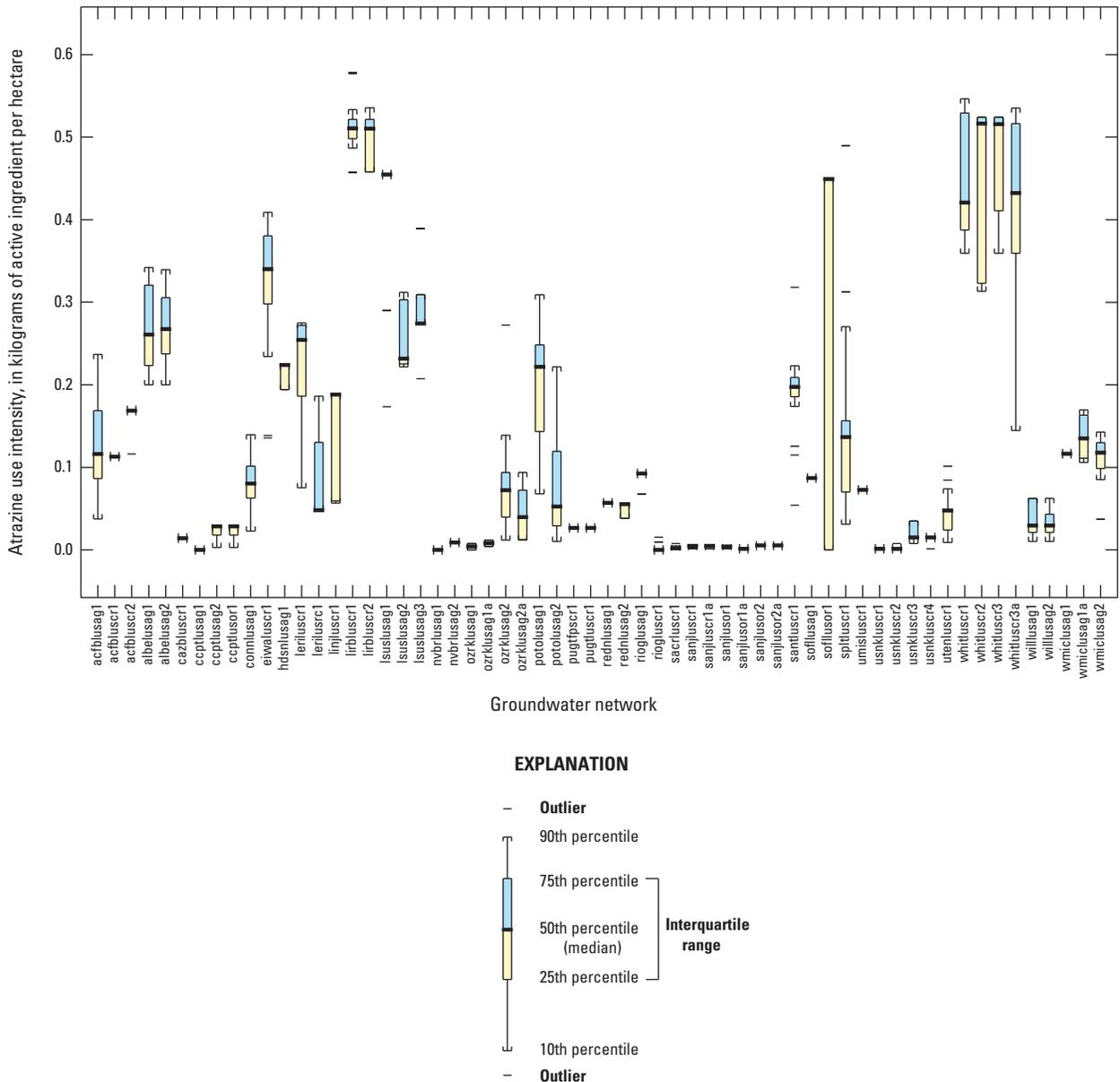


Figure 18. Variations in atrazine use intensity on agricultural land among sites in the groundwater networks examined in the conterminous United States for Phase 1 of this study, 1992–98. Study site locations are shown in figure 1. Descriptions of groundwater networks are provided in appendix C.

The second approach for quantifying the rates of atrazine input at the land surface for this study involved using a spatially uniform value of 2 kilograms of active ingredient per hectare (kg a.i./ha) in all locations of interest. This application intensity represented the median among the atrazine application rates used by 18 field studies of atrazine behavior in the subsurface under corn cultivation (Foy and Hiranpradit, 1989; Sophocleous and others, 1990; Steenhuis and others, 1990; Adams and Thurman, 1991; Frank and others, 1991; Hall and others, 1991; Kalkhoff and others, 1992; Wauchope and others, 1993; Gish and others, 1994; Jayachandran and others, 1994; Sadeghi and Isensee, 1994; Kumar and others, 1998; Baer and Calvet, 1999; Bayless, 2001; Capel and Larson, 2001; Hyer and others, 2001; Malone and others, 2001b, 2004c). These values ranged from 0.8 kg a.i./ha (Frank and others, 1991) to 8.5 kg a.i./ha (Malone and others, 2004c). Most of these rates are consistent with the range of values (0.3 to 3.0 kg a.i./ha) reported for agricultural areas of the United States by the USDA's National Agricultural Statistics Service (Gail Thelin, U.S. Geological Survey, written commun., August 2008), the maximum allowable rate of 2.8 kg a.i./ha per year established by the EPA for corn and sorghum in 1992 (U.S. Environmental Protection Agency, 2003), and the rate of 2 kg a.i./ha used for a large-scale simulation study carried out for the State of Iowa by Eason and others (2004).

During Phase 2, a preliminary set of P-GWAVA-RZ simulations using the areally averaged atrazine application intensities (computed using equation 10) resulted in predicted atrazine concentrations that were less than the reporting limits for the herbicide at all of the sites examined. Because atrazine was detected in shallow groundwater at many of these sites—and given the assumption that the concentrations of any surface-derived contaminant in the vadose zone are most likely to be greater than or similar to those in shallow groundwater beneath the same location—the RZWQM simulations may have underestimated the amounts of solute moving through the soil column. Were this the case, it would have been consistent with the observation by Nolan and others (2010) that in some settings, especially where macropore flow is significant, RZWQM appears to underestimate the rate of transport of nitrate and other conservative solutes (such as bromide) through the vadose zone. To obtain simulated atrazine concentrations that were more closely aligned with those measured in the underlying groundwater during Phase 2, higher intensities of simulated atrazine application were required. Consequently, the final set of P-GWAVA-RZ simulations carried out for Phase 2 used the uniform atrazine application intensity of 2 kg a.i./ha at all sites, a value that was higher than the areally averaged use intensities shown in [figure 2](#) for the Phase 2 study area (0–1.0 kg a.i./ha). Scaling the areally averaged atrazine use intensities ([fig. 2](#)) to align more closely with allowed application rates was not implemented because it may have produced rates of atrazine use exceeding those that were actually applied to the land.

This would have precluded the completion of one aspect of the Phase 2 analysis, in which the proportion of the applied atrazine that the P-GWAVA-RZ model predicted to have passed the 3-m assessment depth—as either unreacted atrazine or DEA—was computed for the 5-year simulation period.

Nitrogen Fertilizers

Although the formation, transport, and fate of nitrate were not simulated during Phase 1, these processes were examined for the P-GWAVA-RZ simulations in Phase 2 of this study. Because of uncertainties regarding variations in its nitrogen content among different regions of the country, manure was not included as a source of applied nitrogen for these simulations. Instead, applications of nitrogen were presumed to have occurred solely through the use of synthetic nitrogen fertilizer. The amounts of synthetic nitrogen fertilizer applied at each site were computed using a method selected from among several state-specific algorithms described by Ahuja and others (2000) for estimating the most appropriate amount of nitrogen to use for growing corn. Of the five approaches described by Ahuja and others (2000), the method recommended by the University of Missouri Soil Testing Laboratory was selected for the initial Phase 2 simulations because it could be implemented without the use of locally derived input data. According to this method, the recommended nitrogen fertilizer application rate is computed as an empirical function of the number of seeds planted per acre, the intended crop yield (in bushels per acre), the mass-based fraction of OM in soil, and an adjustment factor to account for the effect of soil OM and cation exchange on the crop of interest. The values and sources of the input data used for these calculations are presented in [table 14](#).

Estimating Physical and Chemical Property Values for Atrazine and Deethylatrazine

Values for many of the parameters used by PRZM and RZWQM to simulate the physical, chemical, and biological processes that affect the transport and fate of anthropogenic contaminants and their degradates in the hydrologic system have not been published for many of these compounds. In these situations, it is necessary to use one of various methods to estimate a value for the parameter and compound of interest (Barbash and others, 2009). For this study, the methods used to estimate these parameters for atrazine and DEA included quantitative structure-property relations (QSPRs), structure-reactivity relations (QSRRs), property-property relations (QPPRs), and medium-reactivity relations (QMRRs)—approaches that have been used for estimating the properties and reactivities of pesticides and other synthetic organic compounds for at least four decades (for example, Walker, 1974; Hansch and Leo, 1979; Lyman and others, 1990; Roberts and others, 1993; Reinhard and Drefahl, 1999; Schüürmann and others, 2006; Capel and others, 2008).

Partitioning and Mass Transfer of Atrazine and Deethylatrazine

Both PRZM and RZWQM use K_{oc} to characterize the partitioning of organic compounds between soil and water, and the Henry's law constant (K_H) to quantify partitioning between water and air. (However, air-water partitioning was not simulated during Phase 1.) Additionally, RZWQM uses the octanol-water partition coefficient (K_{ow}) to quantify plant uptake of pesticide compounds (Ahuja and others, 2000). Because K_H is more sensitive to temperature variations than either K_{ow} or K_{oc} , temperature corrections were applied to K_H for atrazine and DEA during Phase 2, but not to their K_{ow} or K_{oc} values. RZWQM does not adjust any partitioning or mass-transfer parameters for variations in temperature, however, so these corrections for K_H were carried out externally.

Henry's Law Constant (Phase 2 only)

For atrazine, a K_H value of 2.88×10^{-4} Pascal-cubic meter per mole (Pa-m³/mol) at 25 °C, reported by Mackay and others (1997), was used. Because published K_H values for DEA were not available, an estimate of 7.29×10^{-4} Pa-m³/mol was computed for this parameter by dividing the vapor pressure for DEA at 25 °C (0.0124 Pascals, reported by Neely and Blau, 1985) by its water solubility (17 mol/m³, measured at 22 °C by Mills and Thurman, 1994). The influence of temperature on K_H for atrazine and DEA was accounted for during Phase 2 by using equation 11, adapted from Mackay and others (2000), to adjust the value of K_H for each compound from 298.15 K (25 °C, the temperature for which the K_H value from Mackay and others [1997] was reported) to the average air temperature in May (T_{May}) at each site:

$$K_{H,T_{May}} = K_{H,25C} * \exp \left[\left(\frac{\Delta H_s}{R} \right) * \left(\frac{1}{298.15 K} - \frac{1}{T_{May}} \right) \right] \quad (11)$$

where

- $K_{H,T_{May}}$ is the Henry's law constant at T_{May} ;
- $K_{H,25C}$ is the Henry's law constant at 25 °C (298.15 K);
- ΔH_s is the enthalpy change for transfer from gaseous to solution phase, in kilojoules per mole (kJ/mol); and
- R is the universal gas constant (0.008314 kJ/mol-K).

Because no published ΔH_s values were available specifically for either atrazine or DEA, a value of 47 kJ/mol, computed by Staudinger and Roberts (2001) from K_H data for 197 organic compounds, was used for this parameter. Given the spatial variability of T_{May} within the Corn Belt (fig. 15), the use of equation 11 produced values of K_H that ranged from 0.8×10^{-4} to 4.1×10^{-4} Pa-m³/mol across the Phase 2 study area.

Octanol-Water Partition Coefficient (Phase 2 only)

The data compilation by Mackay and others (1997) included a recommended K_{ow} value for atrazine (562), but none for DEA. (The latter compound was not included among those examined by Mackay and others [1997].) A K_{ow} value for DEA was estimated for the present work by adjusting the atrazine value from Mackay and others (1997) to account for the structural differences between the two compounds. This was accomplished using K_{ow} values computed by Finizio and others (1991) for the two compounds from their respective *retention times* in a reversed-phase, high-performance liquid chromatography (RP-HPLC) column (that is, the amount of time compounds require to migrate through the column under specified conditions). The data reported by Finizio and others (1991) appear to represent the only pair of K_{ow} values for atrazine and DEA that have been measured to date with the same method during the same study. For Phase 2 of the present study, these two values were used with equation 12 to estimate K_{ow} for DEA by scaling the value recommended for atrazine by Mackay and others (1997):

$$\begin{aligned}
 K_{ow}[\text{DEA}] &\approx K_{ow, M+97}[\text{atr}] * \left(\frac{K_{ow, meas, F+91}[\text{DEA}]}{K_{ow, meas, F+91}[\text{atr}]} \right) \\
 &= (562) * \left(\frac{32.4}{407} \right) = 44.6
 \end{aligned}
 \tag{12}$$

where

- $K_{ow}[\text{DEA}]$ is the K_{ow} value used for DEA for this study (dimensionless);
- $K_{ow, M+97}[\text{atr}]$ is the K_{ow} value recommended for atrazine by Mackay and others (1997), and used for the P-GWAVA-RZ simulations for this study;
- $K_{ow, meas, F+91}[\text{DEA}]$ is the K_{ow} value estimated for DEA by Finizio and others (1991) from measurements of its RP-HPLC retention time; and
- $K_{ow, meas, F+91}[\text{atr}]$ is the K_{ow} value estimated for atrazine by Finizio and others (1991) from measurements of its RP-HPLC retention time.

Adapted from the approach described by Barbash and others (2009), equation 12 represents a QSPR that is mathematically analogous to the structural fragment method described by Hansch and Leo (1979) and Lyman (1990) for estimating K_{ow} values. As such, it provides an estimate of the quantitative effect on K_{ow} of replacing the ethyl group in atrazine with a hydrogen atom. Finizio and others (1991) also estimated K_{ow} values for atrazine and DEA using the fragment method of Hansch and Leo (1979). Application of equation 12 in conjunction with these values yielded an estimated K_{ow} of 46.8 for DEA. The arithmetic average of the K_{ow} values obtained for DEA using the RP-HPLC retention time data from Finizio and others (1991) and estimated using the Hansch and Leo (1979) fragment method (that is, 45.7) was the value used for the P-GWAVA-RZ simulations.

Soil-Water Partition Coefficients

For both phases of this study, the partitioning of atrazine (and, during Phase 2, DEA) between soil and water was described using the well-known linear equilibrium sorption model, in which the soil-water partition coefficient (K_d), which is the ratio between the sorbed concentration (C_s) and the concentration in solution (C_{aq}), is presumed to be independent of either concentration:

$$K_d = \frac{C_s}{C_{aq}} \tag{13}$$

Individual values of K_d were computed, as milliliters per gram (mL/g) of soil, in each location of interest using a rearrangement of the equation first introduced by Hamaker and Thompson (1972) to define K_{oc} , that is,

$$K_d = f_{oc} * K_{oc} \tag{14}$$

Values of f_{oc} , in turn, were computed from the mass fraction of OM in the soil (f_{om} , calculated as %om/100 percent), under the assumption that soil OM, on average, is 58 percent carbon by weight (Chiou, 2002), and thus that:

$$f_{oc} = 0.58 * f_{om} \tag{15}$$

For Phase 1, equations 14 and 15 were used to compute a K_d value for each of the 1,224 sites examined, using the depth-averaged f_{om} value (fig. 7) in each location. For Phase 2, equations 14 and 15 were used to calculate a separate K_d value for every soil horizon in each SSURGO component for which a simulation was carried out.

The P-GWAVA-PR simulations used a K_{oc} value of 130 mL/g of organic carbon for atrazine, as this represented the median among 73 measured values taken from 25 published studies (Harris and Warren, 1964; Armstrong and others, 1967; Hance, 1967; Nearpass, 1967; Armstrong and Chesters, 1968; Grover and Hance, 1968; Hayes and others, 1968; Lavy, 1968; Obien and Green, 1969; Bouchard and Lavy, 1985; Gamerdinger and others, 1991; Kladvik and others, 1991; Pignatello and Huang, 1991; Sichani and others, 1991; Franklin and others, 1994; Laird and others, 1994; Mills and Thurman, 1994; Novak and others, 1994; Roy and Krapac, 1994; Mersie and Seybold, 1996; Seybold and Mersie, 1996; Guo and others, 1997; Moreau and Mouvet, 1997; Suzuki and others, 1998; Baer and Calvet, 1999). Use of this value—in conjunction with equations 14 and 15 and the STATSGO-derived f_{om} data for the individual sites—resulted in computed K_d values of 0.98 ± 0.07 mL/g for atrazine among the 1,224 locations examined during Phase 1.

For the initial set of P-GWAVA-RZ simulations during Phase 2, the recommended K_{oc} value of 100 mL/g from Mackay and others (1997) was used for atrazine. Using an approach analogous to that of equation 12, a K_{oc} value for DEA was obtained by scaling the atrazine value with the following equation:

$$K_{oc}[\text{DEA}] \approx K_{oc, M+97}[\text{atr}] * \left(\frac{K_{oc, meas, S+M96}[\text{DEA}]}{K_{oc, meas, S+M96}[\text{atr}]} \right) \quad (16)$$

$$= (100 \text{ mL/g}) * \left(\frac{80 \text{ mL/g}}{140 \text{ mL/g}} \right) = 57 \text{ mL/g}$$

where

$K_{oc}[\text{DEA}]$ is the initial K_{oc} value used for simulating DEA partitioning during Phase 2;

$K_{oc, M+97}[\text{atr}]$ is the K_{oc} value recommended for atrazine by Mackay and others (1997);

$K_{oc, meas, S+M96}[\text{DEA}]$ is the K_{oc} value measured for DEA by Seybold and Mersie (1996) on a clay loam soil; and

$K_{oc, meas, S+M96}[\text{atr}]$ is the K_{oc} value measured for atrazine by Seybold and Mersie (1996) on a clay loam soil.

The K_{oc} values measured and reported by Seybold and Mersie (1996) for atrazine and DEA were selected for use in equation 16 because compared with the other studies that have measured K_{oc} values for both compounds, the value measured by Seybold and Mersie (1996) for atrazine was closest to the

100 mL/g value recommended for the herbicide by Mackay and others (1997). As with equation 12, equation 16 represents a QSPR quantifying the apparent effect that replacing the ethyl group in atrazine with a hydrogen atom exerts on a chemical property of the molecule—in this case, its affinity for soil organic carbon. The observation that the estimated values of K_{ow} (equation 12) and K_{oc} (equation 16) for DEA were lower than their respective values for atrazine reflects the fact that an ethyl group is more hydrophobic than a hydrogen atom. This observation also is consistent with predictions from the fragment method of Hansch and Leo (1979), as well as with the observation that transport rates through soil are higher for DEA than for atrazine (Kruger and others, 1996b).

During Phase 2, preliminary model simulations using P-GWAVA-RZ led to predicted concentrations of atrazine and DEA that were lower than their reporting limits in nearly all locations, even after the spatially uniform intensity of atrazine application was used. These initial model simulations also demonstrated that, consistent with the findings of several previous modeling studies (for example, Boesten and van der Linden, 1991; Dubus and Brown, 2002; Dubus and others, 2003), the simulated concentrations were sensitive to the value of K_{oc} used. Consequently, the K_{oc} values for atrazine and DEA were adjusted downward to bring the simulated concentrations of the two solutes closer to those measured in groundwater, while ensuring that the adjusted K_{oc} values were consistent with the respective ranges reported by previous studies, and that the ratio between the values for the two solutes remained constant. As a result of this process, the K_{oc} values used for the initial set of simulations (100 mL/g for atrazine; 57 mL/g for DEA) were decreased by 75 percent (to 25 mL/g for atrazine and 14 mL/g for DEA) for the final set of P-GWAVA-RZ simulations (tables 4 and 14), leading to concomitant reductions in the K_d values computed using equation 14 for both compounds. (Measured K_{oc} values reported by previous studies range from 13 mL/g [Armstrong and others, 1967] to 1,680 mL/g [Roy and Krapac, 1994] for atrazine, and from 16 mL/g [Thurman and Fallon, 1996] to 2,700 mL/g [Bayless, 2001] for DEA.)

Wash-off Parameters for Crop Foliage and Residue (Phase 2 only)

RZWQM uses the following empirical relations, originally developed by Willis and others (1980), to estimate the concentrations of an applied pesticide on crop foliage and residue (C_f and C_r , respectively) as a function of the initial concentration ($C_{o(f)}$ and $C_{o(r)}$, respectively) and the amount of rain that falls on these materials within a given interval of time:

$$C_f = C_{o(f)} * F_{wo(f)} * e^{-P_{wo(f)} * I_R * \Delta t} \quad (17)$$

$$C_r = C_{o(r)} * F_{wo(r)} * e^{-P_{wo(r)} * I_R * \Delta t} \quad (18)$$

where

- $F_{wo(f)}$ is the wash-off coefficient for foliage, expressed as a fraction (Knisel and Davis, 1999);
- $F_{wo(r)}$ is the wash-off coefficient for residue, expressed as a fraction (Knisel and Davis, 1999);
- $P_{wo(f)}$ is the wash-off power for foliage, per millimeter (mm^{-1});
- $P_{wo(r)}$ is the wash-off power for residue, per millimeter;
- I_R is the rainfall rate during time interval Δt , in millimeters per hour; and
- Δt is the duration of rainfall, in hours.

Following the recommendation of Ahuja and others (2000), for each compound of interest, the values of F_{wo} were presumed to be identical for crop foliage and crop residue, as were the corresponding values for P_{wo} . Consequently, the subscripts “f” and “r” will not be used with these parameters for the remainder of this discussion.

The values of F_{wo} and P_{wo} used for atrazine (0.8 and 0.015 mm^{-1} , respectively) were obtained for the herbicide by Malone and others (2001b) through RZWQM calibration. (Although F_{wo} appears as a fraction in equations 17 and 18 [Knisel and Davis, 1999], it is expressed as a percentage when entered as an input parameter for RZWQM [Ahuja and others, 2000].) Both F_{wo} and P_{wo} appear to be positively related to water solubility (Ahuja and others, 2000). Because published values for F_{wo} and P_{wo} do not seem to be available for DEA, they were estimated for this study on the basis of the contrast in water solubility (S_w) between atrazine and DEA. In one of the few studies that measured S_w for both compounds, Mills and Thurman (1994) reported S_w values of 33.8 mg L^{-1} for atrazine and $3,200 \text{ mg L}^{-1}$ for DEA. Consequently, an F_{wo} value of 0.9 was selected for DEA because it was intermediate between the value of 0.8 reported by Malone and others (2001b) for atrazine and the value of 1.0 recommended by Ahuja and others (2000) for pesticides with water solubilities less than or equal to 10^6 mg L^{-1} . A value of P_{wo} was estimated for DEA using the following quantitative property-property relation (QPPR):

$$P_{wo}[\text{DEA}] \approx P_{wo, \text{M}+01}[\text{atr}] * \left(\frac{P_{wo}[S_w = 10^3 - 10^4]_{\text{A}+00}}{P_{wo}[S_w = 10 - 100]_{\text{A}+00}} \right) \quad (19)$$

$$= (0.015 \text{ mm}^{-1}) * \left(\frac{0.033 \text{ mm}^{-1}}{0.005 \text{ mm}^{-1}} \right) = 0.099 \text{ mm}^{-1}$$

where

- $P_{wo}[\text{DEA}]$ is the wash-off power estimated for DEA, per millimeter;
- $P_{wo, \text{M}+01}[\text{atr}]$ is the wash-off power, per millimeter, reported for atrazine by Malone and others (2001b);
- $P_{wo}[S_w = 10^3 - 10^4]_{\text{A}+00}$ is the wash-off power, per millimeter, assigned by Ahuja and others (2000) for compounds with water solubilities between 10^3 and 10^4 milligrams per liter; and
- $P_{wo}[S_w = 10 - 100]_{\text{A}+00}$ is the wash-off power, per millimeter, assigned by Ahuja and others (2000) for compounds with water solubilities between 10 and 100 milligrams per liter.

Although RZWQM simulates pesticide wash off from both crop foliage and crop residue, this process was expected to be relevant only for the crop residue because the application of atrazine was simulated to occur prior to crop emergence in the spring.

Mass Transfer Rates (Phase 2 only)

Kinetic Controls on Sorption

In addition to simulating the equilibrium partitioning of solutes between water and soil, RZWQM also accounts for the kinetics of adsorption and desorption through its use of two parameters, referred to as $Ek2$ and $Rk2$. The parameter $Ek2$ represents the ratio between the rate constants for adsorption and desorption (Liwang Ma, U.S. Department of Agriculture, written commun., December 2007), and is designated here as the quantity k_{ads}/k_{des} for greater clarity:

$$Ek2 \equiv \frac{k_{ads}}{k_{des}} = K_d * F_{ads} \quad (20)$$

where

- k_{ads} is the rate constant for adsorption;
- k_{des} is the rate constant for desorption; and
- F_{ads} is the fraction of sites on the soil surface that engage in slow, but reversible sorption (Ahuja and others, 2000).

Measured values of most of the parameters in equation 20 are scarce in the published literature, but a study by Guo and others (1997) of atrazine transport in water during miscible displacement through a column containing an unamended silt-loam soil provided estimates of K_d and F_{ads} . The

experiments were conducted at two pore-water velocities: a “slow” rate (approximately 1 cm/h) and a “fast” rate (approximately 5 cm/h). Using equation 20, the data from Guo and others (1997) for the “slow” and “fast” experiments yielded the following estimates, expressed in cubic centimeters per gram (cm³/g), for the ratio of k_{ads} to k_{des} :

$$\left(\frac{k_{ads}}{k_{des}}\right)_{slow} = K_d * F_{ads,slow} = (0.93 \text{ cm}^3/\text{g}) * (0.73) = 0.68 \text{ cm}^3/\text{g} \quad (21)$$

$$\left(\frac{k_{ads}}{k_{des}}\right)_{fast} = K_d * F_{ads,fast} = (0.93 \text{ cm}^3/\text{g}) * (0.67) = 0.62 \text{ cm}^3/\text{g} \quad (22)$$

Taking an average of the two results yielded the selected value for k_{ads}/k_{des} ($Ek2$) of 0.65 cm³/g for atrazine. Given the similarity of the structures of atrazine and DEA, the same value for this parameter also was used for DEA during the P-GWAVA-RZ simulations.

Data from the study by Guo and others (1997) were also used to estimate the RZWQM parameter referred to as $Rk2$, which represents the kinetic rate constant for desorption (Malone and others, 2004b), that is, k_{des} . Using data from the two soil column experiments conducted at different pore-water velocities, Guo and others (1997) reported values for a parameter referred to as a “first-order kinetic rate constant” for sorption. Dimensional analysis suggests that this parameter is equivalent to k_{des} , rather than k_{ads} . From their experiments, Guo and others (1997) estimated values for this parameter of 0.17 per hour (h⁻¹) and 0.06 h⁻¹ for the “fast” and “slow” velocities, respectively. Taking the average of the two values yielded the selected value of 0.12 h⁻¹ used for k_{des} ($Rk2$) for atrazine during the P-GWAVA-RZ simulations. Given the similarity of the structures of atrazine and DEA, and the apparent absence of published data for the degradate, a k_{des} ($Rk2$) value of 0.12 h⁻¹ was also used for DEA.

Solute Exchange Between Micropores and Mesopores

In addition to accounting for kinetic effects on sorption, RZWQM also simulates the exchange of pesticide compounds between micropores and mesopores during infiltration, using the following equation (Ahuja and others, 2000):

$$\frac{\delta C_{meso}}{\delta t} = D_d^{eff} (C_{micro} - C_{meso}) \quad (23)$$

where

- C_{meso} is the solute concentration in the mesopores, in micrograms per gram (µg/g) of soil;
- t is time, in hours;

- D_d^{eff} is the effective diffusion coefficient for micropore-macropore exchange, in square centimeters per hour (cm²/h); and
- C_{micro} is the solute concentration in the micropores (µg/g).

RZWQM does not simulate this process for nitrate because the model assumes instantaneous equilibrium between micropores and mesopores for this solute (Liwang Ma, U.S. Department of Agriculture, written commun., July 2011). The effective diffusion coefficient in equation 23 is calculated as follows (Ahuja and others, 2000):

$$D_d^{eff} = \frac{D_a}{1 + \frac{\rho_{b,sn} * K_{d,sn}}{\theta_{sn}}} \quad (24)$$

where

- D_a is the apparent diffusion coefficient in water (cm²/h);
- $\rho_{b,sn}$ is the bulk density of soil layer n , in grams per cubic centimeter (g/cm³);
- $K_{d,sn}$ is the distribution coefficient for soil layer n , in cubic centimeters of water per gram of soil (cm³/g); and
- θ_{sn} is the volumetric water content of soil layer n , in cubic centimeters of water per cubic centimeter of soil (cm³/cm³).

Thus, equation 24 adjusts the value of D_a to account for the influence of soil density, sorption and water content on the rate of solute exchange between micropores and macropores. The denominator in equation 24 is identical to what is commonly referred to as a retardation factor, or R (Freeze and Cherry, 1979).

The magnitude of D_a for a given solute is determined by the rate at which the molecule diffuses through aqueous solution, and the sinuosity, or *tortuosity* of the path along which it must travel, in this instance, between mesopores and micropores. Methods for determining the rates of diffusion of individual solutes in homogeneous aqueous solution, by either direct measurement or calculation, are well established (Tucker and Nelkin, 1990). A relatively extensive amount of research has also been carried out to understand the factors that control the rates of solute exchange between mobile and immobile waters in the subsurface (for example, van Genuchten and others, 1977; Nielsen and others, 1986; Kookana and others, 1993; Gerke and van Genuchten, 1996; Shaw and others, 2000; Jarvis and others, 2007a). Among the few studies that have explicitly examined the effects of pore size and (or) geometry on this process, however, the investigation by Shaw and others (2000) appears to be the only one that has provided a PTF for predicting the rates of exchange of a solute (in their case, bromide ion) between mobile and immobile water from soil properties for which SSURGO provides data.

As part of their study, Shaw and others (2000) examined the extent to which various soil properties were correlated (if at all) with several key parameters in the system of dual-domain equations introduced by van Genuchten and Wierenga (1976) to describe solute transport through porous media containing regions of mobile and immobile waters. One key parameter was the coefficient of mass transfer between mobile and immobile waters for bromide ion (α_{Br-}). Among the various soil properties examined (which included sand content, clay content, cation exchange capacity, extractable iron content, and the sizes of soil structures larger than individual particles), those with which α_{Br-} was significantly correlated were clay content and cation-exchange capacity normalized to clay content (CECg). As a result, both these properties were incorporated by Shaw and others (2000) into a PTF for predicting the mass-transfer coefficient for bromide.

Because data for both CECg and clay content were provided by SSURGO for most soil horizons examined during Phase 2 of the present study, the following quantitative medium-property relation (QMPR) was used to estimate a value of D_a for atrazine and DEA in each soil horizon for the P-GWAVA-RZ simulations:

$$D_{a,i,sn} = D_{w,i} * \left(\frac{\alpha_{Br-,sn}}{\alpha_{Br-,max}} \right) \quad (25)$$

where

- $D_{a,i,sn}$ is the apparent diffusion coefficient for the exchange of solute i between micropores and mesopores in soil layer n (cm^2/h);
- $D_{w,i}$ is the coefficient of molecular diffusion in homogeneous aqueous solution for solute i (cm^2/h);
- $\alpha_{Br-,sn}$ is the first-order rate constant for exchange of bromide ion between regions of mobile and immobile water in soil layer n , expressed in units of inverse minutes (min^{-1}), and estimated from clay content and CECg using the PTF from Shaw and others (2000); and
- $\alpha_{Br-,max}$ is the maximum value of the first-order rate constant for exchange of bromide ion between regions of mobile and immobile water (min^{-1}), estimated using the PTF from Shaw and others (2000).

Published values for D_w were not available for atrazine or DEA. As a result, D_w values of 0.0211 and 0.0237 cm^2/h for atrazine and DEA, respectively, were estimated from the molar volume of each molecule and the viscosity of water at 25 °C, using the equation of Hayduk and Laudie that was recommended for this purpose by Tucker and Nelkin (1990). Values of $\alpha_{Br-,sn}$ were computed using the following, exponential form of a corrected version of the PTF from Shaw and others (2000):

$$\alpha_{Br-,sn} = \exp \left\{ 4.51 - \left[0.010 * \left(\% \text{clay}_{sn} \right)^2 \right] - \left[0.065 * \text{CECg}_{sn} \right] \right\} \quad (26)$$

where

- $\% \text{clay}_{sn}$ is the weight percentage of clay in soil layer n (from SSURGO); and
- CECg_{sn} is the cation-exchange capacity for soil layer n , in milliequivalents per 100 grams of clay ($\text{meq}/100 \text{ g clay}$), calculated from CEC7 (that is, the value of CEC at pH 7, also provided by SSURGO) and $\% \text{clay}$.

Equation 26 incorporates the correction of an error in the published version of this equation, in which the coefficients 0.010 and 0.065 were inadvertently switched (Professor Joey Shaw, Auburn University, written commun., July 2011). For soil horizons for which no CEC data were provided by SSURGO, values of $\alpha_{Br,sn}$ were computed using the median CECg value among all of the soils used by Shaw and others (2000) to develop equation 26. Finally, $\alpha_{Br,max}$ was computed by setting %clay_{sn} and CECg_{sn} in equation 26 to their minimum values among the soil horizons examined for this study (that is, %clay = 1.0%; CECg = 7.87 meq/100 g clay), yielding a $\alpha_{Br,max}$ value of 54.0 min⁻¹.

Figure 19 illustrates the manner in which $D_{a,sn}$ for atrazine varied as a function of %clay and CECg among the 1,657 soil horizons at the Phase 2 study sites for which SSURGO provided data for both parameters. (Because the D_w values computed for atrazine and DEA were so similar, the corresponding plots for DEA exhibited distributions that were identical to the distributions shown for atrazine, but the $D_{a,sn}$ values were about 12 percent greater for DEA than the values for atrazine.) The data shown in figure 19 indicate that most of the $D_{a,sn}$ values computed for atrazine (and, by extension, for DEA) used values of %clay and CECg that were within the range of values used by Shaw and others (2000) to construct the PTF from which $\alpha_{Br,sn}$ (equation 26), and thus $D_{a,i,sn}$ (equation 25), were estimated.

Atrazine and Deethylatrazine Transformation Rates

The disappearance of atrazine was simulated during Phase 1 of this study, but not the formation, transport, or fate of any of its transformation products. During Phase 2, however, the production of DEA (from atrazine) and its disappearance over time, as well as the disappearance of atrazine, were simulated. For this discussion, the term *disappearance* is used to refer to the aggregate influence of all processes, either biological or abiotic, that convert a compound to one or more transformation products, or *degradates*.

An extensive body of research over the past four decades has elucidated the influence of various physical, chemical, and biological factors on the mechanisms and rates of pesticide transformation in the hydrologic system (Barbash, 2007). To account for several of these effects, different approaches were used for the two phases of this investigation (table 14). During Phase 1, adjustments were made to account for the effect of temperature on the rate of atrazine disappearance in the subsurface. The Phase 2 simulations adjusted the rates of disappearance of atrazine and DEA for temperature variations, accounted for the influence of soil moisture and depth within the soil column on these rates, and adjusted for the effects of temperature, soil OM, and sand content on the rate of conversion of atrazine to DEA.

Atrazine and Deethylatrazine Transformation in the Hydrologic System

Both atrazine and DEA are known to undergo transformation by several mechanisms in soils. As indicated in figure 20, the initial steps in these transformations for both compounds commonly involve either dealkylation or hydrolysis. In the absence of light, atrazine dealkylation (which results in the formation of either DEA or deisopropyl atrazine) occurs primarily through biotransformation, rather than through abiotic processes (Erickson and Lee, 1989). By contrast, atrazine hydrolysis is an abiotic process that does not require microbial assistance; however, the rate of this reaction has been shown to be substantially higher in non-sterile soils than in sterile soils (Erickson and Lee, 1989; Mandelbaum and others, 1993; Rice and others, 2004; Krutz and others, 2008). The atrazine transformation products displayed in figure 20 are also known to undergo several additional reactions in situ that are not shown (Erickson and Lee, 1989; Fenner and others, 2003).

Although several of the reactions shown in figure 20 may be either photochemically driven or microbially mediated, the product yields shown in the figure represent the percentages of reacted compound that have been known to form the designated product in non-sterile soils through *thermal* (that is, non-photochemical) reactions. The product yields were computed from the results reported by between one and nine studies for each reaction, but did not control for the effects of variations in soil temperature, soil OM or pH. Additionally, the yields were not corrected for *microbial adaptation*, that is, increases in the rate of biotransformation that may occur in response to repeated applications of the compound, a phenomenon that has been reported for atrazine by several previous studies (for example, Zablotowicz and others, 2007; Krutz and others, 2008, 2010a, 2010b). The product yields from individual compounds in the figure sum to less than 100 percent because several other products (for example, bound residues, more polar degradates, and so forth) were not accounted for.

In the absence of light, the dealkylation reactions shown in figure 20 appear to require oxic conditions (Nair and Schnoor, 1992; Papiernik and Spalding, 1998; Rügge and others, 1999), presumably because they involve the oxidation of alkyl carbons (to form carbon dioxide). By contrast, hydrolysis does not involve a change in oxidation state, and thus may take place under either oxic or anoxic conditions. Following the approach of McMahon and Chapelle (2007), the term *oxic* is used herein to denote an aqueous environment where dissolved oxygen is detected (at a concentration equal to or greater than 0.5 mg/L), and the term *anoxic* denotes conditions where the dissolved oxygen concentrations are low enough to allow denitrification, iron reduction, manganese reduction and (or) methanogenesis to take place (typically less than 0.5 mg/L). The terms *aerobic* and *anaerobic*, respectively, are also frequently used to describe these two conditions, but are used herein only to refer to the types and activities of microorganisms that are predominant in these environments, not the geochemical conditions themselves.

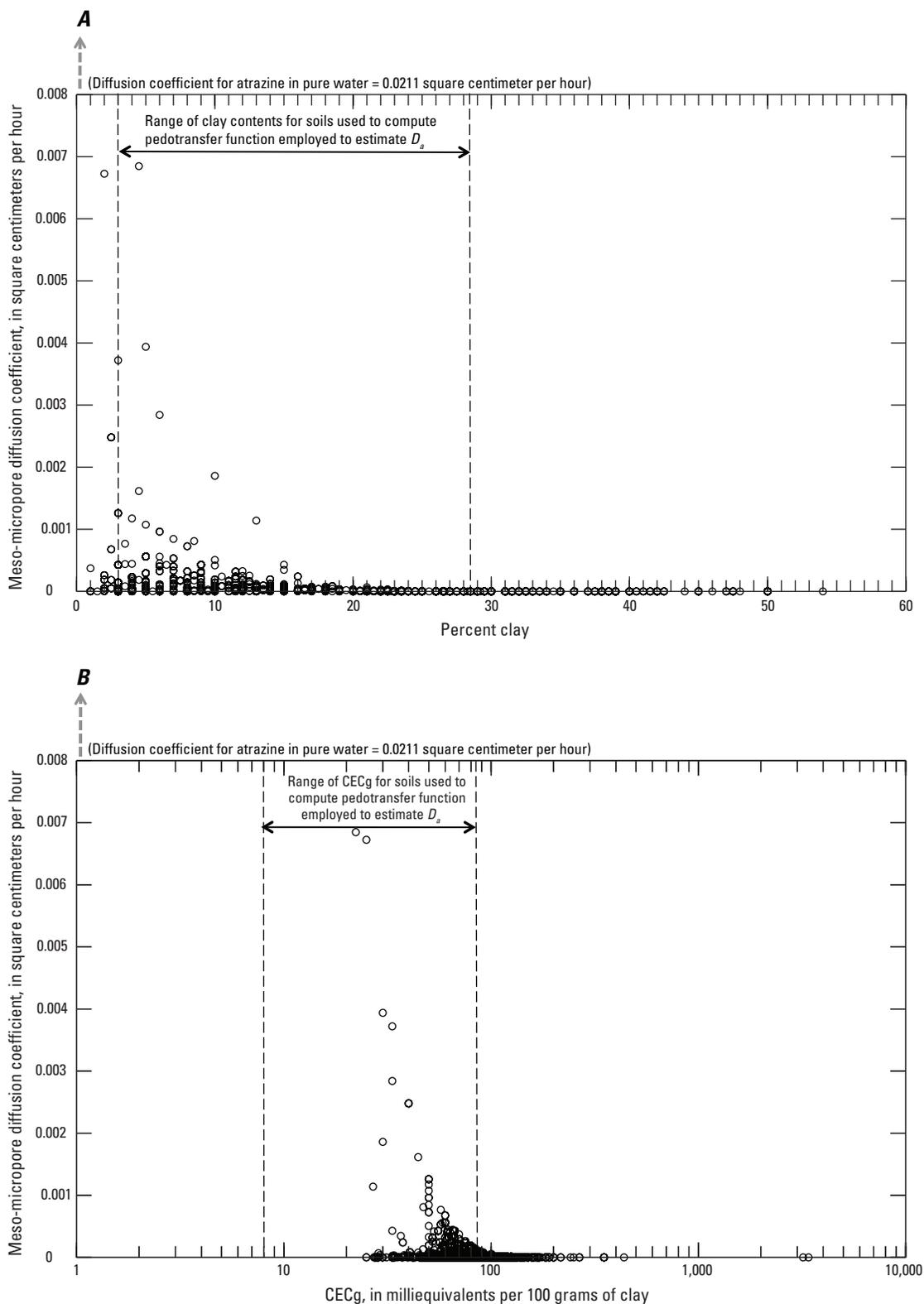


Figure 19. Apparent diffusion coefficient (D_a) for the exchange of atrazine between micropores and mesopores compared with (A) clay content (percent clay), and (B) cation exchange capacity normalized to clay content (CECg) for 1,657 soil horizons at P-GWAVA-RZ (Phase 2) study sites in the 10 northernmost states of the Corn Belt. Values are shown for all Phase 2 soil horizons with available SSURGO data for percent clay and CEC7.

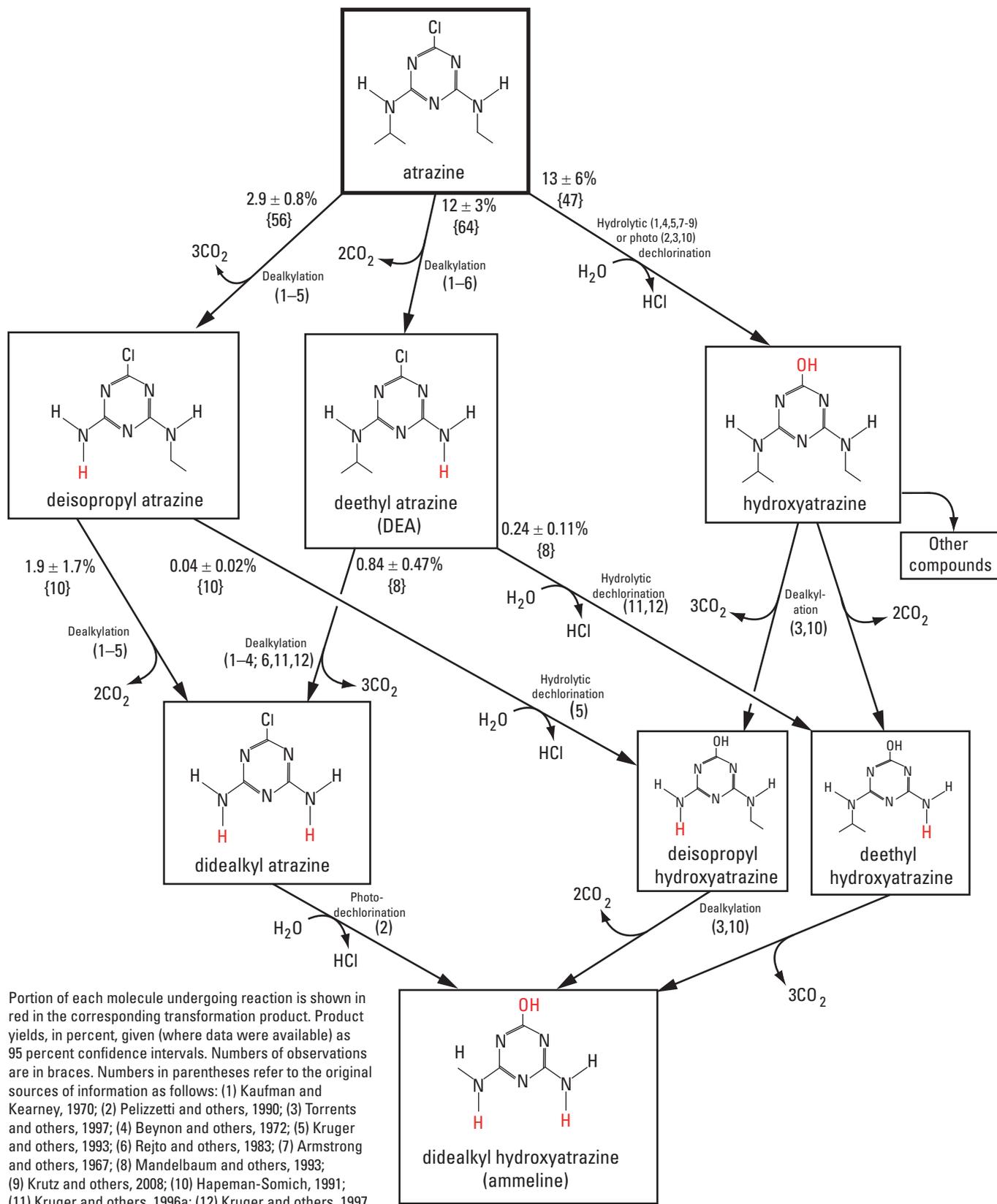


Figure 20. Reactions producing the atrazine transformation products that have been examined most extensively in the hydrologic system.

Atrazine and Deethylatrazine Disappearance Rates in Soil

PRZM quantifies the rate of pesticide disappearance in terms of first-order rate constants (k), whereas RZWQM uses half-lives ($t_{1/2}$) for this purpose. Both approaches are derived from the assumption that the disappearance of the solute of interest displays first-order kinetics, and thus occurs at a rate (dC/dt) that at any given time (t) is directly proportional to the solute concentration at that moment (C_t), that is,

$$\frac{dC}{dt} = k * C_t \quad (27)$$

The half-life for the disappearance of a chemical compound represents the amount of time required for the initial concentration of the compound (C_o) to diminish, through first-order kinetics, by 50 percent—that is, the time interval after which C_t/C_o equals 0.5. The observed half-life ($(t_{1/2})_{obs}$), expressed as a function of the observed rate constant (k_{obs}) for the disappearance of the solute of interest, is obtained by separating variables in equation 27, integrating both sides and solving for t when C_t/C_o equals 0.5:

$$(t_{1/2})_{obs} = \frac{\ln 2}{k_{obs}} = \frac{0.693}{k_{obs}} \quad (28)$$

For many pesticides following application (as well as many of their degradates), k_{obs} commonly represents the sum of several individual rate constants, each of which reflects the combined influence of at least three factors, that is, the mechanism of transformation (for example, hydrolysis, dealkylation, dehydrohalogenation, and so forth), the source of the energy driving the process (thermal versus photochemical), and the presence or absence of biological assistance. Variations in the characteristics of environmental media, such as the presence or absence of solid surfaces, the composition and size of the microbial population, the mass fraction of organic carbon, and the concentrations of other reactive species, may also affect the rates and relative importance of different reaction mechanisms for a given compound (Barbash, 2007).

Atrazine Disappearance Rates

Both PRZM and RZWQM offer the option of simulating pesticide disappearance on the surfaces of plant foliage, crop residues, and soil. PRZM also simulates disappearance in the soil solution and in the soil gas. Owing to a lack of evidence demonstrating its importance, however, atrazine disappearance in soil gas was presumed negligible for this investigation. RZWQM simulates pesticide disappearance through either biotransformation, phototransformation or other abiotic reactions.

Photochemical Transformations

Published estimates of the rates of atrazine transformation on plant surfaces are limited, but the rates of direct phototransformation of atrazine and DEA by sunlight are negligible in homogeneous aqueous solution at neutral pH (Pellizzetti and others, 1990; Lartiges and Garrigues, 1995; Peñuela and Barceló, 2000; Lackhoff and Niessner, 2002; Prosen and Zupančič-Kralj, 2005). Because atrazine is typically applied directly to the soil prior to crop emergence, the transformations of atrazine and DEA on crop foliage were neglected for this study. Following the guidance of Ahuja and others (2000), the rates of disappearance of both compounds on crop residue also were presumed negligible. Results from a limited number of previous investigations indicate that atrazine (Rice and others, 2004) and perhaps DEA (Prosen and Zupančič-Kralj, 2005) may undergo phototransformation at moderate rates in soils exposed to sunlight. However, owing to the absence of appropriate measurements from previous research, the P-GWAVA simulations did not account for the phototransformation of the two compounds on soil surfaces. Therefore, only thermal transformations of atrazine, DEA, or nitrogen species are discussed in the remainder of this report.

Thermal Transformations in Soil

Atrazine reactions in the subsurface may occur in either the dissolved or the sorbed state. Previous research generally indicates that the biotransformation of pesticides and other anthropogenic compounds in soil occurs primarily, if not exclusively in the dissolved state, and that compounds in the sorbed state, including atrazine (Jacobsen and others, 2001), are mostly unavailable to microorganisms for these reactions (Alvarez-Cohen and others, 1993; Barbash and Resek, 1996; Zhang and others, 1998). Results from laboratory studies, however, suggest that atrazine reactions in the subsurface are likely to be most rapid in water that is in intimate contact with non-sterile soil (Erickson and Lee, 1989; Mandelbaum and others, 1993; Rice and others, 2004; Krutz and others, 2008). Additionally, although abiotic atrazine hydrolysis may take place in the sorbed state or in aqueous solution, the reaction occurs more rapidly in the presence of soil than in aqueous solution alone (Armstrong and others, 1967; Skipper and others, 1967; Armstrong and Chesters, 1968; Rice and others, 2004).

Simulations carried out during Phase 1 of this study provided opportunities to examine the relative importance of reactions in the sorbed and dissolved states in influencing the concentrations of atrazine in the vadose zone. Separate P-GWAVA-PR simulations were conducted at every Phase 1 site using four different reaction scenarios. The four scenarios involved simulating reactions (1) solely in the dissolved state, (2) solely in the sorbed state, (3) in both dissolved and sorbed

states, or (4) in neither state (that is, not at all). The atrazine concentrations simulated using the four reaction scenarios were then compared with those measured in groundwater at the same sites, to determine which approach resulted in the closest agreement between the simulated and measured atrazine concentrations.

In contrast with the approach used by PRZM, RZWQM simulates pesticide transformation in the soil as a single medium, without distinguishing between reactions in the aqueous and sorbed states. RZWQM simulates pesticide disappearance in soil under either oxic conditions or anoxic conditions. The model simulates the onset of anoxic conditions after the soil moisture content exceeds specific depth-dependent thresholds for longer than a specified period (Ahuja and others, 2000; Wauchop and others, 2004). In the soil column, RZWQM offers the option of specifying a *lumped process* to account for the simultaneous operation of multiple pathways of transformation. The model requires, however, that each transformation product of interest be generated from a single process. Consequently, the rates of atrazine and DEA disappearance under oxic conditions—and, by extension, the formation of DEA from atrazine dealkylation—were quantified as lumped processes within the soil column, despite the fact that atrazine and DEA undergo transformation by both abiotic and biotic mechanisms (Winkelmann and Klaine, 1991a and 1991b; Kruger and others, 1997). For anoxic conditions, these reaction rates were specified using the RZWQM parameter referred to as the “soil subsurface anerobic [*sic*] biodegradation half-life.”

Initial Disappearance Rates and Temperature Variations

Among the environmental factors that are known to influence the rates of pesticide transformation in the hydrologic system, temperature is one of the most significant. The rates of *thermal reactions* are known to increase with temperature to a maximum value determined either by the thermal stability of the reactants or by the viability of any organisms that may be responsible for facilitating the reactions of interest. Although temperature effects are often observed for some indirect photolytic reactions, the rates of direct photolysis are independent of temperature (Mill and Mabey, 1985). Initial values for the rates of solute transformation at each location of interest during both study phases were computed for the average air temperature in May (T_{May}), when the annual agrichemical applications were assumed to have occurred (see section, “Weather”). During the Phase 2 simulations, the rates of these reactions were also adjusted in response to spatial and temporal variations in temperature, and additional adjustments made to account for the influence of variations in moisture content and depth below the land surface.

During Phase 1 of this study, the initial rate of atrazine disappearance was computed for T_{May} (in K) in each location using the Arrhenius equation (Atkins, 1982):

$$k_{atr} = A_o * \exp\left(\frac{-E_a}{RT_{May}}\right) \quad (29)$$

where

- k_{atr} is the first-order rate constant for atrazine disappearance in non-sterile soil, in inverse days (d^{-1});
- A_o is the Arrhenius pre-exponential factor (d^{-1});
- E_a is the activation energy (kJ/mol); and
- R is the universal gas constant (0.00831 kJ/K-mol).

Values of A_o and E_a for Phase 1 were computed from data reported by Walker and Zimdahl (1981) for the rates of atrazine disappearance at four temperatures (5, 15, 25, and 35 °C) in loam soils from three locations in the United States. Given the similarity in the reported E_a values for the three soils examined (45.4, 50.6, and 51.1 kJ/mol for a Mississippi silt loam, a Colorado clay loam, and a New York sandy loam, respectively), the data from all three sites were combined to compute more representative estimates of the Arrhenius parameters of interest for the Phase 1 simulations ($A_o = 2,920,024 d^{-1}$; $E_a = 46.2 kJ/mol$).

The second phase of this study involved the use of various methods to account for the effects of several environmental factors, in addition to temperature, on the rates of atrazine disappearance in soil. Previous research has established that the rates and mechanisms of transformation of atrazine and other pesticide compounds in the soil—through abiotic and (or) microbially mediated reactions—may be influenced by a wide variety of physical, hydrologic, chemical, and biological factors (Barbash, 2007). Some of this research has led to the development of QMRRs that can be used to predict the rates of atrazine disappearance in non-sterile, oxic soils from various system characteristics, including the temperature, moisture content, organic carbon content, sand content, and pH of the soil, as well as the depth below the land surface and the depth interval over which the transformation rate is to be estimated (Walker, 1978; Walker and Zimdahl, 1981; Dinelli and others, 2000; Fenner and others, 2007).

Among the QMRRs devised by these previous studies, the Fenner-Borsuk relation, a linear, multivariate correlation equation introduced by Fenner and others (2007), accounts for the influence of the widest range of variables determined to be significantly correlated with the rates of atrazine disappearance from thermal reactions in oxic, non-sterile soils. Thus, although RZWQM provides options for adjusting pesticide transformation rates to account for variations in temperature,

soil moisture, and depth below the land surface, the use of an updated version of the Fenner-Borsuk relation (that is, a version in which the original coefficients were recalculated using a larger number of laboratory data, as described in [appendix B](#)) was examined for the Phase 2 simulations, to account for the potential influence of a wider range of explanatory factors on the initial rates of atrazine disappearance.

Preliminary model simulations using the updated version of the Fenner-Borsuk relation to estimate initial atrazine disappearance rates in soil led to predicted atrazine concentrations that were lower than the atrazine reporting limits in nearly all locations in the Phase 2 study area, resulting in simulated concentrations and frequencies of detection that were substantially less than those measured in groundwater at the same sites. This indicated that the updated version of the Fenner-Borsuk relation may have systematically overestimated the actual atrazine disappearance rates. As an alternative approach, atrazine reaction rates obtained directly from data reported by previous laboratory studies, rather than values predicted by the updated version of the Fenner-Borsuk relation, were used to obtain initial estimates of the half-life for the disappearance of atrazine at the soil surface ([table 4](#)). However, the updated Fenner-Borsuk relation was still used to estimate the fraction of reacting atrazine that formed DEA ([appendix B](#)).

For each SSURGO component of interest, the half-life for the disappearance of atrazine in oxic soil was obtained during Phase 2 by adjusting a value selected from the published literature to T_{May} for that location. To select this value, 259 rates of atrazine disappearance in non-sterile, oxic soils in the absence of light at circumneutral pH (that is, pH values between 6 and 8) were retrieved or computed from the results reported by 20 previous laboratory studies. From these data, the median half-life was selected from among the 125 values measured by 7 studies at 25 °C, the temperature at which the largest number of measurements were made (Walker, 1978; Walker and Zimdahl, 1981; Kruger and others, 1993; Topp and others, 1994; Rocha and Walker, 1995; Issa and Wood, 1999; Dinelli and others, 2000). An initial value of the half-life for atrazine disappearance was then calculated for each SSURGO component by adjusting this median value (109 days, measured by Issa and Wood [1999]) to the reference temperature of T_{May} for the location of interest using the following form of the Arrhenius equation:

$$\begin{aligned} (t_{1/2})_{atr,ox,T_{May}} &= (t_{1/2})_{atr,ox,25\text{ }^{\circ}\text{C}} * \exp\left[\left(\frac{E_a}{R}\right) * \left(\frac{1}{T_{May}} - \frac{1}{298.15\text{ K}}\right)\right] \\ &= (109d) * \exp\left[\left(\frac{50.9\text{ kJ/mol}}{0.00831441\text{ kJ/K} - \text{mol}}\right) * \left(\frac{1}{T_{May}} - \frac{1}{298.15\text{ K}}\right)\right] \\ &= (109d) * \exp\left[6,121.9\text{ K} * \left(\frac{1}{T_{May}} - \frac{1}{298.15\text{ K}}\right)\right] \end{aligned} \quad (30)$$

where

- $(t_{1/2})_{atr,ox,T_{May}}$ is the half-life, in days (d), for the disappearance of atrazine in non-sterile, oxic soil in the absence of light at T_{May} ; and
- $(t_{1/2})_{atr,ox,25\text{ }^{\circ}\text{C}}$ is the half-life (d) for the disappearance of atrazine in non-sterile, oxic soil in the absence of light at 25 °C.

The activation energy (E_a) value of 50.9 kJ/mol used in equation 30 represented the median among 31 independent values of this parameter that were either retrieved or computed from the results reported by 6 previous studies of the effects of temperature, moisture, application history, and other factors on the rates of atrazine disappearance in oxic, non-sterile

soils at circumneutral pH in the absence of light (Roeth and others, 1969; Walker, 1978; Walker and Zimdahl, 1981; Rocha and Walker, 1995; Dinelli and others, 2000; and Krutz and others, 2008). Each of the 31 E_a values was obtained from a separate experiment involving a different soil and (or) combination of system conditions. In several instances where individual rate constants or half-lives were provided in the original publications (Walker, 1978; Walker and Zimdahl, 1981; Rocha and Walker, 1995; Dinelli and others, 2000), the E_a value calculated for this study from the published data differed from the value provided by the original authors. In these instances, the E_a value calculated from the original kinetic data was included among those from which the median E_a value was selected, rather than the published E_a value. The E_a value of 50.9 kJ/mol was also used to adjust for the effects of temperature variations on the rates of DEA disappearance in soil under oxic conditions, and on the rates of disappearance of atrazine and DEA in soil under anoxic conditions, given that published data from which E_a values for these other reactions could be retrieved or computed did not appear to be available.

Use of equation 30 for the P-GWAVA-RZ simulations resulted in predicted atrazine concentrations and detection frequencies that were in substantially closer agreement with those measured in shallow groundwater than was the case using the updated Fenner-Borsuk relation. The marked change in the level of agreement between simulated and measured concentrations in response to this change in approach was consistent with the common observation that pesticide concentrations predicted in the subsurface by computer simulations are sensitive to variations in the transformation rate specified for the solute of interest (for example, Wagenet and Hutson, 1986; Boesten and van der Linden, 1991; Soutter and Musy, 1999; Tiktak, 1999; Dubus and Brown, 2002; Dubus and others, 2003; Dann and others, 2006).

Equation 30 was used to estimate the rates of atrazine disappearance in soil under oxic conditions for the RZWQM simulations. To estimate the rates of atrazine disappearance under anoxic conditions, the results from experiments conducted under anoxic conditions by Accinelli and others (2001) with a non-sterile soil collected from a depth interval from 80 to 100 cm (the only soil for which the pH was between 6 and 8) were used. This was accomplished for each SSURGO component of interest at the reference temperature of T_{May} using the following QMRR:

$$k_{atr,anox,T_{May}} \approx k_{atr,ox,T_{May}} * \left(\frac{k_{atr,anox,A+01,15^{\circ}C}}{k_{atr,ox,A+01,15^{\circ}C}} \right) = k_{atr,ox,T_{May}} * \left(\frac{0.00170d^{-1}}{0.00580d^{-1}} \right) = k_{atr,ox,T_{May}} * 0.293 \quad (31)$$

where

$k_{atr,anox,T_{May}}$ is the first-order rate constant for atrazine disappearance in anoxic soil at temperature T_{May} (d^{-1});

$k_{atr,ox,T_{May}}$ is the first-order rate constant for atrazine disappearance in oxic soil at temperature T_{May} (d^{-1});

$k_{atr,anox,A+01,15^{\circ}C}$ is the first-order rate constant for atrazine disappearance measured in anoxic soil by Accinelli and others (2001) at circumneutral pH and 15 °C (d^{-1}); and

$k_{atr,ox,A+01,15^{\circ}C}$ is the first-order rate constant for atrazine disappearance measured in oxic soil by Accinelli and others (2001) at circumneutral pH and 15 °C (d^{-1}).

The data used in equation 31 from the study by Accinelli and others (2001) are consistent with the observation, noted by several previous investigations, that atrazine is more persistent under anoxic conditions than under oxic conditions (for example, Kaufman and Kearney, 1970; Nair and Schnoor, 1992; Papiernik and Spalding, 1998; Rügge and others, 1999; and Larsen and others, 2000).

Expressing the reaction rates in equation 31 in terms of half-lives (using equation 28), substituting the right side of equation 30 for $(t_{1/2})_{atr,ox,T_{May}}$ and collecting terms yields the expression used for computing the half-life for atrazine disappearance in non-sterile soils at the reference temperature of T_{May} whenever anoxic conditions were simulated by RZWQM during Phase 2:

$$\begin{aligned}
 (t_{1/2})_{atr,anox,T_{May}} &= \left(\frac{109d}{0.293} \right) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right] \\
 &= (372d) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right]
 \end{aligned} \quad (32)$$

Use of equations 31 and 32 to estimate the rate of atrazine disappearance under anoxic conditions at temperatures other than 15 °C was predicated on the assumption that the activation energies for the disappearance of atrazine under oxic and anoxic conditions are identical, and thus that the ratio $k_{atr,anox}/k_{atr,ox}$ (in equation 31) is independent of temperature, within the temperature range of interest to the Phase 2 simulations (10–20 °C [fig. 15]). This assumption was necessary because of the apparent lack of published data on the temperature dependence of atrazine disappearance rates in anoxic soil.

As the P-GWAVA-RZ simulation in each SSURGO component progressed, the half-life for atrazine disappearance estimated at the reference temperature of T_{May} using either equation 30 (for oxic conditions) or equation 32 (for anoxic conditions) was adjusted by an internal routine in RZWQM to account for temporal variations in temperature in each soil layer. RZWQM makes these adjustments using the same form of the Arrhenius relation used for equations 30 and 32:

$$\begin{aligned}
 (t_{1/2})_{atr,T_{sn}} &= (t_{1/2})_{atr,T_{May}} * \exp \left[\left(\frac{E_a}{R} \right) * \left(\frac{1}{T_{sn}} - \frac{1}{T_{May}} \right) \right] \\
 &= (t_{1/2})_{atr,T_{May}} * \exp \left[\left(\frac{50.9 \text{ kJ/mol}}{0.00831441 \text{ kJ/K} \cdot \text{mol}} \right) * \left(\frac{1}{T_{sn}} - \frac{1}{T_{May}} \right) \right] \\
 &= (t_{1/2})_{atr,T_{May}} * \exp \left[(6,121.9K) * \left(\frac{1}{T_{sn}} - \frac{1}{T_{May}} \right) \right]
 \end{aligned} \quad (33)$$

where

$(t_{1/2})_{atr,T_{sn}}$ is the half-life for the disappearance of atrazine in soil layer n , in days; and
 T_{sn} is the temperature, in K, of soil layer n .

Equation 33 incorporates a correction to the original version of this equation presented by Ahuja and others (2000), in which the last two temperature terms were inadvertently reversed (Liwang Ma, U.S. Department of Agriculture, written commun., July 2007).

Influence of Soil Moisture on Disappearance Rates (Phase 2 only)

More than three decades of research have established that under unsaturated conditions, the rates at which many pesticides disappear in non-sterile soil generally increase with soil moisture content (for example, Walker, 1974; Gottesbüren, 1991). This effect was first quantified by Walker (1974) using the following QMRR:

$$t_{1/2}(\theta) = a * \theta^{-b} \quad (34)$$

where

- θ is the percent moisture content of interest, expressed on a weight basis (% w/w);
- $t_{1/2}(\theta)$ is the half-life, in days, for the disappearance of the compound of interest at moisture content θ ; and
- a and b are empirical constants.

(Unless specified otherwise, all water contents mentioned in this report are expressed on a weight basis [w/w].) According to equation 34 (also referred to as the Walker equation), at a water content equal to the field capacity of the soil (θ_{FC}), the half-life for the disappearance of a given compound in soil ($t_{1/2}(\theta_{FC})$) may be estimated as follows:

$$t_{1/2}(\theta_{FC}) = a * \theta_{FC}^{-b} \quad (35)$$

Dividing each side of equation 34 by its corresponding side in equation 35 and isolating $t_{1/2}(\theta)$ yields the form of the Walker equation used in RZWQM to adjust pesticide transformation rates for variations in soil moisture:

$$t_{1/2}(\theta) = t_{1/2}(\theta_{FC}) * \left(\frac{\theta}{\theta_{FC}} \right)^{-b} \quad (36)$$

Thus, normalizing the expression for $t_{1/2}(\theta)$ in equation 34 with respect to $t_{1/2}(\theta_{FC})$ from equation 35 yields an expression (equation 36) that requires only one empirical parameter, the Walker exponent b , to compute $t_{1/2}(\theta)$.

At least 13 previous studies have examined the influence of soil water content on the rates of atrazine disappearance in non-sterile soils in the absence of light. Among these investigations, six either reported values for b , or provided the experimental data from which b values could be computed. The results from these studies were used to retrieve or calculate 14 independent values of b (that is, values derived from experiments using different soils or other variations in system conditions) for the disappearance of atrazine in non-sterile soils under oxic conditions at circumneutral pH in the dark at 25 °C (Walker and Zimdahl, 1981; Rocha and Walker, 1995; Dinelli and others, 2000), at 20 °C (Walker, 1978; Krutz and others, 2008), or as an average of values measured at 15 and 28 °C (Baer and Calvet, 1999). For cases where individual studies did not provide the values of θ_{FC} needed to compute b from equation 36, data provided by Saxton and Rawls (2006) were used to infer θ_{FC} from soil texture. Where necessary, bulk density (ρ_b) was used to convert soil water contents from a volumetric basis ($\theta_{(v/v)}$) to a weight basis ($\theta_{(w/w)}$) using the following equation derived from dimensional analysis:

$$\theta_{(w/w)} = \frac{\theta_{(v/v)}}{\rho_b} \quad (37)$$

The median among the 14 independent b values (0.43) was used for atrazine in the P-GWAVA-RZ simulations (table 14). No b data were found in the published literature for DEA, so the atrazine value (0.43) was used for this compound, as well. Owing to a lack of b data in the published literature for anoxic conditions, the quantitative dependence of atrazine and DEA disappearance rates on water content was presumed to be the same in anoxic soils as in oxic ones.

Deethylatrazine Production from Atrazine Reaction in Soil (Phase 2 only)

RZWQM quantifies the production of a pesticide degradate as a fixed proportion of the total amount of the parent compound that reacts over time, a parameter referred to as the *daughter product formation percentage*. For this study, the DEA formation percentage ($F_{atr>DEA}$) was computed using the following equation:

$$F_{atr>DEA} = 100\% * \left(\frac{k_{atr>DEA}}{k_{atr}} \right) \quad (38)$$

where

$k_{atr>DEA}$ is the first-order rate constant for the production of DEA from atrazine in non-sterile, oxic soils in the dark (d^{-1}); and

k_{atr} is the first-order rate constant for the disappearance of atrazine in non-sterile, oxic soils in the dark (d^{-1}).

An analysis of data reported by previous laboratory studies (appendix B) indicated that the magnitude of $k_{atr>DEA}$ is significantly correlated with the same explanatory parameters whose influences on atrazine disappearance rates (k_{atr}) are accounted for by the Fenner-Borsuk relation. Consequently, rather than using a single $F_{atr>DEA}$ value for all of the Phase 2 sites, modified versions of the Fenner-Borsuk relation were used to estimate $k_{atr>DEA}$ and k_{atr} , and thus $F_{atr>DEA}$, for each SSURGO component for the P-GWAVA-RZ simulations. These equations, and the approach used to develop them, are presented in appendix B. Use of equation 38 to estimate $F_{atr>DEA}$ for all of the SSURGO components examined during Phase 2 yielded predicted values of this parameter that ranged from 1.0 to 25.4 percent. These values were well within the range of 0.4 to 51.1 percent spanned by the 58 $F_{atr>DEA}$ values computed from the eight laboratory studies (fig. B1) from which equation B4, used to predict $k_{atr>DEA}$, was derived (Winkelmann and Klaine, 1991a and 1991b; Kruger and others, 1993; Assaf and Turco, 1994; Topp and others, 1994; Kruger and others, 1997; Rodriguez and Harkin, 1997; Zablutowicz and others, 2006).

Deethylatrazine Disappearance Rate in Soil (Phase 2 only)

For the P-GWAVA-RZ simulations, the rates of DEA disappearance in oxic soils were estimated by scaling the atrazine values using a QSRR, rather than taking the DEA reaction rates directly from the published literature. This approach was used because of the similarities between DEA and atrazine in relation to their structure and their reactivities (fig. 20), and because the number of reported measurements of atrazine disappearance rates in non-sterile, oxic soils at circumneutral pH is substantially larger than the number of

reported measurements for DEA. (Only 4 such measurements at circumneutral pH have been reported to date for DEA, whereas at least 259 measurements are available for atrazine.)

The rate of DEA disappearance at T_{May} was estimated by adjusting the atrazine disappearance rate at T_{May} with the following QSRR:

$$k_{DEA,ox,T_{May}} \approx k_{atr,ox,T_{May}} * \left(\frac{k_{DEA,ox,K+97,24^{\circ}C}}{k_{atr,ox,K+97,24^{\circ}C}} \right) = k_{atr,ox,T_{May}} * \left(\frac{0.0038d^{-1}}{0.0034d^{-1}} \right) = k_{atr,ox,T_{May}} * 1.1 \quad (39)$$

where

- $k_{DEA,ox,T_{May}}$ is the first-order rate constant (d^{-1}) for the disappearance of DEA in oxic, non-sterile soil at temperature T_{May} ;
- $k_{atr,ox,T_{May}}$ is the first-order rate constant (d^{-1}) for the disappearance of atrazine in oxic, non-sterile soil at temperature T_{May} , estimated using equations 28 and 30;
- $k_{DEA,ox,K+97,24^{\circ}C}$ is the first-order rate constant for the disappearance of DEA in oxic, non-sterile soil at circumneutral pH, measured at $24^{\circ}C$ by Kruger and others (1997); and
- $k_{atr,ox,K+97,24^{\circ}C}$ is the first-order rate constant for the disappearance of atrazine in oxic, non-sterile soil at circumneutral pH, measured at $24^{\circ}C$ by Kruger and others (1997).

Equation 39 quantifies the inferred influence of replacing the ethyl group in atrazine with a hydrogen atom (fig. 20) on the rate of disappearance of the molecule in oxic, non-sterile soil at circumneutral pH. The investigation by Kruger and others (1997) was used as the source of the kinetic data in equation 39 because it reports disappearance rates for DEA and atrazine in the same soil at the same temperature under oxic, non-sterile conditions at circumneutral pH in the dark. The data used by equation 39 from Kruger and others (1997) were measured using a soil sample collected from a depth interval from 90 to 120 cm, the only soil examined with a pH between 6 and 8. Expressing the reaction rates in equation 39 in terms of disappearance half-lives (using equation 28), substituting the right side of equation 30 for $(t_{1/2})_{atr,ox,T_{May}}$ and collecting terms yields the expression used to estimate the half-life for DEA disappearance in oxic soils at T_{May} for each SSURGO component of interest:

$$\begin{aligned} (t_{1/2})_{DEA,ox,T_{May}} &= \frac{(t_{1/2})_{atr,ox,T_{May}}}{1.1} = \left(\frac{109d}{1.1} \right) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right] \quad (40) \\ &= (99d) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right] \end{aligned}$$

The use of equations 39 and 40 for estimating the rate of DEA disappearance at temperatures other than $24^{\circ}C$ (equation 39) was predicated on the assumption that the activation energy for the disappearance of DEA in soil is identical to that for atrazine, and thus that the ratio $k_{DEA,ox}/k_{atr,ox}$ is independent of temperature, within the temperature range of interest for the Phase 2 simulations ($10-20^{\circ}C$ [fig. 15]). Support for this assumption is provided by the similarity in structure between the two compounds, as well as the similarities in the reactions that transform them in soil (fig. 20).

Kruger and others (1997) also measured the rates of atrazine and DEA disappearance in soil under anoxic conditions. Consequently, data from that study were used to estimate the rates of DEA disappearance under anoxic conditions. The DEA disappearance rates were estimated with the following QSRR, which scaled the rate of atrazine disappearance under

anoxic conditions ($k_{atr,anox,T_{May}}$, from equation 31) using the ratio of rate constants for DEA and atrazine disappearance measured under anoxic conditions by Kruger and others (1997):

$$\begin{aligned}
 k_{DEA,anox,T_{May}} &\approx k_{atr,anox,T_{May}} * \left(\frac{k_{DEA,anox,K+97,24^{\circ}C}}{k_{atr,anox,K+97,24^{\circ}C}} \right) \\
 &= k_{atr,anox,T_{May}} * \left(\frac{0.0086d^{-1}}{0.013d^{-1}} \right) = k_{atr,anox,T_{May}} * 0.66
 \end{aligned}
 \tag{41}$$

where

- $k_{DEA,anox,T_{May}}$ is the first-order rate constant for DEA disappearance in anoxic soil at temperature T_{May} (d^{-1});
- $k_{DEA,anox,K+97,24^{\circ}C}$ is the first-order rate constant for DEA disappearance measured in anoxic soil by Kruger and others (1997) at circumneutral pH and 24 °C; and
- $k_{atr,anox,K+97,24^{\circ}C}$ is the first-order rate constant for atrazine disappearance measured in anoxic soil by Kruger and others (1997) at circumneutral pH and 24 °C.

Expressing the reaction rates in equation 41 in terms of half-lives (using equation 28), substituting the right side of equation 32 for $(t_{1/2})_{atr,anox,T_{May}}$, and collecting terms yields the expression used to compute the half-life for DEA disappearance in soil for the reference temperature of T_{May} whenever anoxic conditions were simulated by RZWQM during Phase 2:

$$\begin{aligned}
 (t_{1/2})_{DEA,anox,T_{May}} &= \left(\frac{372d}{0.66} \right) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right] \\
 &= (562d) * \exp \left[(6,121.9K) * \left(\frac{1}{T_{May}} - \frac{1}{298.15K} \right) \right]
 \end{aligned}
 \tag{42}$$

The use of equation 42 to estimate the rate of DEA disappearance under anoxic conditions at temperatures other than the temperature for which equation 41 was derived (24 °C) was predicated on the assumption that the activation energies for the disappearance of DEA and atrazine under anoxic conditions are identical, and thus that the ratio $k_{DEA,anox}/k_{atr,anox}$ is independent of temperature, within the temperature range of interest to the Phase 2 simulations (10–20 °C [fig. 15]). This assumption was necessary given the apparent absence of published data on the temperature dependence of atrazine and DEA disappearance rates in anoxic soil. As for atrazine, the half-life for the disappearance of DEA estimated at T_{May} using either equation 40 (for oxic conditions) or 42 (for anoxic conditions) was adjusted by RZWQM for temporal variations in temperature in each soil layer during the course of the simulation for each SSURGO component of interest, using the corresponding version of equation 33, that is:

$$(t_{1/2})_{DEA,T_{sn}} = (t_{1/2})_{DEA,T_{May}} * \exp \left[(6,121.9K) * \left(\frac{1}{T_{sn}} - \frac{1}{T_{May}} \right) \right]
 \tag{43}$$

where

- $(t_{1/2})_{DEA,T_{sn}}$ is the half-life for the disappearance of DEA in soil layer n , in days, at the temperature of the soil layer (T_{sn}); and
- $(t_{1/2})_{DEA,T_{May}}$ is the half-life for the disappearance of DEA, in days, at the site of interest at a temperature of T_{May} .

Atrazine and Deethylatrazine Disappearance Rate Adjustments with Depth Below Land Surface

Numerous studies have established that, all other factors being equal, the rates of pesticide transformation in the subsurface generally decrease with increasing depth below the land surface (Barbash and Resek, 1996). This reduction in reaction rates with depth may be attributable to concomitant decreases with depth in one or more of several factors, including the populations of the microorganisms that are responsible for these reactions, the concentrations of the soil OM and nutrients upon which the microorganisms feed, and temperature (Jury and others, 1987; Erickson and Lee, 1989; Alvey and Crowley, 1996; Issa and Wood, 1999; Zablutowicz and others, 2006). For pesticide compounds that exhibit this pattern, RZWQM can simulate variations in transformation rates with depth in the vadose zone. In RZWQM, this involves using a transformation rate that is uniform from the land surface to a depth of 25 cm, decreases in a linear fashion from 25 to 100 cm depth, and is uniform at depths greater than 100 cm (Ahuja and others, 2000). Results from previous studies of relations between persistence and depth within the vadose zone are consistent with this pattern for atrazine (for example, Roeth and others, 1969; Kruger and others, 1993; Stolpe and Shea, 1995; Kruger and others, 1997; Issa and Wood, 1999; Larsen and others, 2000; Accinelli and others, 2001; Jacobsen and others, 2001) and DEA (Kruger and others, 1997). The decrease in reaction rate within the vadose zone over the depth interval between 25 and 100 cm beneath land surface is simulated by RZWQM using the following QMRR:

$$(t_{1/2})_z = (t_{1/2})_{z=0} * \left\{ 1 + \left[(V_{mhf} - 1) * \left(\frac{z-25}{75} \right) \right] \right\} \quad (44)$$

where

- $(t_{1/2})_z$ is the half-life for compound disappearance in oxic soil at a depth of z beneath the land surface ($25 \text{ cm} \leq z \leq 100 \text{ cm}$);
- $(t_{1/2})_{z=0}$ is the half-life for compound disappearance in oxic soil at the land surface ($z = 0$);

and

$$V_{mhf} = \frac{(t_{1/2})_{z=100}}{(t_{1/2})_{z=0}} \quad (45)$$

where

- $(t_{1/2})_{z=100}$ is the half-life for compound disappearance in oxic soil at a depth of 100 cm beneath the land surface.

Equation 44 incorporates a correction to the original form of this relation presented by Ahuja and others (2000) and Wauchope and others (2004), wherein the parameter V_{mhf} appeared alone, rather than as $(V_{mhf} - 1)$.

Given the relation presented earlier between the rate constant and half-life for first-order reactions (equation 28), the following equation was used to estimate the most appropriate value of V_{mhf} from published data on the rates of atrazine and DEA transformation as functions of depth below the land surface:

$$V_{mhf} \equiv \frac{(t_{1/2})_{z=100}}{(t_{1/2})_{z=0}} = \frac{[(\ln 2) / k_{z=100}]}{[(\ln 2) / k_{z=0}]} = \left(\frac{k_{z=0}}{k_{z=100}} \right) \approx \left(\frac{k_{z=0}}{k_{z \sim 100}} \right) \quad (46)$$

where

- $k_{z=0}$, $k_{z=100}$,
and $k_{z \sim 100}$ represent the first-order rate constants for the disappearance of the compound of interest at the soil surface, at a depth of 100 cm, and at a depth of approximately 100 cm, respectively.

Because the data reported by previous investigations did not always include a measurement at a depth of precisely 100 cm, the parameter $k_{z \sim 100}$ represents the transformation rate measured at the depth closest to 100 cm for that location.

At least 12 previous studies have examined the extent to which atrazine persistence in non-sterile, oxic, unsaturated soils in the absence of light varies with depth below the land surface. Among the investigations that measured reaction rates at a uniform temperature in soil samples collected from the land surface and from a depth of (or near) 100 cm, the largest number of observations was reported by the three studies that measured atrazine disappearance rates at 25 °C (Kruger and others, 1993; Stolpe and Shea, 1995; Issa and Wood, 1999). Calculations using the results from these three studies yielded a median of 6.58 among 11 independent values of $(k_{z=0} / k_{z \sim 100})$. Consequently, this was the value of V_{mhf} used for atrazine during the P-GWAVA-RZ simulations (table 14). For DEA, results from measurements carried out at 25 °C by Winkelmann and Klaine (1991b) and at 24 °C by Kruger and others (1997) appear to be the only published data available for estimating $(k_{z=0} / k_{z \sim 100})$. Calculations using the results from these two studies yielded the V_{mhf} value of 7.95 used for DEA for the P-GWAVA-RZ simulations (table 14).

Formation, Transport, and Fate of Nitrate (Phase 2 only)

Figure 21 depicts the compartments and processes associated with the cycling of nitrogen through water, soils, and biota in agricultural systems, highlighting those that are accounted for by RZWQM. (For this report, the term *compartment* refers to an environmental medium, such as soil organic matter, plant tissues, crop residues, groundwater, or surface water.) Values for most RZWQM input parameters associated with the formation, transport, and fate of nitrate (table 14) were those recommended by the model documentation (Ahuja and others, 2000; Agricultural Research Service, 2010; Bartling and others, 2011).

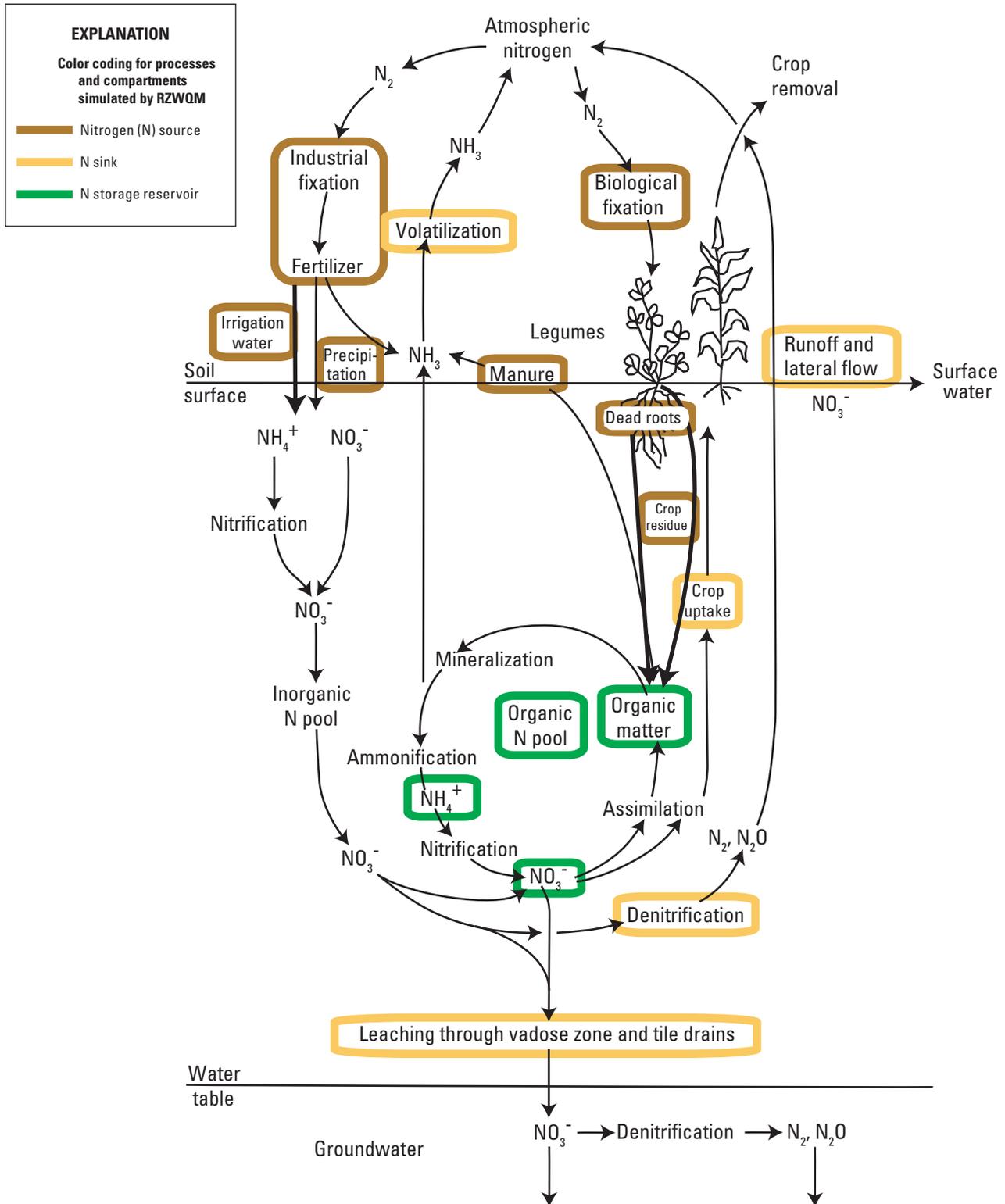


Figure 21. Processes and storage compartments for nitrogen cycling through water, soil, and biota in agricultural systems. Adapted from Makuch and Ward (1986). Highlighted processes and compartments are those that Root-Zone Water-Quality Model (RZWQM) accounts for as either nitrogen sources, sinks, or storage compartments.

One of the exceptions was related to the relative sizes of the three pools of soil OM that show fast, intermediate, and slow rates of oxidation (Ahuja and others, 2000). For the initial model simulations, the RZWQM default values were used for the relative proportions among these fractions (that is, 2, 18, and 80 percent, respectively). However, to achieve closer agreement between the nitrate concentrations predicted by the model and those measured in groundwater, these relative proportions were subsequently adjusted for all sites to 10, 20, and 70 percent, respectively (tables 4 and 14).

Model Formulation and Output

Both PRZM and RZWQM simulate the movement of water within the vadose zone in response to precipitation, irrigation, and ET. Both models also simulate the transport and fate of agrichemicals and their transformation products in the vadose zone in response to (1) the rates, timing, and method of their application to the land (for pesticides and fertilizers); (2) their formation in situ (for nitrogen species and pesticide degradates formed by microbial or abiotic processes); (3) their uptake and release by plants; (4) their transformations; and (5) the effects of biogeochemical conditions (such as temperature, pH, oxygen concentrations, soil organic matter, and microbial activities) on these processes. Table 14 provides a summary of the processes simulated, initial and boundary conditions, and input parameter values. In addition to the selection of input parameter values and approaches for simulating various physical, chemical, biological, and hydrologic processes, efforts also were required to determine the most appropriate sizes of the grid cells to be used for the simulations carried out by the two models.

Soil Column Discretization

Phase 1

Previous studies have demonstrated that the solute concentrations predicted by PRZM in the subsurface are highly sensitive to the sizes of the computational grid cells used for the simulations (for example, Jones and Mangels, 2002; Nolan and others, 2005). Thus, after initial simulations using the P-GWAVA-PR model predicted negligible concentrations of atrazine at the 1-m assessment depth in many study locations where the herbicide had been detected in shallow groundwater, the effect of adjusting the grid discretization on the simulated concentrations was examined. These adjustments, however, were applied only to the deeper parts of the soil column; following a suggestion by Carsel and others (1998), a grid-cell thickness of 0.1 cm was used for the top 10 cm of the soil for all model simulations. To select the most appropriate discretization for the depth interval between 10 and 100 cm beneath the land surface, model simulations

were done using three grid-cell thicknesses: 1 cm, 10 cm and the maximum value of 30 cm recommended by Carsel and others (1998). To ensure that unsaturated conditions were present from the land surface down to the Phase 1 assessment depth of 1 m in all the locations examined, the analysis was restricted to sites where the average DTW exceeded 1 m.

To avoid the potential influence of uncertainties regarding the prevalence, timing, and magnitude of irrigation near any of the sites of interest, this exercise was done without simulating irrigation, and only in those locations where the NRI data indicated that irrigation was not used (fig. 17). Additionally, the analysis was carried out using the areally averaged intensities of atrazine application, because preliminary model simulations indicated that the atrazine concentrations predicted in the vadose zone by the P-GWAVA-PR simulations were in closer agreement with those measured in groundwater when the areally averaged intensities of atrazine application were used than when the use intensities were presumed to be spatially uniform (see section, “Effect of Spatial Variability of Atrazine Application Intensities on Simulation Results”).

Phase 2

RZWQM uses three discretization schemes for the soil column to (1) capture the variations in hydraulic and other properties among individual soil horizons at the site of interest, (2) simulate the redistribution of water and solutes within the soil column, and (3) simulate infiltration and heat flow (Ahuja and others, 2000). The first scheme uses site-specific data to delineate the boundaries between the horizons within the soil column. At each site for the P-GWAVA-RZ simulations, these boundaries were set to coincide with those between adjacent soil horizons, as indicated by the SSURGO data. Where necessary, and following the guidance of Ahuja and others (2000), slight adjustments were made to the layer thicknesses to ensure that grid-cell boundaries always coincided with horizon boundaries. To simulate the processes of water and solute redistribution, infiltration and heat flow, these layers were subdivided further into 1-cm grid cells throughout the entire length of the simulated soil column (that is, from the land surface to the 3-m assessment depth).

Quantifying Solute Concentrations from Model Output

At any location within the simulated soil column, PRZM quantifies solute amounts in terms of concentrations (mass [M] per unit volume [length cubed], or ML^{-3}), whereas RZWQM does so in terms of mass fluxes (mass per unit area [length squared] per unit time, or $ML^{-2}T^{-1}$). Because PRZM and RZWQM use different approaches to quantify model outputs, slightly different methods were used to compute the concentrations simulated by the two models at their respective

assessment depths. At each site, predictions of solute mass and water flow were aggregated over time and combined to obtain simulated values of the flow-weighted mean (FWM) concentration (C_{FWM}) at the assessment depth of interest. Each FWM concentration represented the ratio between the simulated flux of the solute and the simulated flow of water at the assessment depth of interest over the entire 5-year simulation period. For the P-GWAVA-PR simulations, the following equation was used to compute C_{FWM} :

$$C_{FWM} = \frac{\sum_{j=1}^{(t_{sim} * 365)} (C_j * Qw_j)}{\sum_{j=1}^{(t_{sim} * 365)} Qw_j} \quad (47)$$

where

- t_{sim} is the simulation period over which C_{FWM} was computed, in years (5 years for both study phases);
- j is the daily time-step number;
- C_j is the simulated concentration of the solute of interest (ML^{-3}) at the assessment depth, at time step j ; and
- Qw_j is the simulated water flow (volume per unit time, or L^3T^{-1}) at the assessment depth, at time step j .

For the P-GWAVA-RZ simulations, the following equation was used for each SSURGO component examined:

$$C_{FWM} = \frac{\sum_{j=1}^{(t_{sim} * 365)} Qs_j}{\sum_{j=1}^{(t_{sim} * 365)} Qw_j} \quad (48)$$

where

- Qs_j is the solute flux ($ML^{-2}T^{-1}$) past the assessment depth at time step j .

Because the P-GWAVA-RZ simulations were done for more than one SSURGO component in many of the map units of interest, it was necessary to combine the C_{FWM} values from multiple components in these locations. This was accomplished for each solute by using equation 48 to compute a C_{FWM} value for each component, and then using the following equation to combine the C_{FWM} values from the individual components, in proportion to the percentages of the map unit that they occupied:

$$C_{FWM} = \frac{\sum_{i=1}^{N_c} (C_{FWM,i} * P_i)}{\sum_{i=1}^{N_c} P_i} \quad (49)$$

where

- N_c is the number of soil components for which P-GWAVA-RZ simulations were carried out in the SSURGO map unit of interest;
- i is the soil component number;
- $C_{FWM,i}$ is the flow-weighted mean concentration of the solute of interest for component i , computed using equation 48; and
- P_i is the percentage of the map unit area occupied by component i .

The denominator in equation 49 was less than 100 percent for those map units of interest where one or more components were disregarded for one or both of the reasons mentioned earlier—that is, because of an absence of data for one or more of the required soil parameters, or because the component represented less than 10 percent of the map-unit area (see section, “Physical and Chemical Properties of Soils”). An analogous version of equation 49 was used to compute a simulated flow-weighted mean recharge value ($Q_{w,FWM}$) for each SSURGO map unit from the recharge values simulated for its individual components ($Q_{w,FWM,i}$).

Accounting for the Potential Effects of Corn and-Soybean Rotations on Agrichemical Occurrence

The use of corn-and-soybean crop rotations (rather than planting corn each year, often referred to as *continuous corn*) is widespread in the Corn Belt, and thus has occurred at many of the Phase 2 sites. (Locations where corn-and-soybean rotations are used are referred to herein as *corn-and-soybean areas*.) Because atrazine is not applied during soybean cultivation (U.S. Environmental Protection Agency, 2003), the use of corn-and-soybean rotations likely results in spatial and temporal patterns of variation in atrazine and DEA occurrence in the subsurface that differ from those associated with continuous corn cultivation. Similarly, because the annual amounts of nitrogen fertilizer applied to soybeans in the United States are between 11 and 24 percent of the amounts applied to corn (Economic Research Service, 2011), the patterns of nitrate occurrence in the subsurface during corn-and-soybean rotations also are likely to differ from those during continuous corn cultivation. This disparity for nitrate may be diminished to some extent because as legumes, soybeans add nitrogen to the soil through fixation.

Detailed information on crop rotation schedules across the Nation was not available during Phase 2 of this study. Consequently, all the P-GWAVA simulations assumed that corn was grown every year (table 14). As such, the simulations did not account for the spatial and temporal fluctuations in atrazine or nitrogen fertilizer input that would have been related to variations in the prevalence of corn cultivation—relative to soybeans—among individual locations. The analysis of the Phase 2 results, therefore, included an examination of the potential influence of corn-and-soybean rotations on the extent of agreement between the agrichemical concentrations simulated in the vadose zone by the P-GWAVA-RZ model and those measured in the underlying shallow groundwater.

To determine whether or not the assumption of continuous corn during the Phase 2 simulations may have affected the accuracy of the P-GWAVA-RZ predictions, statistical correlations were examined between the average percentage of the land area where corn was grown between 1995 and 2005 and the model residuals for the concentrations of the three solutes of interest. For the purposes of this study, a *model residual* for a given constituent concentration or detection frequency is defined as the value simulated by the P-GWAVA model at a specific depth in the vadose zone (usually the assessment depth), minus the value measured in shallow groundwater at the same site. Thus, positive residuals denote overpredictions by the model and negative residuals denote underpredictions. For each county where one or more Phase 2 sites were located, data obtained from the USDA National Agricultural Statistics Service (2010b) were used to compute the average annual percentage of land area where corn was grown during the simulation period ($p_{c,avg}$) using the following equation:

$$p_{c,avg} = \frac{\sum_{t=1995}^{2005} \left[100\% * \left(\frac{A_{c,t}}{A_{c,t} + A_{s,t}} \right) \right]}{11 \text{ yr}} \quad (50)$$

where

- $A_{c,t}$ is the number of acres from which corn was harvested for either grain or silage in the county of interest in year t ; and
- $A_{s,t}$ is the number of acres from which soybeans were harvested in the county of interest in year t .

P-GWAVA Simulation and Groundwater Sampling Results

Several approaches were used to compare the results from the P-GWAVA model simulations with the results from groundwater sampling or with data obtained from other sources. Although measured rates of groundwater recharge were not available for most sites examined for this study, nationwide results from a separate approach for estimating groundwater recharge rates, known as the base-flow index (BFI) method, provided a set of independent estimates of recharge against which to compare the rates of groundwater recharge predicted by the P-GWAVA simulations. The BFI approach uses an automated hydrograph separation technique to estimate annual rates of groundwater recharge in a given watershed from the amount of flow in unregulated streams that is inferred to be supplied by groundwater discharge. Wolock (2003) computed the BFI-derived estimates of recharge for a 1-km² grid for the conterminous United States by calculating point values using streamflow data from 1951 to 1980 at 8,249 individual streamgages across the country and interpolating between the streamgage sites using an inverse-distance weighting method.

For each solute of interest to this study, three levels of spatial aggregation were used to compare the flow-weighted mean concentrations predicted in the vadose zone by the P-GWAVA simulations with the concentrations measured in groundwater at the same locations: (1) concentrations at individual sites, (2) detection frequencies in individual groundwater sampling networks, and (3) overall detection frequencies among all of the sites in each study area. Some of the key characteristics of the groundwater sampling networks are listed in table 2 and appendix C. For the first two levels of aggregation, the extent of agreement between simulation and measurement was assessed by examining the statistical distributions of model residuals, as well as through correlation analyses. In several instances, the data are presented graphically through the use of scatter plots (to compare the absolute magnitudes of simulated and measured values at individual sites) as well as cumulative distribution plots of the model residuals (to display the statistical distributions of model over- and underpredictions among all sites examined). All the detection frequencies that were computed from the simulated solute concentrations or measured concentrations in groundwater were obtained from locations representing subsets of the Phase 1 or Phase 2 sites (figs. 1 and 2, respectively). In selected locations, the simulated distributions of atrazine and DEA between the dissolved and sorbed states were also examined, as were the distributions of nitrogen among various chemical forms and environmental compartments.

At sites where simulated and measured aqueous concentrations of a given analyte were compared graphically or through the use of model residuals, but one or both values were less than the analytical reporting limit, a concentration of 0.0001 µg/L was assigned for a non-detection of atrazine or DEA, and a value of 0.01 mg/L as N was assigned for a non-detection of nitrate. All of these values were substantially less (by at least 80 percent) than the minimum reporting limits used for their respective compounds (fig. 4). Because simulations were carried out for different periods during the two phases of this study (table 1), in some locations the measured concentrations against which the simulated values were compared may have been measured during different years. Consequently, at some of the sites examined for both Phase 1 and Phase 2, the measured atrazine concentration used for comparison with the Phase 1 prediction was different from the value used for comparison with the Phase 2 prediction.

Examination of DEA and atrazine during Phase 2 made it possible to compare the P-GWAVA-RZ predictions in the vadose zone with measured values of the DEA fraction (f_{DEA}) in groundwater. This parameter is the molar proportion represented by DEA among all the atrazine-derived compounds detected in a given sample (that is, atrazine and DEA for this study), and was computed as follows:

$$f_{DEA} \equiv \frac{[DEA]}{([atrazine] + [DEA])} \quad (51)$$

where

[DEA] is the DEA concentration, in moles per liter;
and

[atrazine] is the atrazine concentration, in moles per liter.

DEA fractions thus span a range from 0 (when only atrazine is detected) to 1 (when only DEA is detected). Because of the manner in which they are calculated, f_{DEA} values were not computed for sites where neither solute was detected in groundwater, or where the simulated concentrations for both were less than their respective reporting limits.

In several locations examined, the average depth to the water table was shallower than the assessment depth used for the simulations (fig. 16). As a result, contrasts between the simulated solute concentrations and the concentrations measured in groundwater—or between the simulated recharge values and the BFI-derived estimates of recharge—might have been affected by the possible occurrence of saturated conditions at depths shallower than the assessment depth during part or all of the simulation period in these locations. To avoid this potentially confounding influence, during the analyses of the effects of different simulation approaches on

model residuals, all sites were excluded where the average water-table depth (fig. 16) was less than the assessment depth (1 m for Phase 1, 3 m for Phase 2). However, because the P-GWAVA system can simulate recharge and solute concentrations anywhere in the conterminous United States—regardless of whether or not the DTW is known—the assessments of agreement between the simulated and measured concentrations (or between the simulated and the BFI-derived recharge values) were done using (1) all of the sites, and (2) only those sites where the average DTW was greater than the assessment depth. This approach made it possible to assess the extent to which the accuracy of the P-GWAVA predictions may have been influenced (if at all) by the fact that the assessment depth was below the water table during some part of the simulation period in some of the study locations.

Phase 1 (P-GWAVA-PR)

Preliminary simulations were carried out with the P-GWAVA-PR model during Phase 1 to determine the most appropriate simulation approach with respect to various model features, process formulation, and inputs. These preliminary simulations examined the effects of grid discretization, atrazine application intensities, the sites of atrazine transformation (dissolved versus sorbed state), the presence or absence of irrigation, and the degree of spatial averaging of soil properties (STATSGO versus SSURGO) on the level of agreement between the atrazine concentrations or detection frequencies predicted in the vadose zone by the simulations and those measured in groundwater.

Soil Column Discretization for Simulations

The extent of agreement between the atrazine concentrations predicted in the vadose zone at the 1-m assessment depth by the P-GWAVA-PR simulations using the three discretization schemes and those measured in shallow groundwater is shown in figure 22. Results are shown for the three discretization schemes, which used 0.1-cm grid cells between the land surface and a depth of 9.9 cm for all simulations, and grid cells with thicknesses of 1, 10, or 30 cm for the interval from 10 to 100 cm. These results indicate that the atrazine concentrations predicted by the P-GWAVA-PR simulations increased with increasing grid-cell size in the depth interval between 10 and 100 cm. (The reasons the atrazine concentrations predicted by the P-GWAVA-PR simulations increased with increasing grid-cell size, however—rather than decreasing, as is typically observed for finite-difference models—remain unclear.)

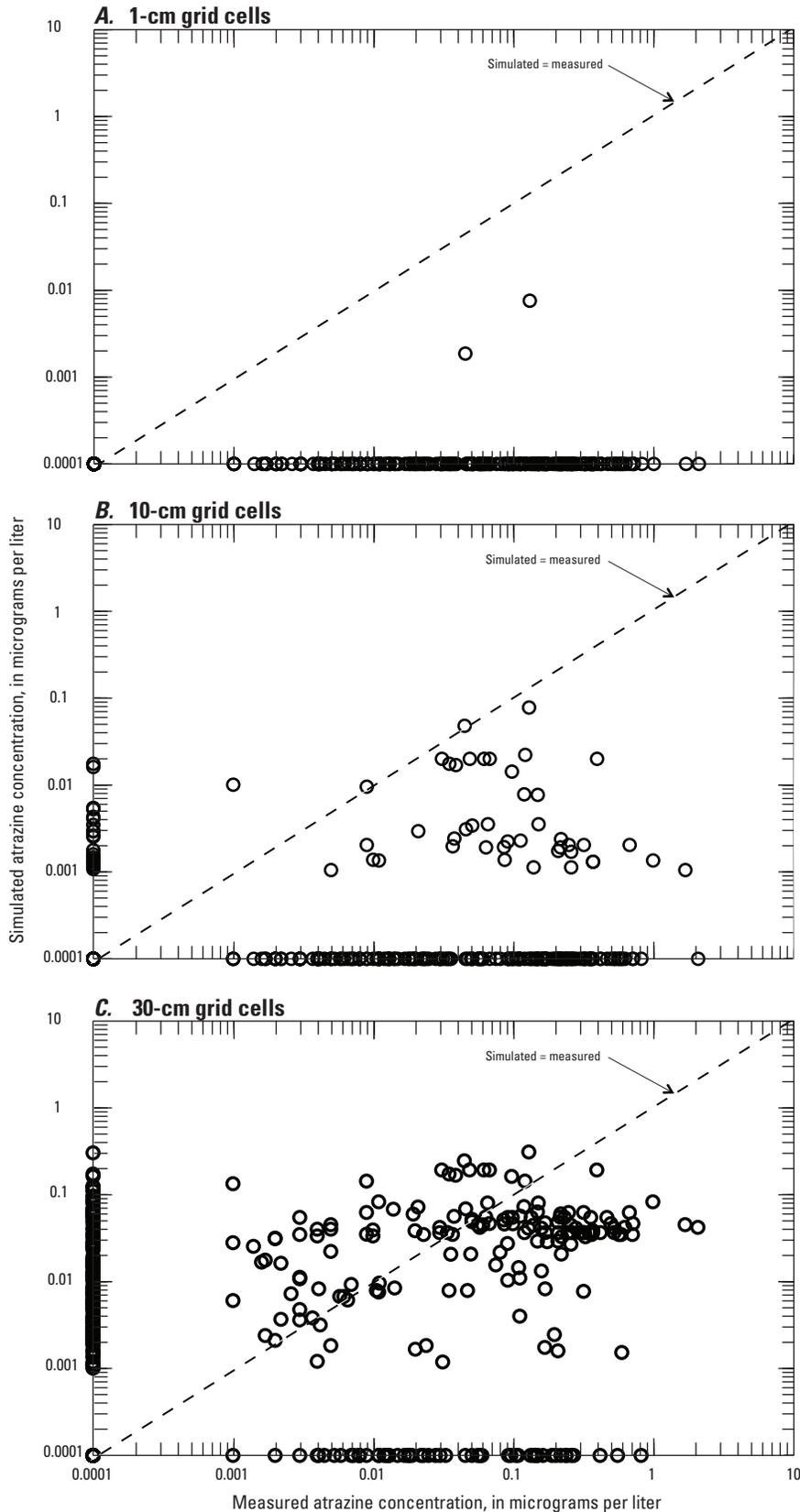


Figure 22. Effect of model grid discretization in the 10–100 centimeter depth interval on the degree of agreement between atrazine concentrations simulated at an assessment depth of 100 centimeters (1 meter) by the P-GWAVA-PR (Phase 1) model and measured in shallow groundwater at 331 sites in unirrigated agricultural areas in the conterminous United States with average depths to water greater than 1 meter. Simulations were carried out with areally averaged atrazine use intensities, and irrigation was not simulated. A grid-cell size of 0.1 centimeter was used for the upper 10 centimeters for all simulations. All atrazine concentrations (simulated or measured) less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purpose of display.

Additionally, the data summarized in table 5 indicate that the use of a grid-cell size of 30 cm within the 10–100 cm depth interval resulted in simulated atrazine concentrations that were more strongly correlated with those measured in groundwater than the concentrations simulated using either the 10-cm or the 1-cm cell sizes. Consequently, the 30-cm grid cells were used for the 10-100 cm depth interval for the Phase 1 simulations (figure 22C, table 4). The only simulations for which the 30-cm discretization between 10 and 100 cm depth was not used were simulations carried out to compare the results obtained using the SSURGO-derived soil property values with those derived from the STATSGO data. This exception was required because the 30-cm discretization did not always align with the soil layering specified by the SSURGO data.

The 30-cm grid-cell size used for the 10–100 cm depth interval is the maximum value recommended by Carsel and others (1998), and larger than most values that have been used for previous studies. However, grid-cell sizes of this magnitude are not without precedent for PRZM simulations. The EPA Office of Pesticide Programs has sometimes used grid-cell sizes of as much as 20 cm for PRZM simulations

of pesticide transport (Dirk Young, U.S. Environmental Protection Agency Office of Pesticide Programs, oral commun., August 21, 2009). Modeling investigations seldom provide information on the discretizations used, but grid-cell sizes of 5 cm (Sauer and others, 1990; Parrish and others, 1992) and as much as 10 cm (Garratt and others, 2002) have been reported by earlier studies using PRZM.

Effect of Spatial Variability of Atrazine Application Intensities on Simulation Results

To examine the degree to which the spatial variability of simulated atrazine applications may have influenced the extent of agreement between the concentrations of atrazine predicted in the vadose zone with the P-GWAVA-PR model and those measured in shallow groundwater, separate sets of simulations were done using the spatially uniform application intensity of 2 kg a.i./ha and the areally averaged application intensities computed with equation 10 (and shown in fig. 1).

Table 5. Effects of model grid discretization in the 10–100 centimeter depth interval on the level of agreement between atrazine concentrations simulated at the 100-centimeter (1 meter) assessment depth in the vadose zone using P-GWAVA-PR (Phase 1) and those measured in shallow groundwater at 331 unirrigated agricultural sites where the average depth to the water table was greater than 1 meter in the conterminous United States, 1992–98.

[All P-GWAVA-PR simulations used grid cells that were 0.1 centimeter (cm) in thickness for the depth interval from 0–9.9 cm below land surface, and the areally averaged intensities of atrazine use. Irrigation not simulated. For the purposes of these calculations, all atrazine concentrations—either simulated or measured—below the Phase 1 reporting limit of 0.001 microgram per liter ($\mu\text{g/L}$) were assigned a value of 0.0001 $\mu\text{g/L}$. **Selected statistical characteristics:** Model residuals calculated as the simulated concentration minus the measured concentration at each site. Simulated concentrations are flow-weighted mean concentrations in the vadose zone at a depth of 1 meter, derived from P-GWAVA-PR simulations and calculated using equation 47. Measured concentrations are those observed in groundwater during the NAWQA program. **Spearman ρ :** Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. **P (ρ):** Probability associated with the Pearson correlation coefficient (R^2) for the relation between the ranks of the simulated and measured atrazine concentrations. **95th percentile:** for each case, 95 percent of the model residuals were smaller than the value shown. \leq , less than or equal to]

Thickness of grid cell used between 10 and 100 cm depth (cm)	Relations between atrazine concentration simulated by P-GWAVA-PR in the vadose zone and concentration measured in groundwater at each site			
	Nonparametric rank correlations		Selected statistical characteristics of model residuals ($\mu\text{g/L}$)	
	Spearman ρ	P (ρ)	Median	95th percentile
30	0.24	≤ 0.0001	0.0000	0.068
10	0.15	0.005	0.0000	0.0012
1	0.07	0.22	0.0000	0.0000

The simulations presumed that atrazine transformation occurred in the sorbed and dissolved states. As with the analysis of the effects of grid discretization on the model predictions, the potential influence of irrigation was avoided by conducting the simulations without irrigation, and restricting the analysis to unirrigated areas.

Cumulative distribution plots (fig. 23) were used to compare the model residuals for the atrazine concentrations predicted by the P-GWAVA-PR simulations using the areally averaged atrazine application intensities with those predicted by the simulations using the spatially uniform application intensity. Substantially closer agreement was noted between the simulated and measured atrazine concentrations when the areally averaged application intensities were used than when the spatially uniform intensity was used. The fact that the atrazine concentrations simulated using the spatially uniform application intensity were almost always greater than those simulated using the areally averaged intensities is consistent with the fact that the spatially uniform application intensity (2 kg a.i./ha) was greater than the areally averaged intensities for most of the Phase 1 sites (fig. 1).

The effects of 15 modeling approaches on the extent of agreement between the atrazine concentrations predicted by the P-GWAVA-PR simulations at the 1-m assessment depth in the vadose zone and the concentrations measured in shallow groundwater at all 1,125 Phase 1 sites where the average DTW exceeded 1 m are shown in table 6. The table provides a summary of the results from statistical analyses of correlations (if any) between the simulated and measured atrazine concentrations for each modeling approach. When irrigation was simulated at all Phase 1 sites and atrazine transformations were simulated in the sorbed and dissolved states, the use of the areally averaged application intensities led to a correlation (table 6) between the simulated and measured atrazine concentrations that was statistically significant ($P[\rho] \leq 0.0001$), whereas the use of the spatially uniform application rate did not ($P[\rho] > 0.05$). Consequently, the final set of predicted atrazine concentrations for Phase 1 were derived from the P-GWAVA-PR simulations that used areally averaged atrazine application intensities, instead of the spatially uniform application rate (table 4).

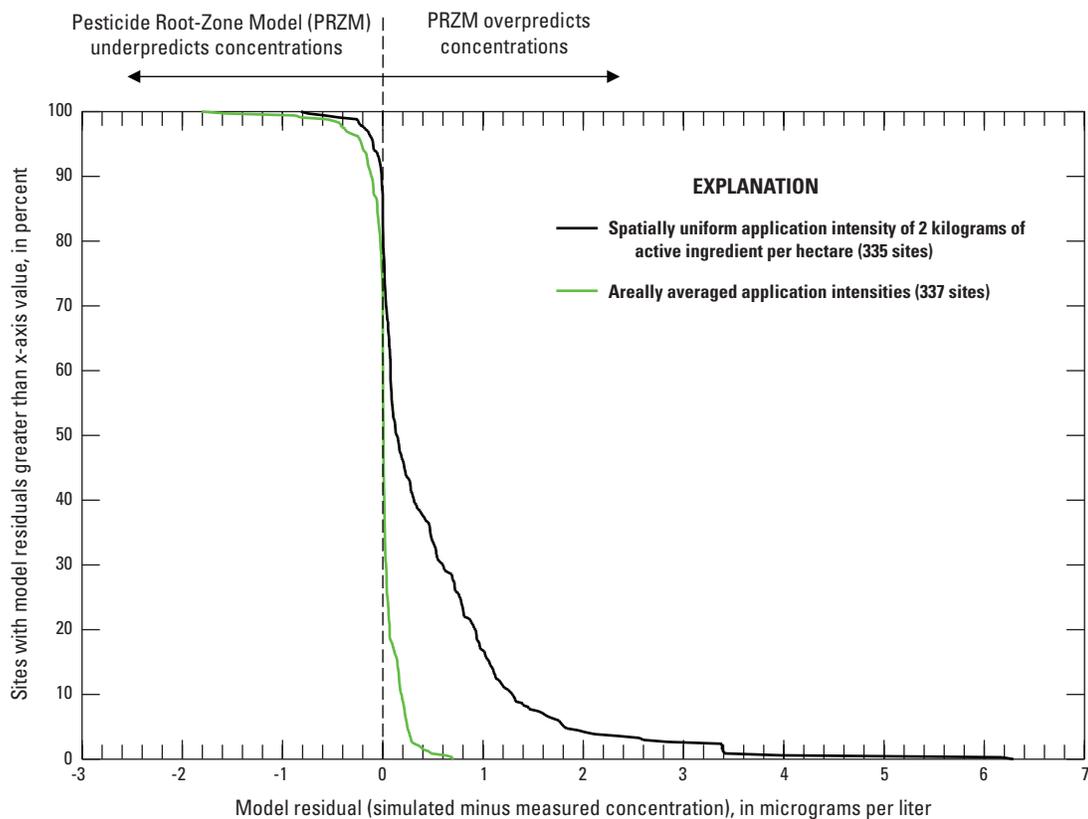


Figure 23. Effect of spatial variability of atrazine application intensities on model residuals for atrazine concentrations measured in shallow groundwater beneath unirrigated agricultural areas where the average depth to water was greater than 1 meter in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–98. Transformations of atrazine were simulated in the dissolved and the sorbed states; irrigation was not simulated. All simulated or measured atrazine concentrations less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations.

Table 6. Effects of 15 modeling approaches on the extent of agreement between atrazine concentrations predicted at the 1-meter assessment depth in the vadose zone by the P-GWAVA-PR (Phase 1) simulations and concentrations measured in shallow groundwater in agricultural areas where the depth to water exceeded 1 meter in the conterminous United States, 1992–98.

[Simulated concentrations are flow-weighted mean concentrations in the vadose zone, derived from the P-GWAVA-PR simulations and calculated using equation 47. For the purposes of these calculations, all concentrations of atrazine below the Phase 1 reporting limit of 0.001 microgram per liter ($\mu\text{g/L}$)—either measured or simulated—were assigned a value of 0.0001 $\mu\text{g/L}$. **Spatial variability of atrazine application:** *Uniform* indicates a spatially homogeneous application intensity of 2 kilograms of active ingredient per hectare (kg a.i./ha). **Sites irrigated:** Indicates whether or not irrigation was simulated by P-GWAVA-PR for all sites. *Stochastic* denotes simulations for which sites were selected at random for irrigation, in the proportion at which irrigation was implemented in the surrounding area, estimated using equation 8. **Spearman ρ :** Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. **$P(\rho)$:** The probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the simulated and measured values. **Model residuals:** Calculated for each site as the atrazine concentration simulated by P-GWAVA-PR at the assessment depth (1 meter) in the vadose zone minus the concentration measured in shallow groundwater in the same location. **95th percentile:** For each case, 95 percent of the model residuals were less than the value shown. $<$, less than; \leq , less than or equal to]

Spatial variability of atrazine application	Sites irrigated	Reaction site(s) where atrazine transformation was simulated (all occurrences)	Correlation (if any) between simulated and measured atrazine concentrations		Model residuals		Number of sites
			Spearman ρ	$P(\rho)$	Median ($\mu\text{g/L}$)	95th percentile ($\mu\text{g/L}$)	
Areally averaged	None	Sorbed and dissolved	0.17	\leq 0.0001	0.000	0.25	1,125
	Stochastic		0.13	\leq 0.0001	0.005	0.35	1,125
	All		0.15	\leq 0.0001	0.049	0.93	1,125
Areally averaged	None	Sorbed	0.16	\leq 0.0001	0.000	0.55	1,125
	Stochastic		0.13	\leq 0.0001	0.011	0.74	1,125
	All		0.14	\leq 0.0001	0.078	2.0	1,125
Areally averaged	None	Dissolved	0.19	\leq 0.0001	0.37	9.1	1,125
	Stochastic		0.18	\leq 0.0001	0.88	9.4	1,125
	All		0.21	\leq 0.0001	2.3	12	1,125
Areally averaged	None	None	0.14	\leq 0.0001	2.4	120	1,125
	Stochastic		0.12	\leq 0.0001	5.9	122	1,125
	All		0.14	\leq 0.0001	18	155	1,125
Uniform	None	Sorbed and dissolved	0.06	0.034	0.064	2.4	1,123
	Stochastic		-0.009	0.76	0.47	25	1,123
	All		-0.05	0.095	2.4	28	1,123

Effect of Transformation Site (Dissolved versus Sorbed State) on Simulation Results

To examine the extent to which the agreement between predicted and measured atrazine concentrations was influenced by the location(s) in the subsurface where atrazine transformation was simulated by PRZM, the results from four P-GWAVA-PR simulation scenarios were compared. These scenarios involved the simulation of atrazine transformation in (1) the dissolved state alone, (2) the sorbed state alone, (3) both states, and (4) neither state (that is, no reaction). The simulations were carried out at all unirrigated Phase 1 sites where the DTW was 1 m or more; irrigation was not simulated. All four scenarios used the areally averaged intensities of atrazine application at all the sites of interest.

The results from this analysis (fig. 24), indicate that the atrazine concentrations measured in groundwater matched the concentrations predicted in the vadose zone most closely when atrazine transformation was simulated in both the dissolved and the sorbed states. A similar conclusion was reached from the statistical analyses of the model residuals obtained when irrigation was simulated at all sites and irrigated sites were included among those examined (table 6). As a result, atrazine transformation was presumed to occur in both the sorbed and the dissolved states for the final set of P-GWAVA-PR model simulations (table 4)—an approach that is consistent with the fact, noted earlier, that the rate of atrazine transformation in water is known to increase in the presence of soil (Armstrong and others, 1967; Skipper and others, 1967; Armstrong and Chesters, 1968; Erickson and Lee, 1989; Mandelbaum and others, 1993; Rice and others, 2004; Krutz and others, 2008).

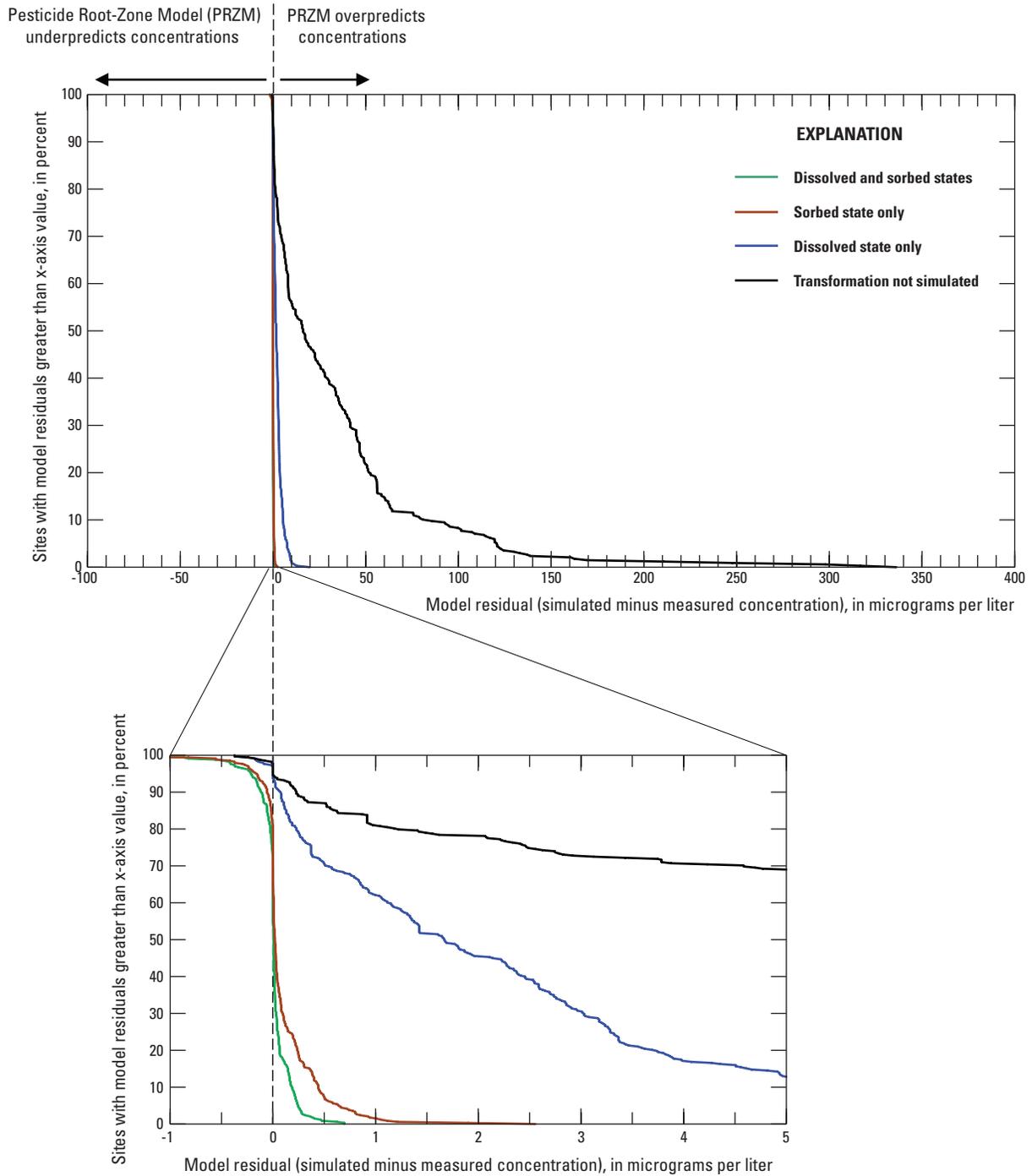


Figure 24. Effect of the location of simulated atrazine transformation (that is, in the sorbed and [or] dissolved state) on model residuals for atrazine concentrations in shallow groundwater beneath unirrigated agricultural areas where the average depth to water was greater than 1 meter (337 sites) in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–98. Simulated concentrations were obtained assuming areally averaged atrazine application intensities, and without simulating irrigation. All simulated or measured atrazine concentrations less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations.

The results shown in figure 24 and table 6 indicate that during the P-GWAVA-PR simulations, transformation in the sorbed state exerted a more pronounced effect on the predicted atrazine concentrations than transformation in the dissolved state. This is likely a consequence of the differences between the atrazine concentrations predicted in the sorbed and dissolved states. At a site in central Washington, for example, 93 percent of the atrazine remaining in the soil column at the end of the 5-year simulation period was present in the sorbed state, rather than in the dissolved state (fig. 25). As indicated by equation 27, for any compound that reacts by first-order kinetics (as is presumed to be the case for the thermal transformations of atrazine in soil or water), the rate of disappearance at any moment is directly proportional to the concentration of the compound at that time. The higher concentrations of atrazine in the sorbed state relative to the dissolved state might have been expected to lead to higher predicted rates of atrazine transformation in the sorbed state, relative to its rates of transformation in solution. This, in turn, would have contributed to the contrast in the relative influence of the two reaction locations indicated by the results shown in figure 24 and table 6.

Approaches for Distributing Irrigation

The approach for selecting the sites where irrigation was to be simulated during Phase 1 was anticipated to influence the level of agreement between the simulated and measured atrazine concentrations. To assess the potential importance of irrigation, the results from three modeling scenarios were examined. These scenarios involved simulating irrigation (1) at all the sites of interest; (2) at sites selected randomly in proportion to the percentage of irrigated land nearby (equation 8; fig. 17); and (3) at none of the sites. Despite its inclusion in this part of the analysis, the approach of assigning irrigation randomly in individual sampling networks was devised primarily for predicting frequencies of atrazine detection, rather than atrazine concentrations in individual locations. The simulations for all three scenarios involved assuming that atrazine was applied with areally averaged use intensities, allowing transformation of the herbicide to take place in both the dissolved and the sorbed states, and focusing solely on those locations where the average DTW exceeded 1 m. For both phases of this investigation, irrigation was simulated at each location by applying water only when soil moisture was below specified thresholds (table 14), rather than by applying water in fixed amounts on specified schedules.

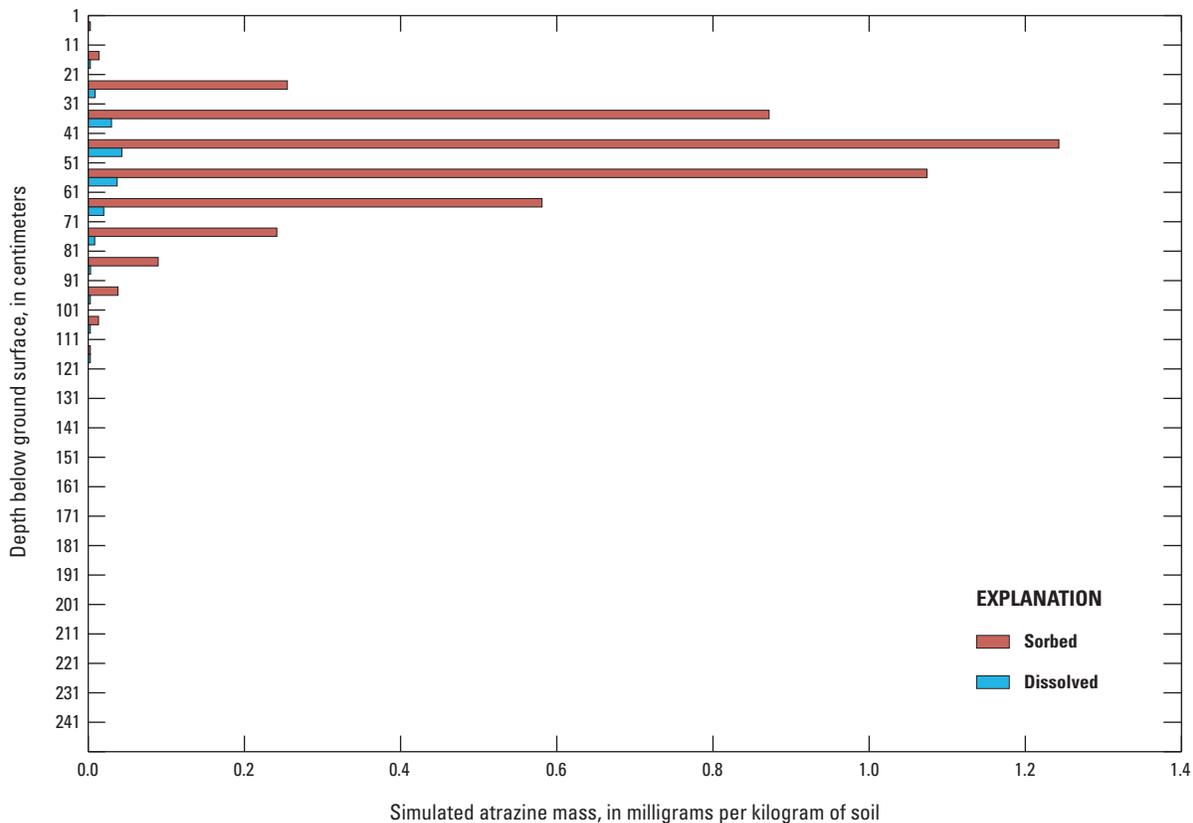


Figure 25. Amounts of atrazine predicted in sorbed and dissolved states in soil at the end of a 5-year P-GWAVA-PR (Phase 1) simulation in an agricultural area (site 2086) in Grant County, Washington, 1991–95.

Statistical analyses of the results from the three irrigation scenarios indicated that all three scenarios led to simulated atrazine concentrations that were significantly correlated with the measured values (see the first three entries in table 6). Simulating irrigation at all of the sites resulted in a greater degree of overprediction of atrazine concentrations—but a lower degree of underprediction—than for the non-irrigated and stochastically distributed irrigation scenarios (fig. 26). This is consistent with the general pattern reported by previous field studies, which have commonly observed increases in pesticide concentrations in subsurface waters in response to recent recharge (Barbash and Resek, 1996).

The spatial distributions of the P-GWAVA-PR model residuals for the frequencies of atrazine detection at agricultural sites with depths to water greater than 1 m (in groundwater networks with 10 or more such sites) are shown in figure 27 for two of the irrigation scenarios. These results indicate that when irrigation was not simulated at any of the

sites (fig. 27A), the geographic distribution of model residuals for the atrazine detection frequencies reflected the distribution of precipitation in the conterminous United States (Daly, 2010), with most areas of underprediction corresponding to more arid regions, and areas of overprediction generally corresponding to more humid regions. This relation was considerably less evident when irrigation was simulated at all of the sites (fig. 27B). Consistent with these observations, the model residuals for the atrazine detection frequencies in the 46 groundwater networks were positively correlated with mean annual precipitation (from 1961 to 1990 [PRISM Climate Group, 2009]) when irrigation was not simulated ($R^2 = 0.55$; $P \leq 0.0001$) or stochastically distributed ($R^2 = 0.31$; $P \leq 0.0001$), but not when irrigation was simulated at all sites ($P = 0.22$). These results demonstrate the importance of accounting for irrigation during the P-GWAVA-PR simulations, to counteract the spatial bias caused by the uneven distribution of precipitation across the Nation.

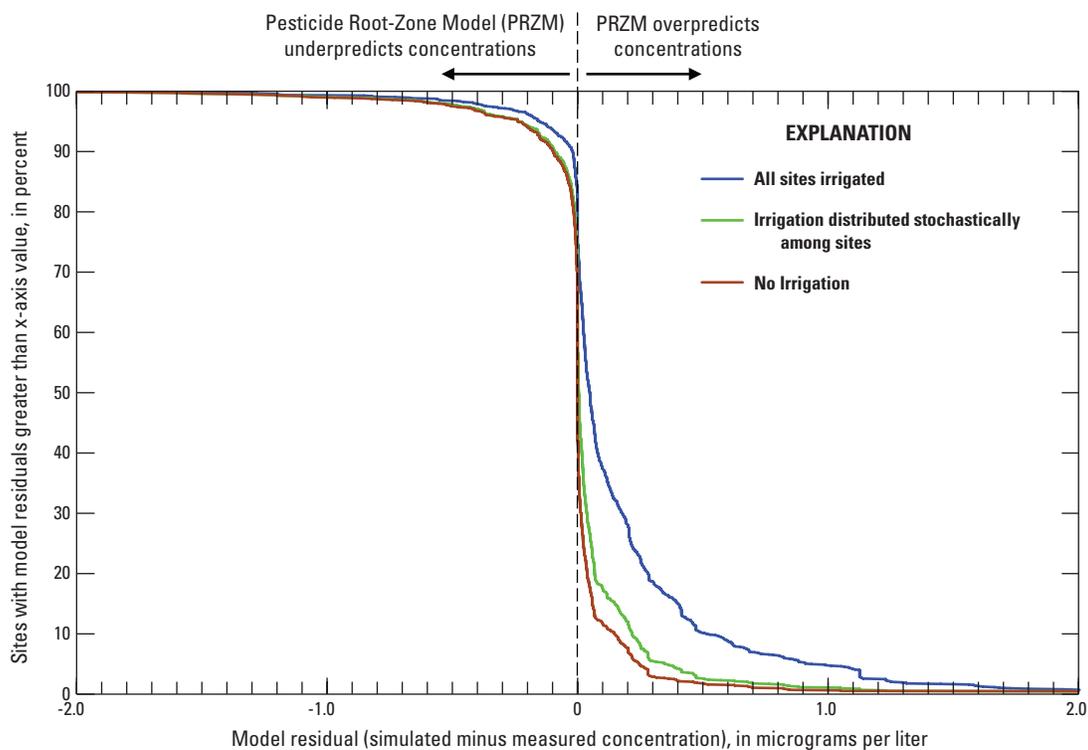


Figure 26. Effect of irrigation simulation approach on model residuals for atrazine concentrations in shallow groundwater beneath agricultural areas where the average depth to water was greater than 1 meter (1,124 sites) in the P-GWAVA-PR (Phase 1) study area in the conterminous United States, 1992–98. Simulated concentrations were obtained using areally averaged atrazine application intensities and assuming that atrazine transformation occurred in both the sorbed and dissolved states. All simulated or measured atrazine concentrations less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations.

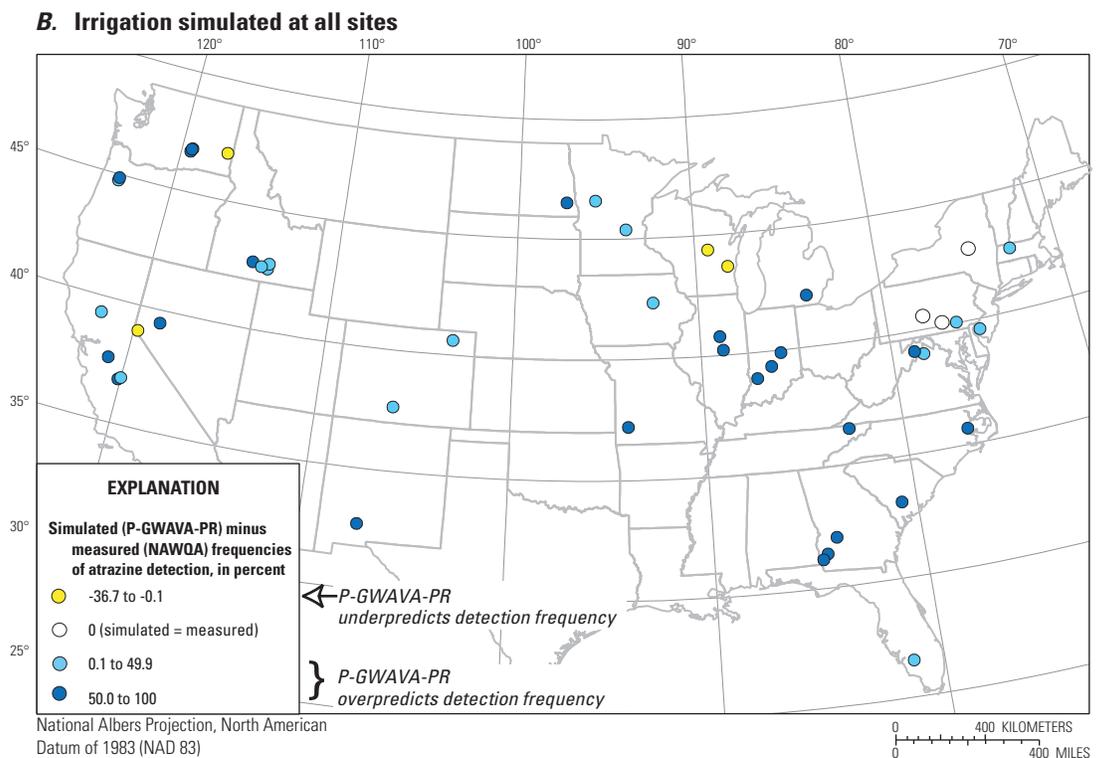
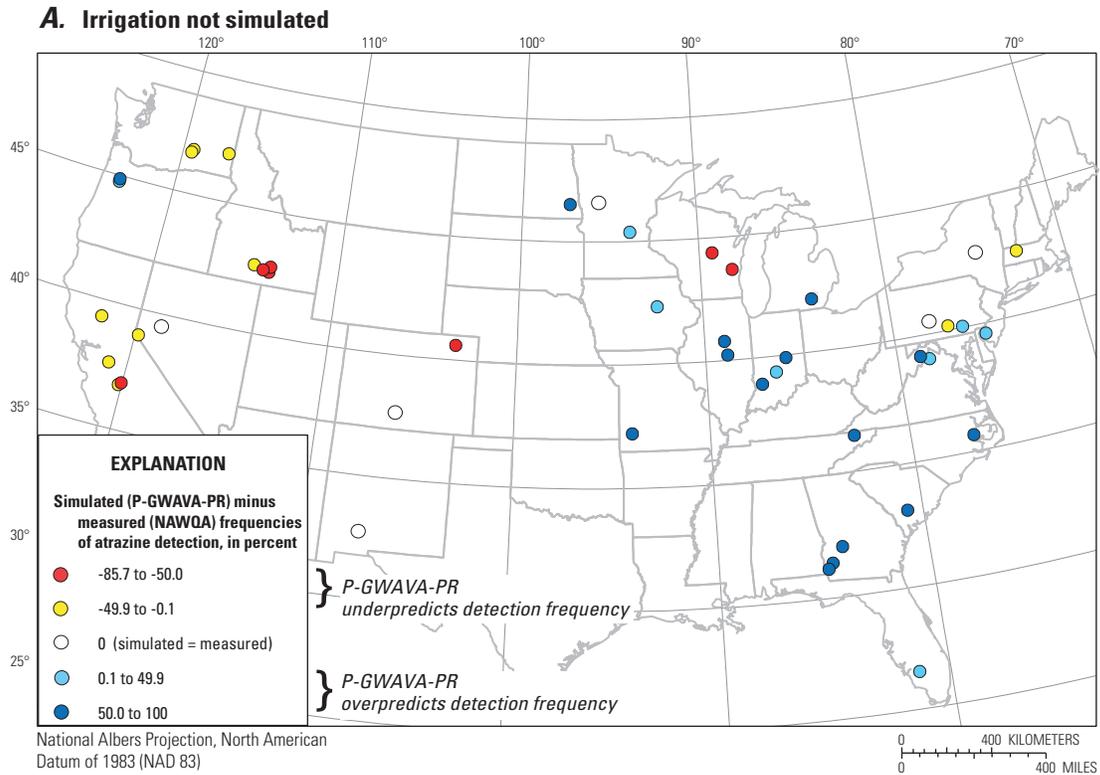


Figure 27. Effect of irrigation simulation approach on P-GWAVA-PR model residuals for frequencies of atrazine detection in groundwater networks with 10 or more sites when (A) irrigation was not simulated at any sites and (B) irrigation was simulated at all sites across the conterminous United States for Phase 1 of this study, 1992–98. All sites included in the analysis had average depths to water greater than 1 meter (46 groundwater networks; 1,051 sites). Model simulations used an assessment depth of 1 m and areally averaged intensities of atrazine use, and assumed that atrazine transformation occurred in both the sorbed and dissolved states.

Spatial Averaging of Soil Parameter Values

Soil parameter values from the STATSGO data—rather than from the more detailed SSURGO data—were used as input for the Phase 1 model simulations, after being averaged both areally and with depth (fig. 7). To examine the potential effects of this spatial averaging on the atrazine concentrations predicted by the P-GWAVA-PR model, the results from a series of 10-year simulations using soil parameter values derived from STATSGO (spatially averaged) were compared with results from an analogous set of simulations using soil property data from SSURGO (as is). These comparisons were carried out at multiple sites in two agricultural locations: four sites in an arid, irrigated area with relatively low atrazine use in central Washington State, and six sites in a humid, unirrigated area with higher atrazine use in Wisconsin. All the simulations in both locations used the areally averaged intensities of atrazine application and assumed that atrazine transformation occurred in both the sorbed and the dissolved states.

For a preliminary set of simulations at the four Washington sites, the 0.1-cm discretization was used for the upper 10 cm of the soil column as recommended by Carsel and others (1998), and 1-cm grid cells used from 10 cm to an assessment depth of 153 cm. The 153-cm assessment depth was used for these analyses to take maximal advantage of all the available data on soil properties—data that are provided to at least this depth in all STATSGO and SSURGO map units. The 1-cm grid cells were used for depths below 10 cm to obtain closer alignment with the SSURGO soil layer boundaries for the model simulations. The average depths to the water table at the four Washington sites ranged from 3.8 to 37.8 m, substantially greater than the 1.53-m assessment depth.

As anticipated from the results shown in figure 22A, the atrazine fluxes predicted by these initial simulations were negligible when the 1-cm discretization was used below 10 cm (data not shown). Given the positive relation between grid-cell sizes and the concentrations predicted at a depth of 100 cm (fig. 22), an additional set of P-GWAVA-PR simulations was done using the same discretization scheme for the upper 93 cm, but with 10-cm grid cells (rather than 1-cm cells) occupying the depth interval from 93 to 153 cm. The results (fig. 28) showed clear differences between the atrazine chemographs created using the STATSGO and SSURGO data at some sites, especially at the times of the annual peak concentrations. However, the differences between the chemographs for the two approaches were not systematic in time or space; all four of the sites exhibited reversals in the

relative magnitudes of the atrazine concentrations simulated by the two approaches over time. Furthermore, although the atrazine concentrations predicted using the spatially averaged soil parameter values from STATSGO exceeded those predicted using the data from SSURGO throughout most of the 10-year simulation at one of the sites (site 2098), the opposite pattern was observed in most years at the other three sites.

Similar results were observed when the simulations were repeated using grid-cell thicknesses that were equal to those of the SSURGO layers for both cases. The atrazine concentrations predicted by the P-GWAVA-PR simulations using this approach in conjunction with the SSURGO and STATSGO soil property data at the four Washington sites are compared with the concentrations measured in shallow groundwater at the same sites in figure 29. As anticipated from the results shown in figure 28, the atrazine concentrations simulated using the two sets of soils data were in relatively close agreement at all four sites. All of the simulated concentrations, however, were substantially higher than the atrazine concentrations measured in groundwater at the four sites, only one of which was greater than the reporting limit.

Analogous comparisons were carried out at six sites with atrazine detections in groundwater beneath a humid, unirrigated agricultural area in Portage County, Wisconsin (fig. 30), where atrazine use is considerably higher than at the Washington sites. As with the four locations examined in Washington, the average depths to the water table at all six Wisconsin sites were greater than the 1.53-m assessment depth, ranging from 6.1 to 22.4 m beneath the land surface. Using the same approach as at the Washington sites, atrazine concentrations measured in groundwater at the Wisconsin sites were compared with concentrations predicted by P-GWAVA-PR simulations using either (1) the original SSURGO data with grid-cell thicknesses equal to those of the SSURGO layers, or (2) the spatially averaged STATSGO data with grid-cell thicknesses equal to those of the SSURGO layers. At five of the six sites, the concentrations simulated using the SSURGO data were in closer agreement with those measured in groundwater than was the case for those simulated using the STATSGO data—none of which were greater than the reporting limit at any of the six sites (fig. 31). Although the reasons for the differences between the atrazine concentrations simulated using the two sets of soil property data are unclear, these results provided support for the use of the SSURGO data to characterize soil properties—instead of the spatially averaged STATSGO values—during Phase 2 of this project.

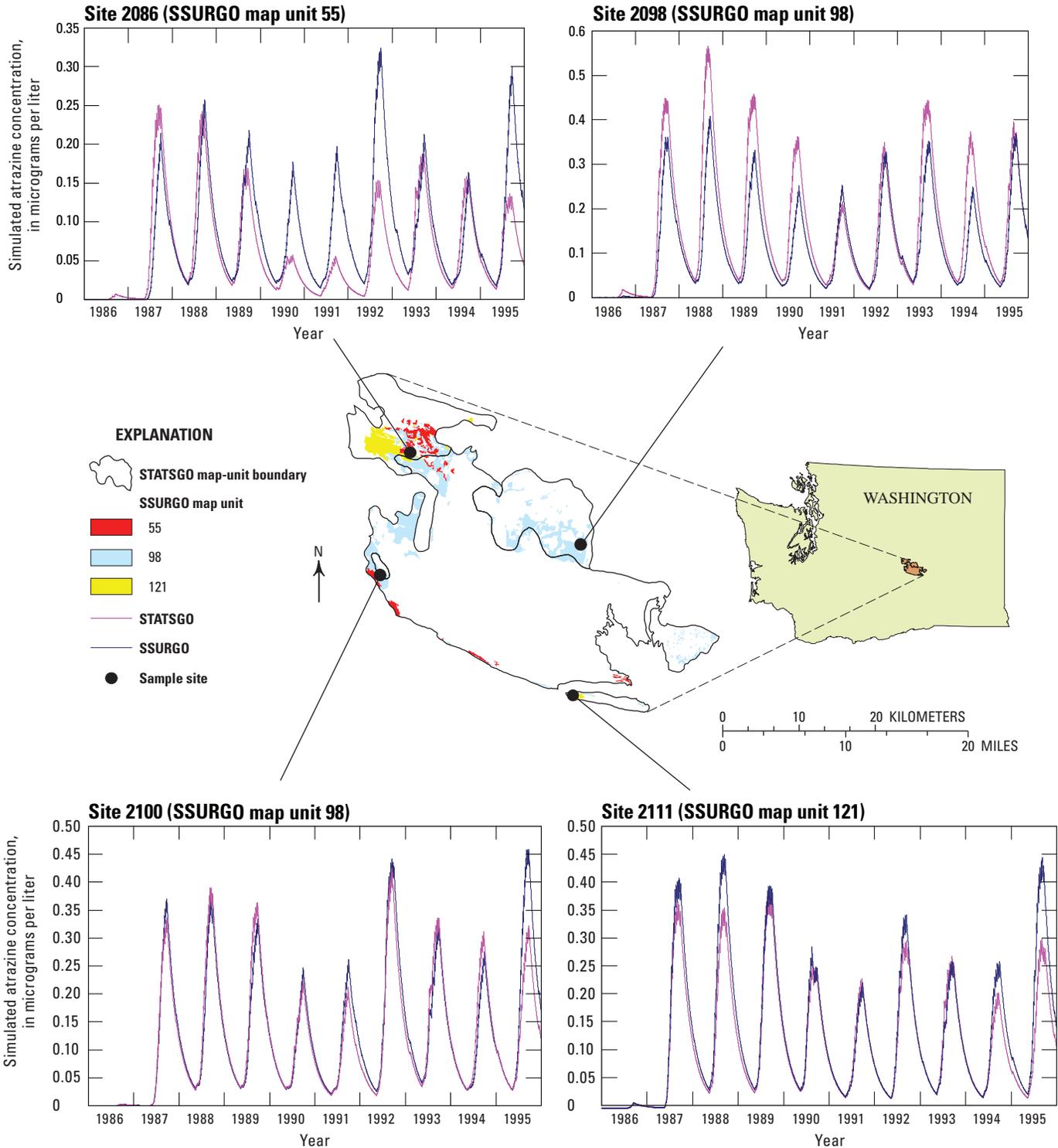


Figure 28. Influence of spatial averaging of soil parameter values on atrazine chemographs simulated at a depth of 153 centimeters in the vadose zone by the P-GWAVA-PR (Phase 1) model using spatially averaged State Soil Geographic database (STATSGO) values and the original Soil Survey Geographic database (SSURGO) values for soil parameters at four agricultural sites in central Washington State, 1986–95. All model simulations used areally averaged intensities of atrazine application and assumed that atrazine transformation occurred in both the sorbed and dissolved states.

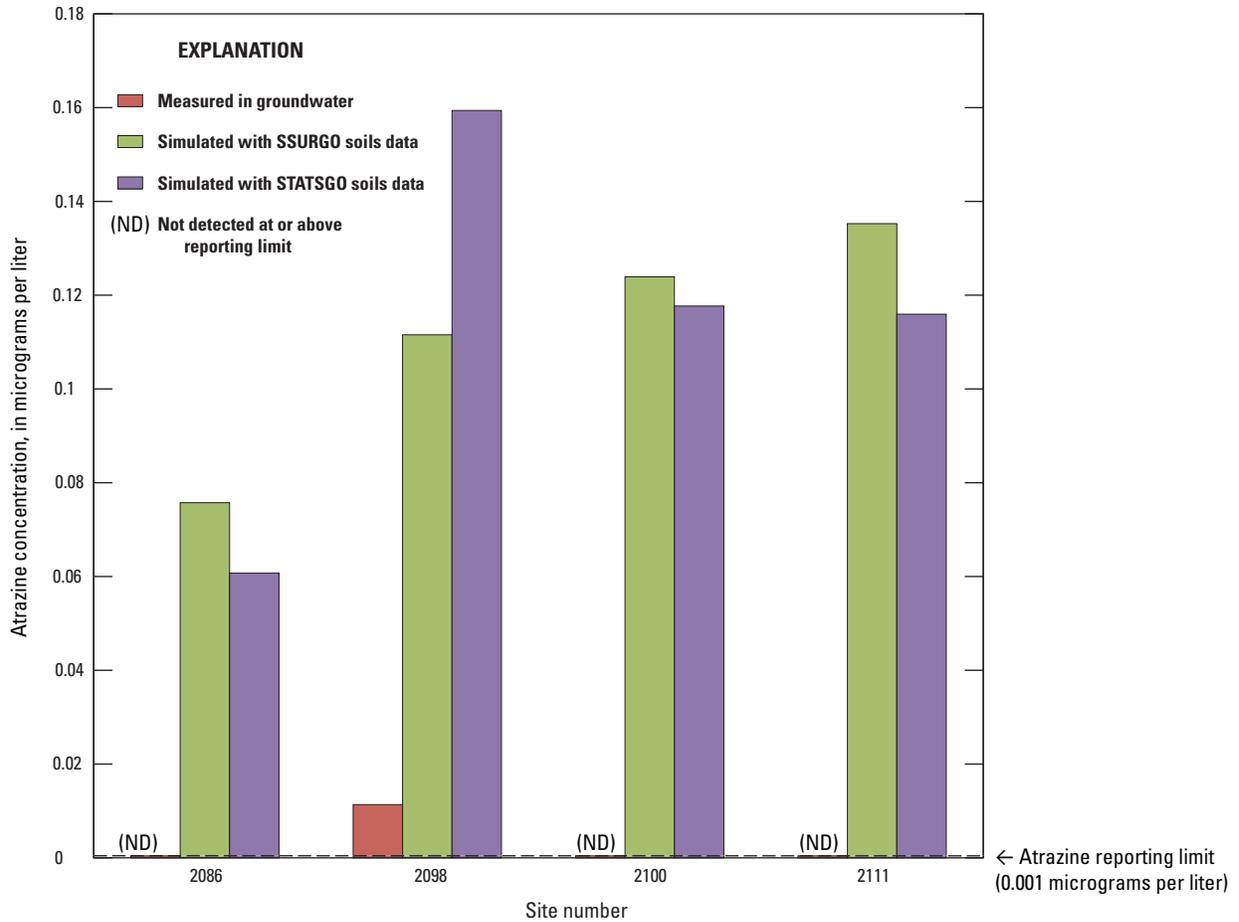


Figure 29. Influence of spatial averaging of soil parameter values on the extent of agreement between atrazine concentrations predicted at a depth of 153 centimeters in the vadose zone by a set of 10-year simulations using the P-GWAVA-PR model (1986–1995) and atrazine concentrations measured in shallow groundwater at four irrigated agricultural sites in central Washington State, 1992–95. Model simulations used areally averaged intensities of atrazine application and assumed that atrazine transformation occurred in both the sorbed and dissolved states. The simulations used grid-cell thicknesses equal to the soil-layer thicknesses specified by the Soil Survey Geographic database (SSURGO) and either the spatially averaged State Soil Geographic database (STATSGO) values or the original SSURGO values for soil parameters. See figure 28 for site locations.



Figure 30. Locations where atrazine concentrations predicted by the P-GWAVA-PR (Phase 1) simulations were compared with atrazine concentrations measured in shallow groundwater at six unirrigated agricultural sites in an agricultural area of Portage County, Wisconsin.

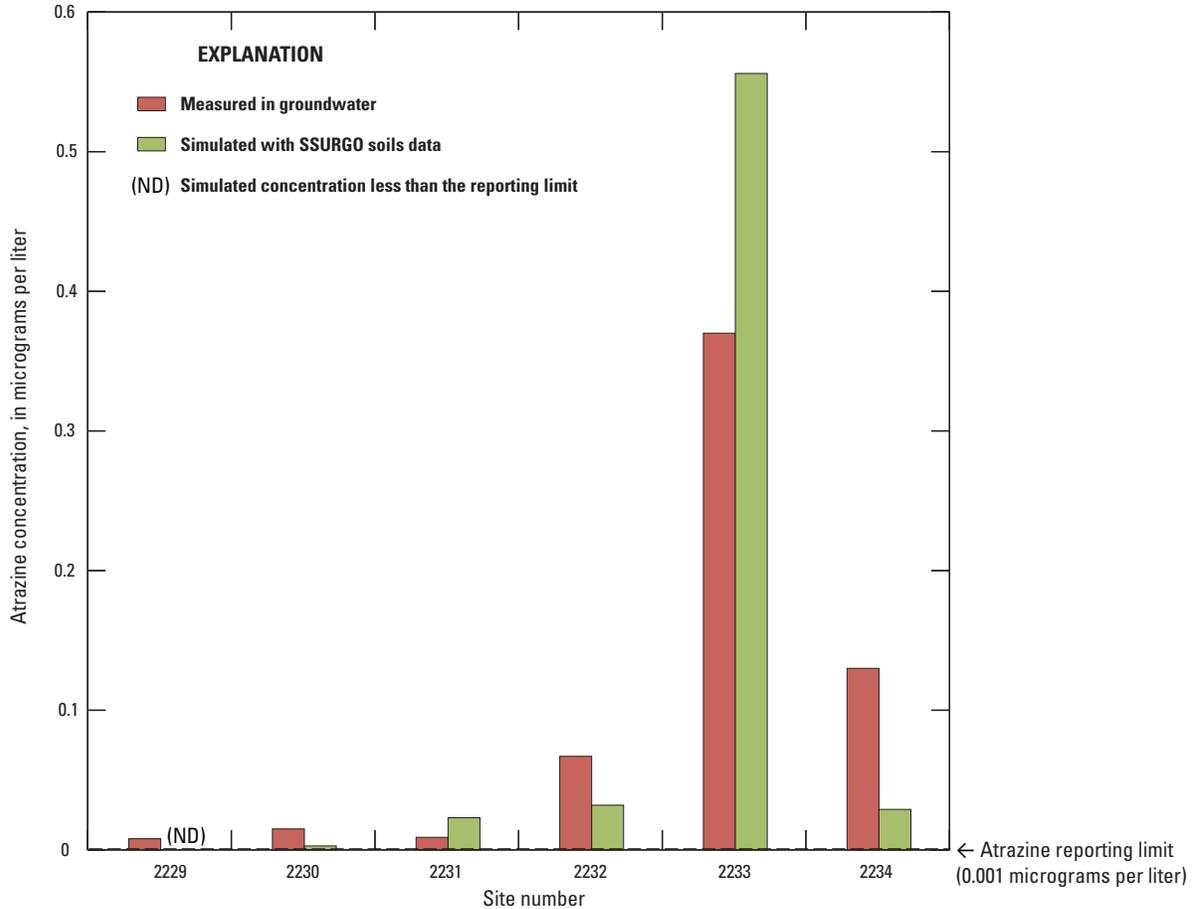


Figure 31. Influence of spatial averaging of soil parameter values on the extent of agreement between atrazine concentrations predicted at a depth of 153 centimeters in the vadose zone by a set of 10-year P-GWAVA-PR simulations (1986–1995) and atrazine concentrations measured in shallow groundwater at six unirrigated agricultural sites in Portage County, Wisconsin, 1992–95. Model simulations used areally averaged intensities of atrazine application, and assumed that atrazine transformation occurred in both the sorbed and dissolved states. Irrigation not simulated. The simulations used grid-cell thicknesses equal to the soil-layer thicknesses specified by the Soil Survey Geographic database (SSURGO) and either the spatially averaged State Soil Geographic database (STATSGO) values or the original (unaggregated) SSURGO values for soil parameters. None of the simulations using the STATSGO values for soil parameters resulted in predicted atrazine concentrations above the reporting limit. See [figure 30](#) for site locations.

Temporal Variability of Atrazine Concentrations and Water Flow

The temporal variations in atrazine concentrations simulated by the P-GWAVA-PR model were consistent with variations commonly seen in relation to the timing of recharge and pesticide applications during field studies of pesticide transport and fate in the subsurface (for example, Bottcher and others, 1981; McKenna and others, 1988; Barbash and Resek, 1996). As indicated by the atrazine chemographs shown in [figure 32](#) for one of the sites in Portage County, Wisconsin, these patterns included familiar features such as the abrupt increases in atrazine concentration in response to major recharge events (rather than immediately following the annual applications of the herbicide in the spring of each year) and the gradual tailing of each atrazine peak (caused by hydrodynamic dispersion) after the maximum concentration passed. The results from a simulation using the (unaggregated) SSURGO soils data ([fig. 32B](#)) show the same general features as the corresponding atrazine chemograph derived from the (aggregated) STATSGO data for the same site ([fig. 32A](#)), but at concentrations that were substantially closer to the value measured in shallow groundwater at this site—as anticipated from the results shown in [figure 31](#).

Modeling Approaches and Simulation Results

Preliminary simulations were carried out during Phase 1 to examine the effects of (1) the spatial variability of atrazine use intensity (areally averaged or uniform), (2) the approach for selecting sites where irrigation was simulated (all sites, no sites, or selected stochastically in proportion to the amount of irrigated land nearby), and (3) the location(s) of atrazine transformation in the subsurface (in the sorbed state, the dissolved state, both, or neither). The influences of these modeling approaches on the extent of agreement between the simulated and the measured atrazine concentrations at the Phase 1 sites are shown in [figure 33](#). The residuals displayed in the figure were compiled for all Phase 1 study sites, regardless of whether or not the DTW was greater than the 1-m assessment depth. The box plots in the figure display the distributions of model residuals for the atrazine concentrations predicted by each of the 15 simulation approaches explored with the P-GWAVA-PR model.

Modeling Approach for Final P-GWAVA-PR Simulations

A nonparametric multiple comparisons test—the Dwass-Steel-Christchlow-Fligner (DSCF) test (Christchlow and Fligner, 1991)—was applied to the 15 sets of model residuals ([fig. 33](#)) to determine which sets of residuals were significantly different from one another (Dr. Robert Black, U.S. Geological Survey, written commun., January 2011). The results from this analysis are shown in [figure 33](#). Scenarios with statistical distributions of ranks not significantly different from one another ($P > 0.05$) are labeled with identical letters;

those with significantly different distributions of ranks are assigned different letters. These results indicate that all four P-GWAVA-PR modeling scenarios that simulated atrazine concentrations that were in closest agreement with concentrations measured in groundwater used the areally averaged atrazine use intensities. Three of the four scenarios involved simulating atrazine transformation in both the sorbed and the dissolved state, and the fourth scenario involved transformation in the sorbed state only. These observations represent the combined influence of the factors examined separately in [figures 23, 24, and 26](#).

The preceding discussion appears to support two approaches for selecting the sites where irrigation was to be simulated (if at all) during Phase 1. For atrazine concentrations, the distributions of model residuals indicate that the most appropriate approach would have been to not simulate irrigation ([fig. 26; table 6](#)). However, when the model residuals were expressed in terms of atrazine detection frequencies, the statistically significant geographic bias introduced by precipitation (see section, “[Approaches for Distributing Irrigation](#)”) was eliminated only when irrigation was simulated at all the sites ([fig. 27](#)). As a compromise between the two approaches (that is, simulating irrigation at all sites or at none of the sites), the stochastic method of assigning irrigation to the sites (using equation 8) was used for the final set of P-GWAVA-PR simulations, along with the previously mentioned approaches of using areally averaged intensities of atrazine application and simulating atrazine transformation in the sorbed and the dissolved states ([table 4](#)). This approach resulted in a 95th percentile for the model residuals with respect to atrazine concentrations among all of the 1,224 Phase 1 sites ($0.39 \mu\text{g/L}$) that was similar to the value observed for the non-irrigated scenario ($0.27 \mu\text{g/L}$). These model residuals are an order of magnitude smaller than the Maximum Contaminant Level (MCL) of $3 \mu\text{g/L}$ established by the EPA for atrazine in water (U.S. Environmental Protection Agency, 2003), indicating a low probability of the P-GWAVA-PR model either under- or overpredicting atrazine concentrations by margins greater than the MCL.

The cumulative distribution plots displayed in [figure 34](#) for the model residuals for atrazine concentrations from the final set of P-GWAVA-PR simulations indicate that the inclusion of all sites in the analysis—regardless of the average DTW—exerted a negligible effect on the extent of agreement between the simulated and measured atrazine concentrations at the Phase 1 sites, relative to the level of agreement when sites with depths to water equal to or shallower than the 1-m assessment depth were excluded. One reason for this observation may have been that the 77 sites with depths to water of 1 m or less represented a relatively small percentage of the full set of 1,224 Phase 1 sites. The results displayed in [figure 34](#) also indicate that at the sites with depths to water equal to or less than the 1-m assessment depth, the P-GWAVA-PR model was more likely to overpredict the atrazine concentrations than to underpredict them.

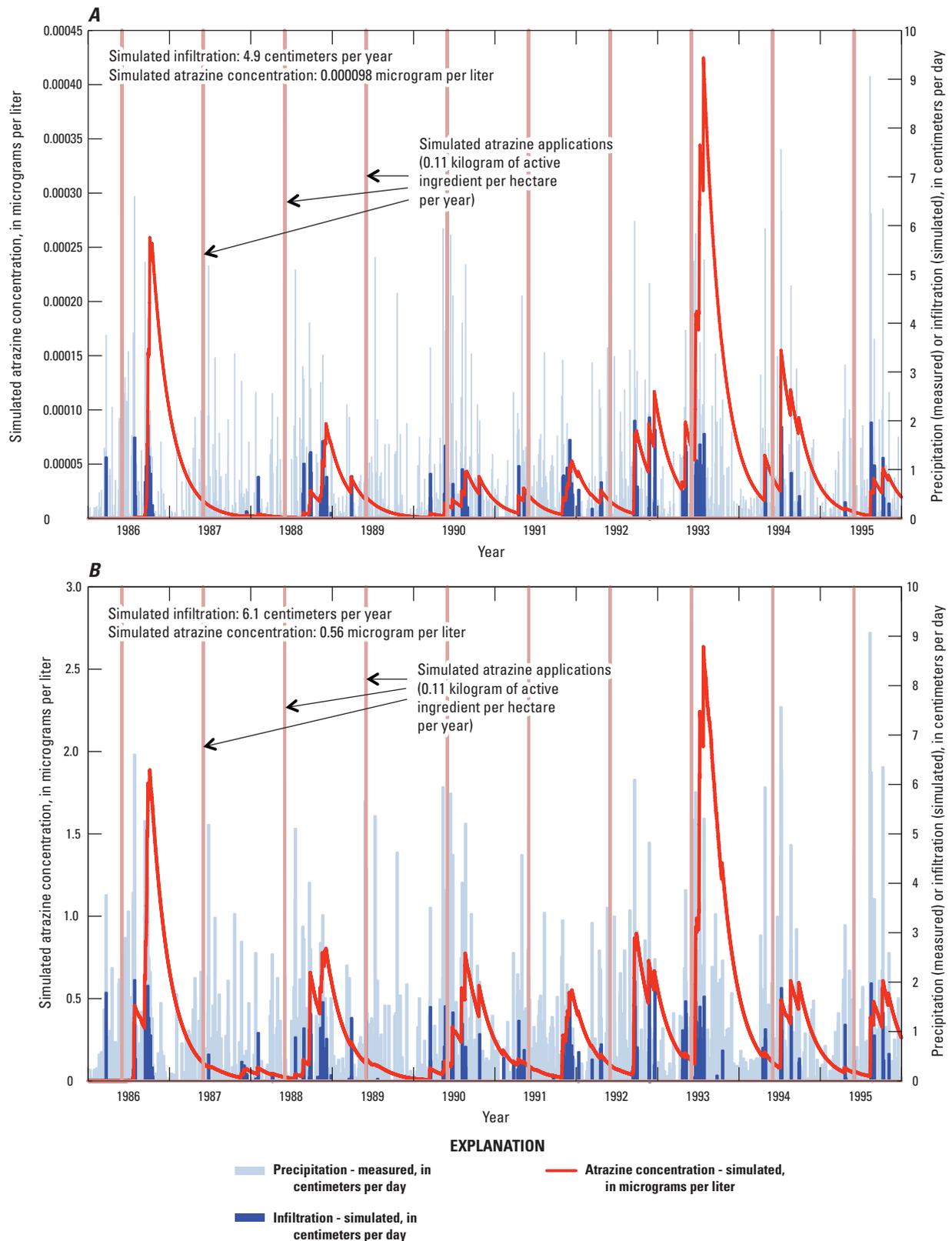
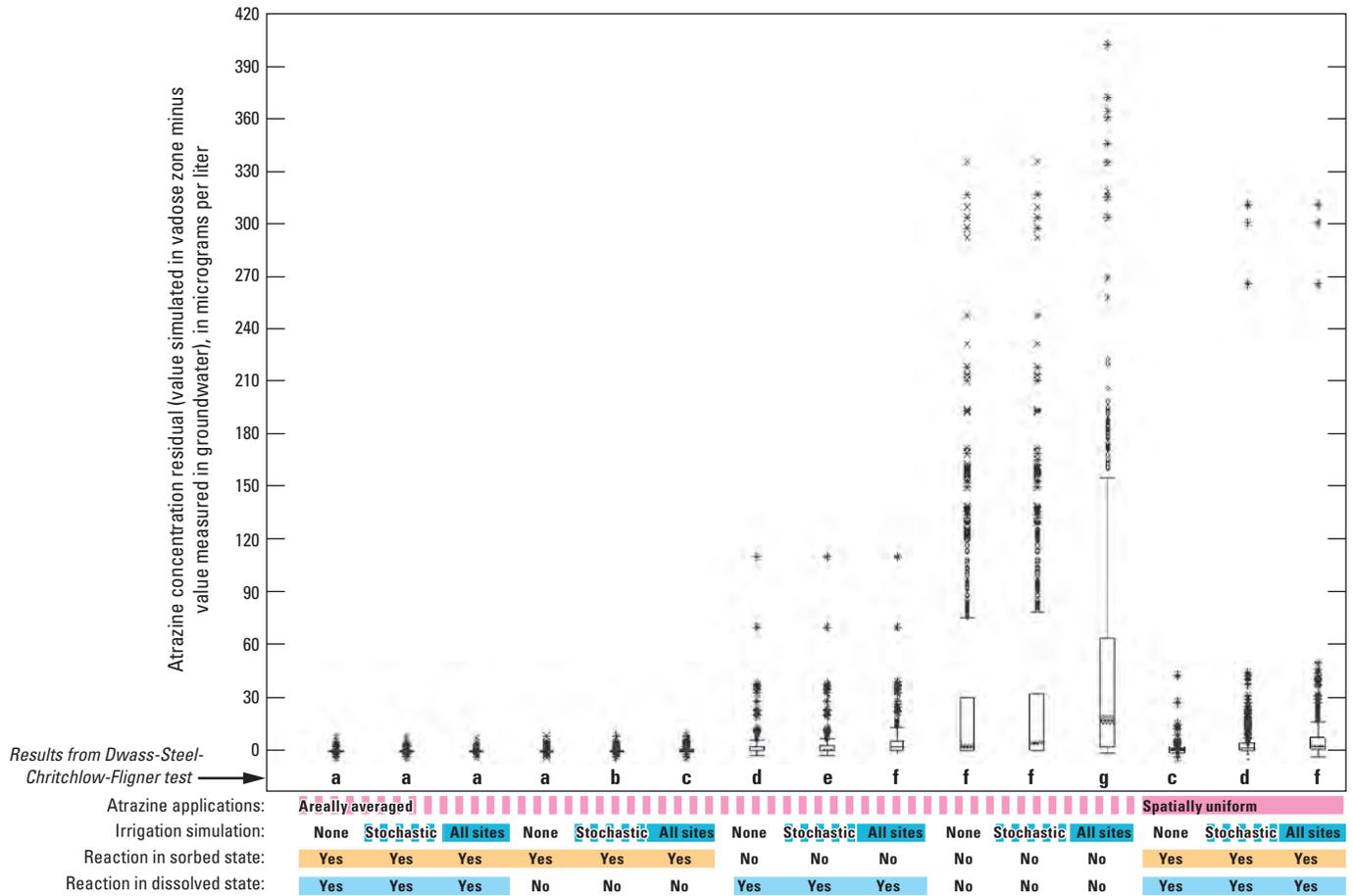


Figure 32. Temporal variability in measured precipitation, and in the infiltration and atrazine concentrations simulated at an assessment depth of 153 centimeters using the P-GWAVA-PR (Phase 1) model at site 2233 in an unirrigated agricultural area of Portage County, Wisconsin, during the 1986–95 simulation period. Model simulations used areally averaged intensities of atrazine application, and assumed that atrazine transformation occurred in both the sorbed and dissolved states. Irrigation not simulated. Soil property values used for the simulations were either (A) spatially averaged using data from the State Soil Geographic database (STATSGO), or (B) the original (unaggregated) data from the Soil Survey Geographic database (SSURGO). Atrazine concentration measured in shallow groundwater at this site was 0.37 microgram per liter; estimated recharge (from the base-flow index) was 35.6 centimeters per year. See figure 30 for site location.

Atrazine concentration residuals for all P-GWAVA-PR simulations
 (N = 1,224 sites for spatially variable atrazine applications; N = 1,220 sites for uniform applications)



EXPLANATION

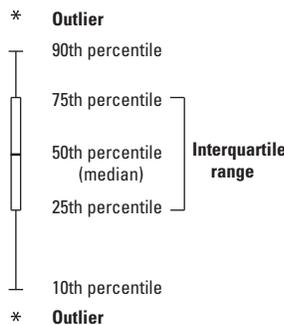


Figure 33. Influence of different modeling approaches on the P-GWAVA-PR model residuals for atrazine concentrations at all of the Phase 1 study sites (regardless of water-table depth) in agricultural areas of the conterminous United States, 1992–98. Each boxplot displays the statistical distribution of model residuals for a different permutation of simulation approaches related to (1) the spatial variability of atrazine applications, (2) the approach used for selecting sites where irrigation was simulated (if at all), and (3) whether atrazine transformation was simulated in the sorbed state and (or) the dissolved state (if at all). All non-detections of atrazine, either simulated or measured, were assigned a concentration of 0.0001 microgram per liter for the purposes of the calculations. Letters beneath individual boxplots display the results from a nonparametric multiple comparison among the sets of residuals for all 15 modeling approaches, using the Dwass-Steel-Chritchlow-Fligner (DSCF) test (Chritchlow and Fligner, 1991). The distributions of model residuals from simulation runs with different letters were significantly different from one another (P less than or equal to 0.05).

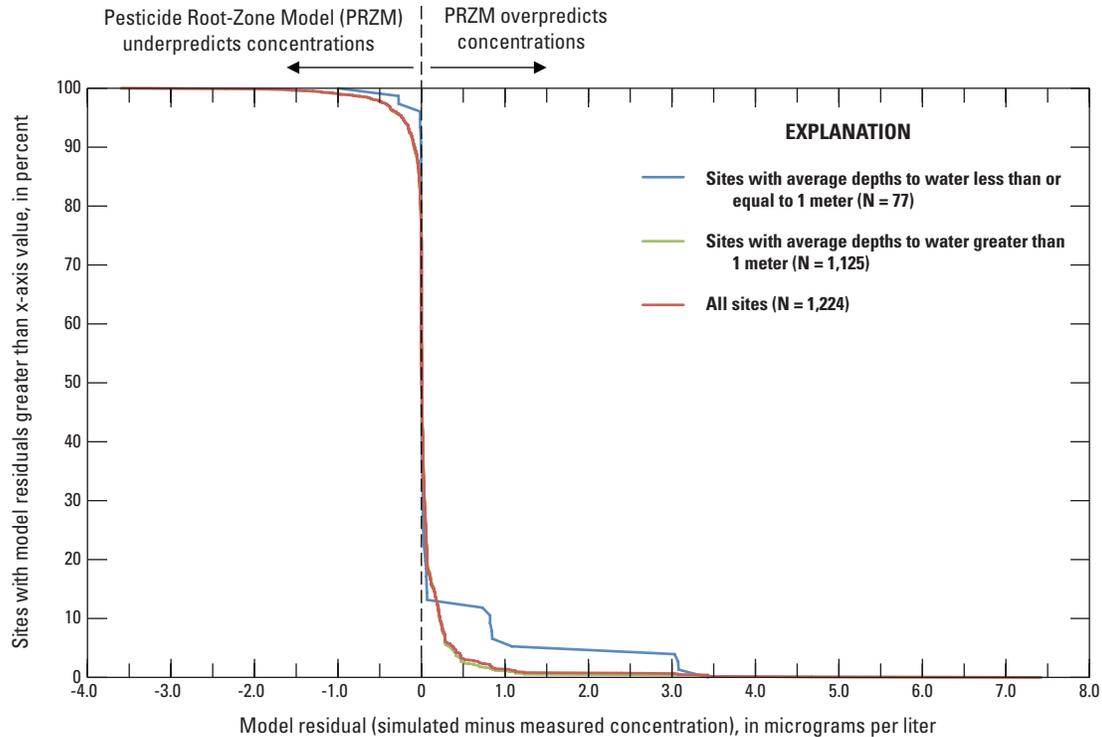


Figure 34. Cumulative distributions of model residuals for atrazine concentrations at Phase 1 study sites for the final set of P-GWAVA-PR simulations (table 4) in agricultural areas of the conterminous United States, 1992–98. All atrazine concentrations (simulated or measured) less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations. Descriptive statistics for the model residuals are presented in table 7.

Water Flow

The mean annual rates of groundwater recharge predicted at the Phase 1 sites by the P-GWAVA-PR simulations are compared with the computed base-flow index (BFI) values in figure 35. To avoid the potential influence of irrigation on this analysis, the BFI values excluded water flows contributed by irrigation (Wolock, 2003), the P-GWAVA-PR simulations were carried out without irrigation, and the analysis was restricted to sites that were unirrigated (fig. 17). The correlation between the estimates of annual recharge provided by the P-GWAVA-PR simulations and the BFI at all of the unirrigated sites where the DTW was greater than 1 m was moderate but statistically significant (Spearman $\rho = 0.30$; $P[\rho] \leq 0.0001$; 676 sites).

Atrazine Concentrations and Detection Frequencies

Summary statistics describing the extent of correlation between the atrazine concentrations predicted at the 1-m assessment depth in the vadose zone by the final set of P-GWAVA-PR simulations and the concentrations measured at the same sites in shallow groundwater are presented in table 7. These final simulations assumed that the atrazine use intensities were areally averaged, that atrazine transformation took place in the sorbed and dissolved state, and that irrigation was distributed stochastically among sites in each sampling network (table 4). Moderate, but statistically significant correlations were observed ($P[\rho] \leq 0.0001$; Spearman rank correlations) when the analysis included all the Phase 1 sites or just those where the water table was deeper than 1 m (table 7).

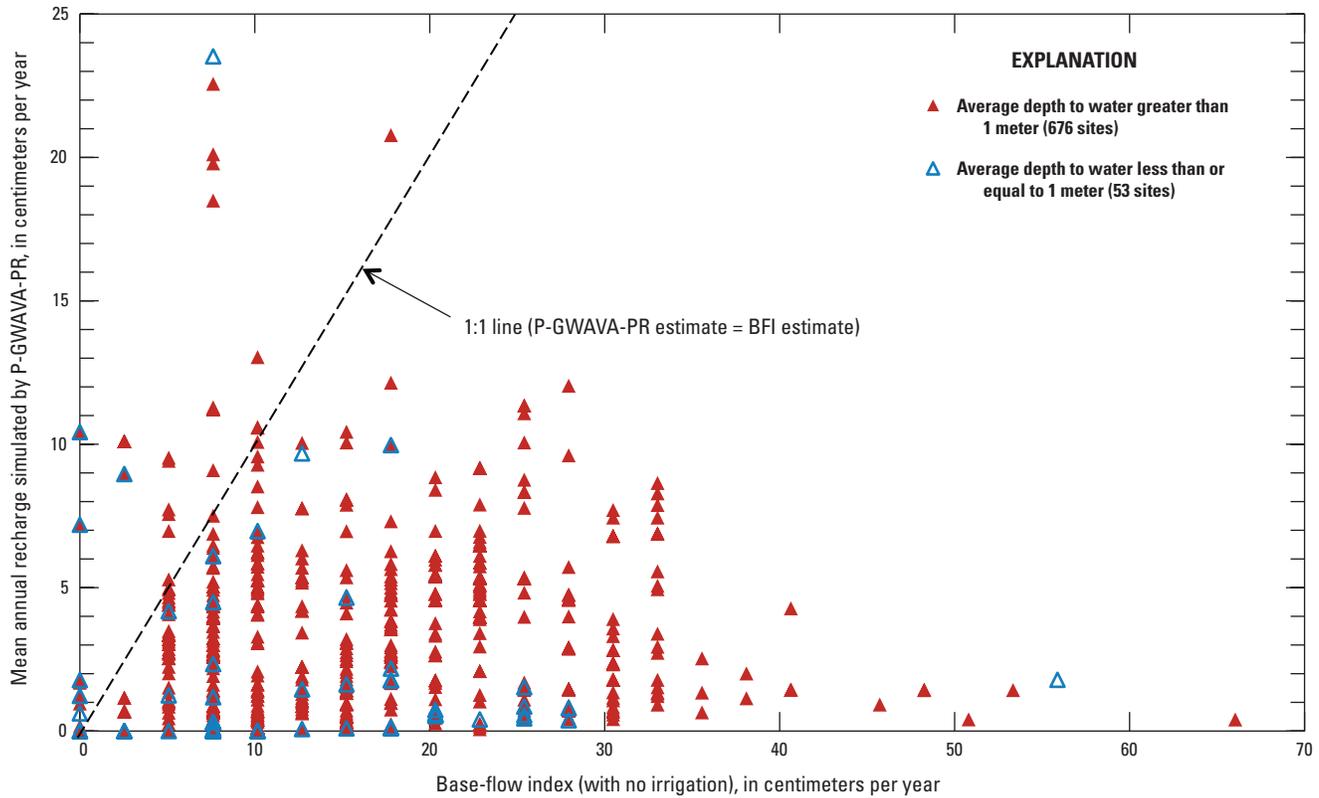


Figure 35. Mean annual groundwater recharge rates simulated by the P-GWAVA-PR (Phase 1) model with no irrigation, and by the base-flow index (BFI) method excluding irrigation, at all of the unirrigated agricultural sites in the conterminous United States where the depth to water was known. BFI data from Wolock (2003).

Table 7. Correlations between atrazine concentrations simulated by the P-GWAVA-PR (Phase 1) model at the 1-meter assessment depth in the vadose zone and concentrations measured in shallow groundwater at the same locations in agricultural areas of the conterminous United States, 1992–98.

[Concentrations of atrazine simulated by the P-GWAVA-PR system were obtained by using areally averaged intensities of atrazine use, and by simulating atrazine transformation in both the dissolved and sorbed states. Irrigation was simulated at locations selected at random using equation 8. For the purposes of these calculations, non-detections of atrazine—either simulated or measured—were assigned a concentration of 0.0001 microgram per liter (µg/L). **Range of depths to water:** Average annual values for each site. **Spearman ρ:** Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. **P(ρ):** The probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the simulated and measured values. **Model residuals:** The model residual for a given parameter is equal to the value predicted in the vadose zone by the P-GWAVA simulation minus the value measured in groundwater at the same site. **95th percentile:** For each case, 95 percent of the model residuals were less than the value shown. **Abbreviations:** m, meter; <, less than; ≤, less than or equal to]

Range of depths to water (m)	Correlation (if any) between simulated and measured concentrations		Model residuals (simulated minus measured values) (µg/L)		Number of sites
	Spearman ρ	P(ρ)	Median	95th percentile	
<1	0.021	0.86	0.001	1.5	77
1.01–178.27	0.13	≤0.0001	0.005	0.35	1,125
All sites ¹	0.14	≤0.0001	0.002	0.39	¹ 1,224

¹Depth-to-water measurements were not available for 22 of the sites.

No significant correlation was observed, however, between the simulated and measured atrazine concentrations ($P[p] > 0.05$) when the analysis was restricted to sites where the water table was shallower than the 1-m assessment depth, perhaps in part because of the relatively small sample size (77 sites) and narrower depth range examined (0–1 m). However, the transport and persistence of atrazine under the unsaturated conditions simulated by the model are also likely to have been substantially different from what occurred under the intermittently saturated conditions at depths shallower than 1 m during part or all of the simulation period at these locations.

The atrazine concentrations predicted by the final set of P-GWAVA-PR simulations in the vadose zone at all of the Phase 1 sites are compared with those measured in groundwater in the same locations in figure 36. Consistent with the results shown in figures 33 and 34, figure 36 indicates that despite a considerable degree of scatter, the model residuals for the final set of P-GWAVA-PR simulations were relatively evenly distributed between over- and underprediction of the measured atrazine concentrations over more than three orders of magnitude.

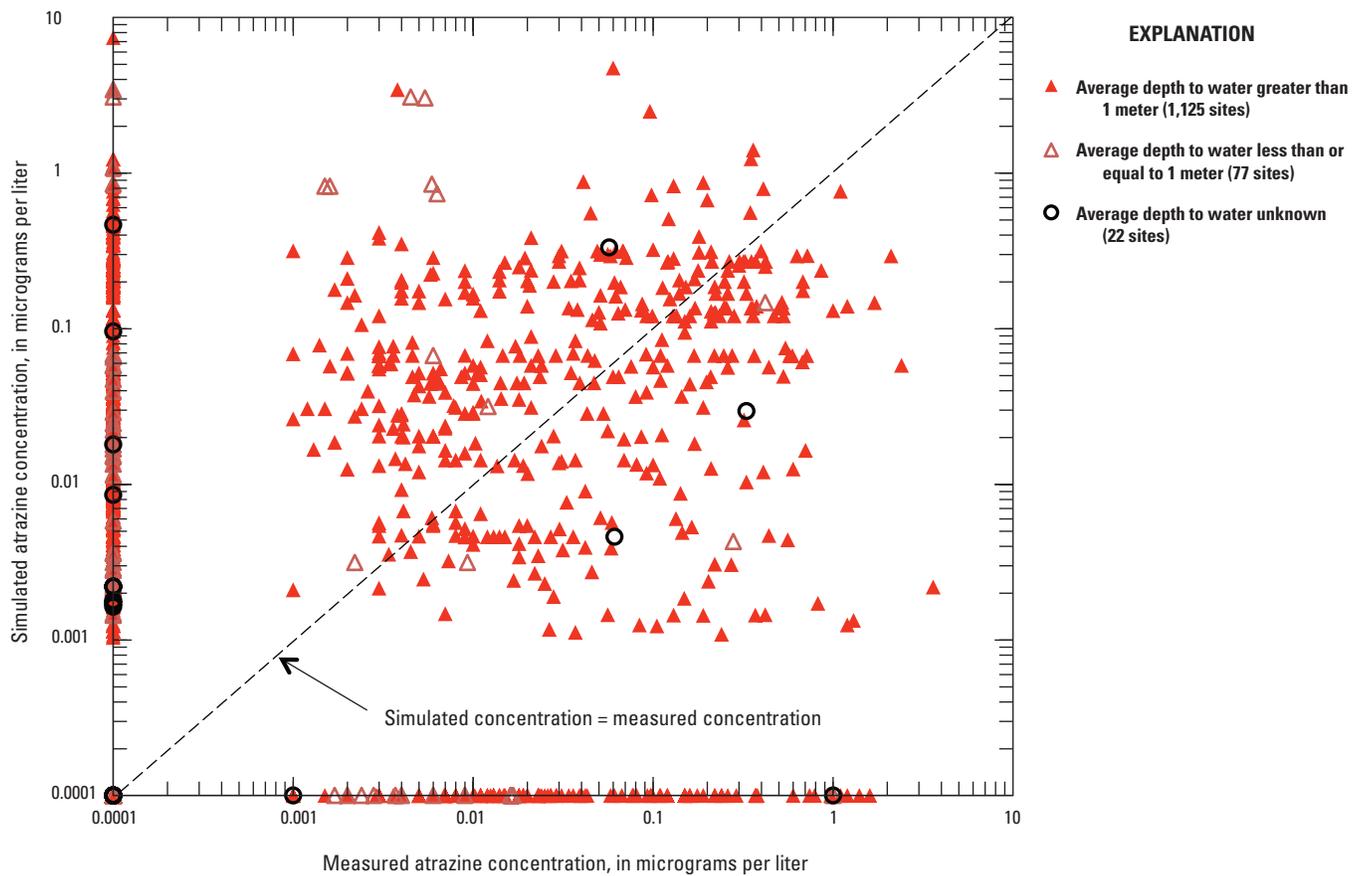


Figure 36. Atrazine concentrations simulated in the vadose zone by the P-GWAVA-PR system and concentrations measured in groundwater at Phase 1 sites in the conterminous United States, 1992–98. The P-GWAVA-PR simulations used areally averaged intensities of atrazine application, atrazine transformation in both the sorbed and dissolved states, and a stochastic distribution of irrigation (table 4). All atrazine concentrations (simulated or measured) less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of display.

The frequencies of atrazine detection (at concentrations equal to or greater than a reporting limit of 0.001 µg/L) predicted by the final set of P-GWAVA-PR simulations in the 47 groundwater networks in the Phase 1 study area are compared with those measured in shallow groundwater in [figure 37](#). The results for 2 subsets of sites are shown: all sites in networks with 10 or more wells ([fig. 37A](#)), and sites where the depths to water were greater than the 1-m assessment depth in all networks with 10 or more such wells ([fig. 37B](#)). No significant correlations were observed between the simulated and the measured frequencies of atrazine detection, regardless of the range of water-table depths examined ($P[p] > 0.05$; Spearman rank correlations).

Geographic Distribution of Model Residuals

The geographic distribution of P-GWAVA-PR model residuals for the frequencies of atrazine detection at or above a reporting limit of 0.001 µg/L in all 47 of the groundwater networks with 10 or more wells in agricultural areas of the conterminous United States is shown in [figure 38](#). These results are derived from the final set of P-GWAVA-PR simulations, which used stochastically distributed irrigation, areally averaged atrazine application intensities, and atrazine transformation in the sorbed and dissolved states ([table 4](#)). The data are shown for all Phase 1 sites, regardless of water-table depth. As was the case when no irrigation was simulated ([fig. 27A](#)), most locations where the atrazine detection frequencies were underpredicted were in the arid West, in the Northeast, and in the highly permeable soils of central Wisconsin. In contrast, the simulations overpredicted atrazine detection frequencies in areas with low-permeability soils, such as central Illinois, southwestern Indiana, and the Southeast. These patterns may have been a consequence of the spatial averaging of the SSURGO data used to create the STATSGO database—a procedure that would have tended to contract the range of values spanned by each parameter of interest. For the present example, such averaging may have influenced the spatial distributions of model residuals shown in [figure 38](#) by reducing the highest permeabilities (for example, in Wisconsin) and increasing the lowest permeabilities (for example, in Illinois, Indiana, and Georgia), relative to the range of values provided by the original SSURGO data. Along the Atlantic coast, the distribution of model residuals shown in [figure 38](#) reflects the influence of precipitation, with overpredictions predominating in the more humid Southeast, and underpredictions confined to the Northeast, where precipitation is somewhat lower (Daly, 2010). Overpredictions of atrazine detection frequencies in Florida, Georgia, and New Jersey also may have been abetted by irrigation, which is otherwise uncommon across most of the eastern United States ([fig. 17](#)). Some of the regional patterns indicated by [figure 38](#) are also evident in [figure 39](#), which displays the cumulative distribution functions for the

model residuals with respect to atrazine concentrations for the Phase 1 sites in the West, the Corn Belt, the Northeast, and the Southeast. Consistent with the patterns evident in [figure 38](#), these results indicate that many of the largest overpredictions (and smallest underpredictions) of atrazine concentrations occurred in the humid Southeast, with some of the more substantial underpredictions occurring in the Northeast. The sites examined in the West and Corn Belt, however, showed similar distributions of model residuals.

Statistical Correlations with Site Characteristics

To examine the extent to which the level of agreement between the simulated and measured frequencies of atrazine detection may have been related to site characteristics, the degrees of correlation (if any) between the P-GWAVA-PR model residuals for the atrazine detection frequencies and various site characteristics related to chemical use, soil properties, and climate ([table 8](#)) were evaluated. All values used to quantify the soil parameters were computed as depth- and component-weighted averages from the STATSGO data (Wolock, 1997; David Wolock, U.S. Geological Survey, written commun., April 2009), using the approach shown in [figure 7](#). The analysis encompassed all of the Phase 1 groundwater networks that included 10 or more wells ([fig. 38](#)), and included all of the sites in each network, regardless of the DTW.

The results summarized in [table 8](#) indicate that the model residuals for atrazine detection frequencies were not significantly correlated with spatial variations in the intensity of atrazine use among the Phase 1 sites. Use of the areally averaged intensities of atrazine application for the P-GWAVA-PR simulations thus seemed to account adequately for the effects of spatial variations in atrazine use on the predicted frequencies of atrazine detection (and, by extension, the predicted atrazine concentrations). These results are consistent with the observations that other factors may exert greater control over the spatial variability in atrazine detection frequencies (Kolpin and others, 2002; Stackelberg and others, 2006) and concentrations in groundwater (Stackelberg and others, 2012) than atrazine use intensity. For example, the results shown in [table 8](#) indicate that the extent to which the P-GWAVA-PR simulations overpredicted the atrazine detection frequencies in shallow groundwater was positively correlated with soil clay content, runoff, precipitation, and temperature, and negatively correlated with soil permeability ($P < 0.05$; Pearson and Spearman [rank] correlations). The positive correlation with clay content and inverse correlation with vertical permeability were consistent with the geographic pattern of agreement shown in [figure 38](#), and indicate that the P-GWAVA-PR system may underestimate the effect of hydraulic conductivity on the downward movement of atrazine through the soil.

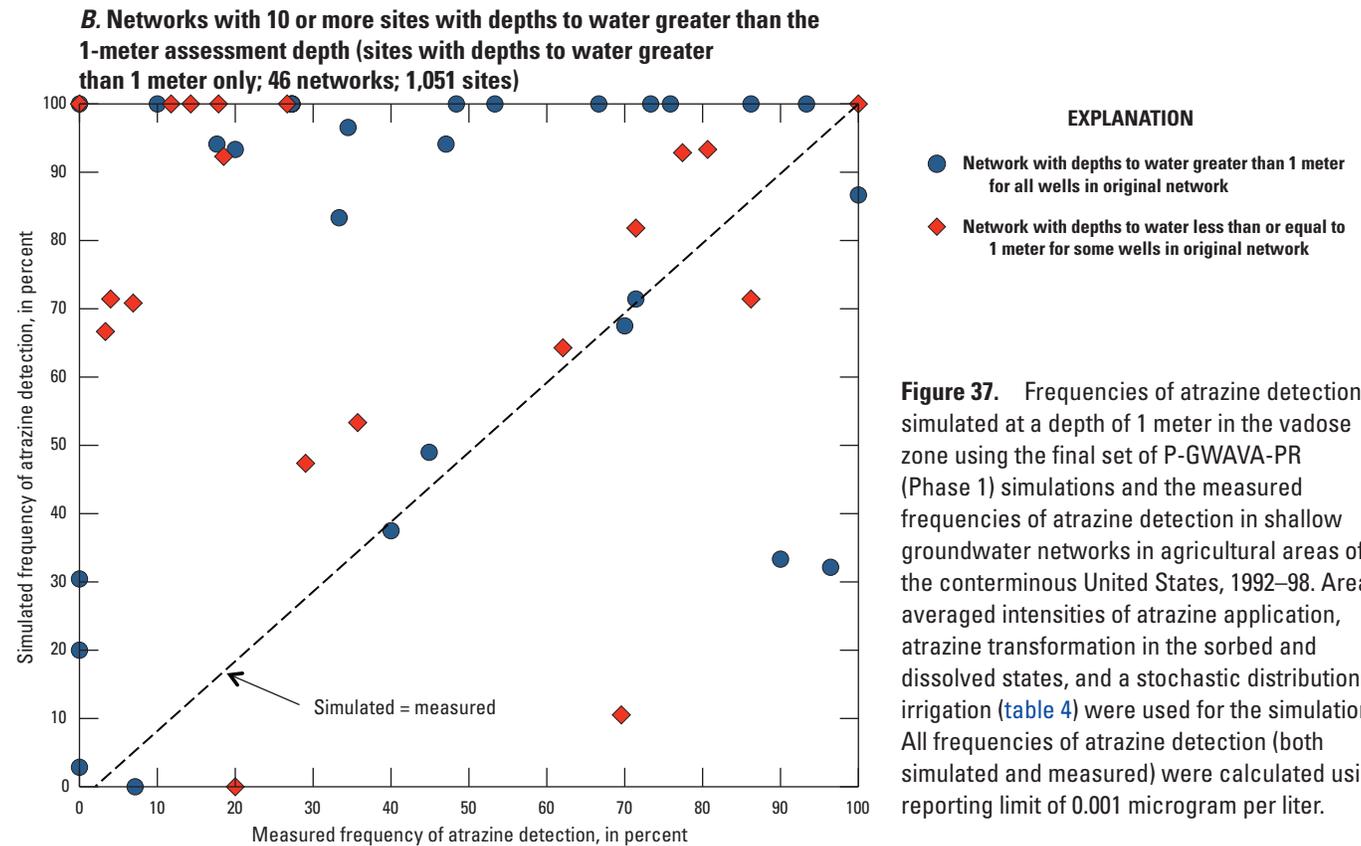
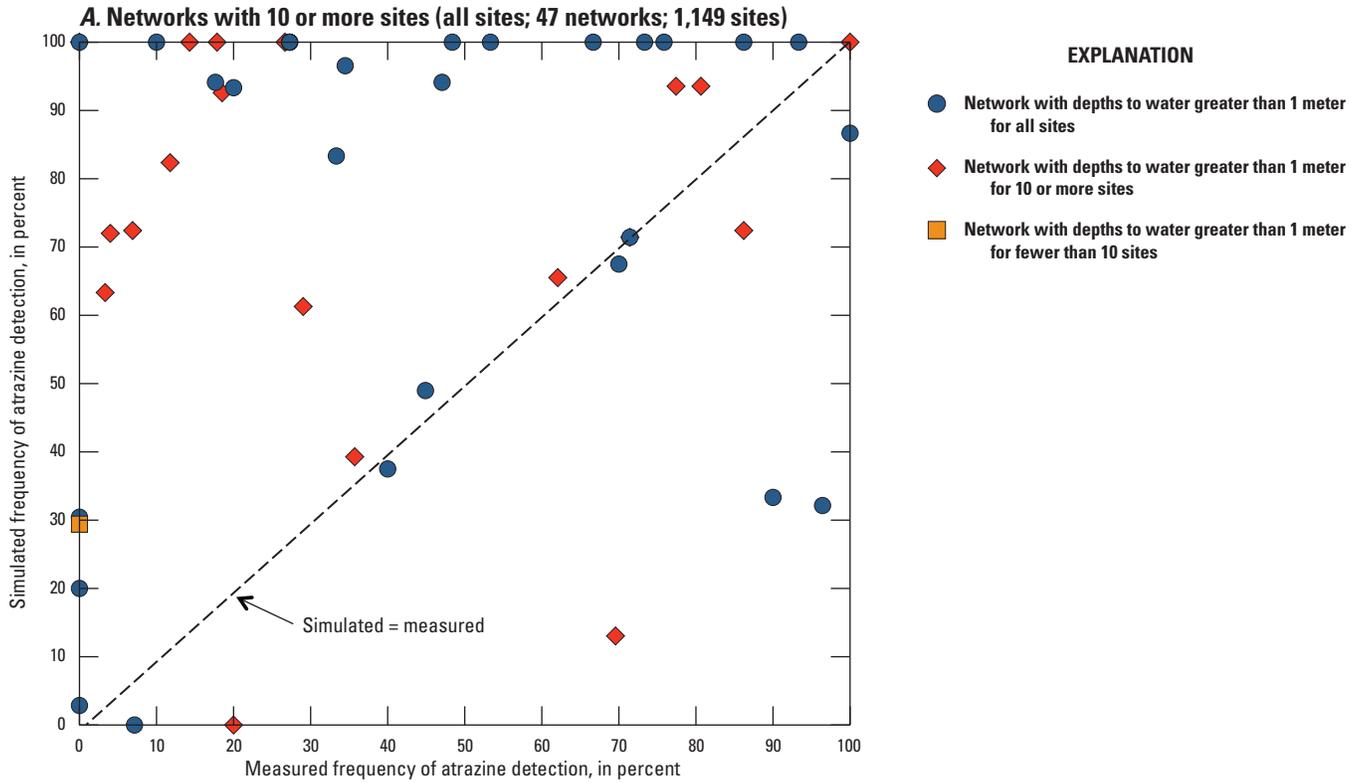


Figure 37. Frequencies of atrazine detection simulated at a depth of 1 meter in the vadose zone using the final set of P-GWAVA-PR (Phase 1) simulations and the measured frequencies of atrazine detection in shallow groundwater networks in agricultural areas of the conterminous United States, 1992–98. Areal averaged intensities of atrazine application, atrazine transformation in the sorbed and dissolved states, and a stochastic distribution of irrigation (table 4) were used for the simulations. All frequencies of atrazine detection (both simulated and measured) were calculated using a reporting limit of 0.001 microgram per liter.

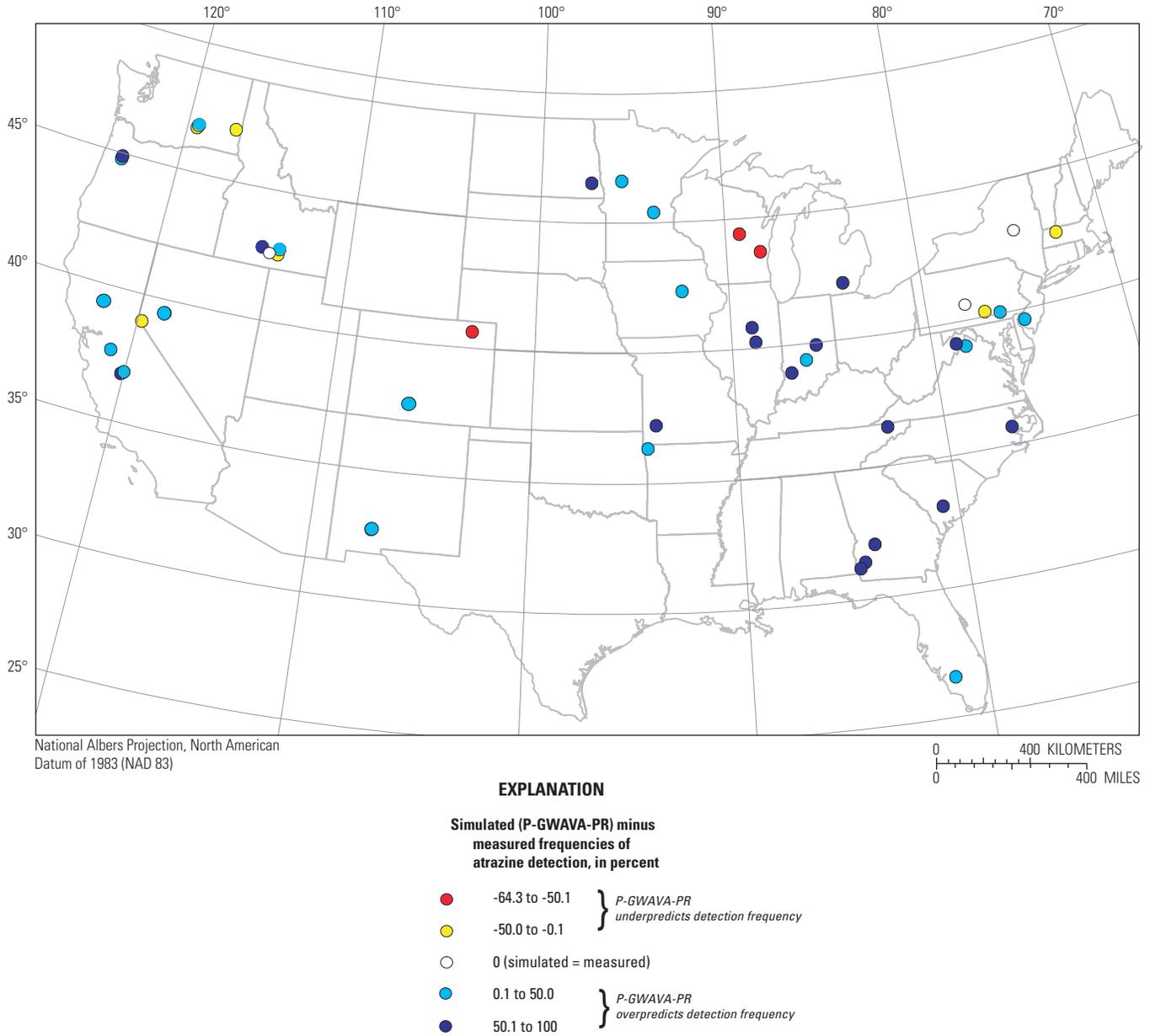


Figure 38. Distribution of P-GWAVA-PR (Phase 1) model residuals for atrazine detection frequencies in 47 groundwater networks in agricultural areas of the conterminous United States, 1992–98. Predicted detection frequencies were derived from the final set of P-GWAVA-PR simulations, which assumed areally averaged atrazine applications, atrazine transformation in the sorbed and dissolved states, and a stochastic distribution of irrigation (table 4). Data for all sites in networks containing 10 or more wells are shown, regardless of depth to water. All frequencies of atrazine detection (simulated and measured) were calculated using a reporting limit of 0.001 microgram per liter.

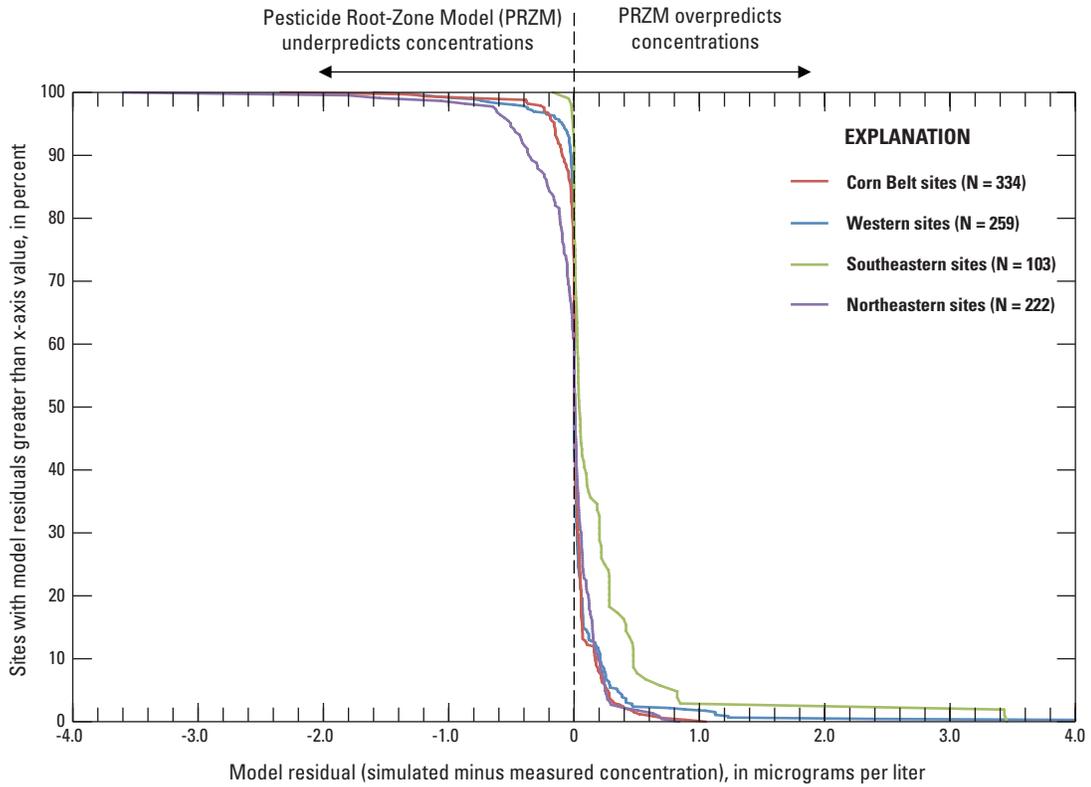


Figure 39. Cumulative distributions of P-GWAVA-PR model residuals for atrazine concentrations at Phase 1 study sites in agricultural areas of the Corn Belt and western, southeastern, and northeastern regions of the United States. Simulations were done assuming areally averaged atrazine applications, atrazine transformation in the sorbed and dissolved states, and a stochastic distribution of irrigation (table 4). All atrazine concentrations (simulated or measured) less than the 0.001 microgram per liter ($\mu\text{g/L}$) reporting limit were assigned a value of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations.

Table 8. Correlations between the P-GWAVA-PR (Phase 1) model residuals for atrazine detection frequencies in shallow groundwater in 47 groundwater networks in agricultural areas of the conterminous United States, 1992–98 (1,149 sites), and selected site characteristics.

[The geographic distribution of the networks is shown in figure 38. Detection frequencies were computed using simulated and measured atrazine concentrations at all sites in networks containing 10 or more wells for which the required ancillary data were available, regardless of water-table depth. The P-GWAVA-PR simulations used areally averaged intensities of atrazine use, atrazine transformation in both the sorbed and dissolved states, and irrigation at sites selected at random in each network using equation 8. Detections—either simulated or measured—were determined using a uniform reporting limit of 0.001 microgram per liter ($\mu\text{g/L}$). Areally averaged atrazine use intensities were computed using equation 10. Network-based values for soil-related site characteristics were computed as depth- and component-weighted averages from STATSGO data for the entire area encompassed by each network (Wolock, 1997; David Wolock, U.S. Geological Survey, written commun., April 2009). Mean annual precipitation and temperature data were computed for 1980–97; mean annual runoff data were for 1951–80. R^2 : Pearson correlation coefficient. $P(R^2)$: Probability associated with the Pearson correlation coefficient. **Spearman ρ** : Spearman rank correlation coefficient. $P(\rho)$: Probability associated with the Spearman correlation coefficient for the correlation between the ranks of the simulated and measured values. Results from statistically significant correlations ($P < 0.05$) are shown in **boldface**. **Abbreviations:** cm, centimeter; in., inch; in/hr, inch per hour; kg a.i./ha, kilograms of active ingredient per hectare; $^{\circ}\text{C}$, degrees Celsius; <, less than; \leq , less than or equal to]

Site feature	Correlations between model residuals and site feature			
	R^2	$P(R^2)$	Spearman ρ	$P(\rho)$
Areally averaged atrazine use intensity (kg a.i./ha)	0.041	0.17	0.26	0.079
Clay content (weight percent)	0.13	0.012	0.39	0.0074
Silt content (weight percent)	0.007	0.58	-0.080	0.59
Sand content (weight percent)	0.012	0.46	-0.057	0.70
Soil organic matter content (weight percent)	0.033	0.22	-0.13	0.38
Available water capacity (volume percent)	0	0.995	-0.052	0.73
Vertical permeability (in/hr)	0.089	0.041	-0.30	0.044
Mean annual runoff (in.)	0.089	0.042	0.27	0.07
Mean annual precipitation (cm)	0.17	0.004	0.49	0.0006
Mean annual air temperature ($^{\circ}\text{C}$)	0.23	0.0006	0.57	\leq 0.0001

The positive correlations between the model residuals for the atrazine detection frequencies and both runoff and precipitation (table 8) indicate that the degree to which the P-GWAVA-PR simulations overpredicted atrazine concentrations in groundwater tended to increase with increasing recharge. This is in agreement with the statistical patterns noted earlier for the simulated concentrations in response to irrigation (fig. 26) or increased precipitation, as well as the geographic pattern of model residuals for detection frequencies shown in figure 38. Finally, because the degree of overprediction of the detection frequencies was positively correlated with temperature, the model likely underpredicted the extent to which atrazine transformation rates increase with temperature. Thus, the activation energy value used during Phase 1 (46.2 kJ/mol [table 14]) may have been too low.

Phase 2 (P-GWAVA-RZ)

The P-GWAVA-RZ (Phase 2) simulations were carried out assuming a spatially uniform intensity of atrazine use (2 kg a.i./ha-yr) and applying irrigation on demand, in response to soil moisture deficits, at all sites (tables 4 and 14).

As with Phase 1, comparisons between the predictions from the P-GWAVA-RZ simulations and measurements in groundwater focused on multiple subsets of sites, depending on whether the average depth of the water table in each location was greater or less than the Phase 2 assessment depth (3 m). Although many of the time series examined here spanned the full 7 years of the simulations (that is, the 2-year stabilization period followed by the 5-year period of the actual simulations), all of the water fluxes and solute concentrations calculated from the final set of P-GWAVA-RZ simulations were computed from the last 5 years of the simulation period, 2000–2004 (table 1).

Spatial and Temporal Patterns of Material Transport

Water Flow

The temporal and spatial patterns of water distribution and flow predicted by the P-GWAVA-RZ simulations were consistent with those that are commonly observed in the subsurface. Using the results from a site in south-central Wisconsin (Marquette County) as an example, figure 40

illustrates the temporal variations in water inputs (precipitation and irrigation) and losses (deep seepage, runoff, crop transpiration, and evaporation) predicted during the course of the 7-year P-GWAVA-RZ simulation at that location. As expected, irrigation and transpiration occurred only during the growing season (May through September) each year,

and deep seepage tended to occur more readily when natural precipitation was augmented by irrigation. (Transpiration was confined to the growing season because it was simulated only in the corn plants.) Additionally, evaporation fluxes were higher during warmer times of the year, but lower during periods of high transpiration in late summer.

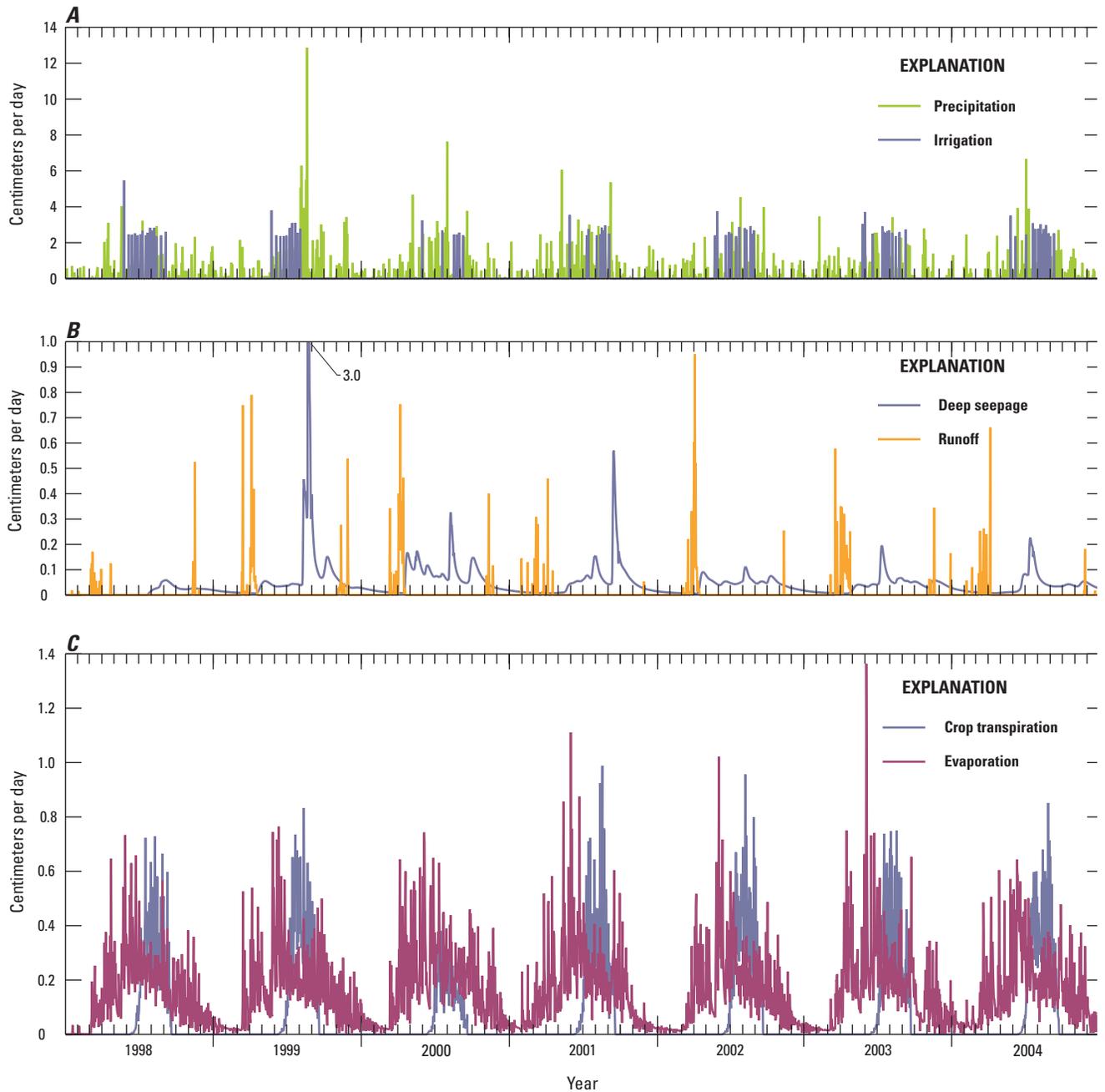


Figure 40. Temporal patterns of water fluxes estimated for (A) precipitation and irrigation, (B) deep seepage and runoff, and (C) crop transpiration and evaporation at a site in south-central Wisconsin (Soil Survey Geographic database [SSURGO] component 21840; Marquette County) during the P-GWAVA-RZ (Phase 2) simulation period, 1998–2004.

Model simulation results at the Wisconsin site are shown from a spatial perspective in [figure 41](#), displaying the vertical variations in water content, pressure head, and solute mass predicted by P-GWAVA-RZ in the soil on the last day of the 7-year simulation period. Data indicating the variations in soil texture in the soil column (from SSURGO) are also shown. The model predictions displayed in the figure indicate a pattern of water distribution in the shallow vadose zone that is commonly observed following several days without a major recharge event ([figs. 40A and 40B](#)). The discontinuities in the soil-water-content profile for this site ([fig. 41A](#)) reflect the influence of variations in water-holding capacity among the layers, with the highest values simulated in the sandy loam (layer 3) and the lowest gradient simulated in the sand (layer 4). The effects of an extended period of soil drainage without any major recent recharge events are indicated by the simulated increases in water content ([fig. 41A](#)) and pressure head ([fig. 41B](#)) with depth in each layer.

The average annual groundwater recharge rates predicted by the P-GWAVA-RZ simulations are compared with the values estimated at the same sites using the BFI method in [figure 42](#). The recharge rates predicted by the P-GWAVA-RZ simulations were computed for the 5-year simulation period from 2000 to 2004 ([table 1](#)), as was done for all final solute concentrations computed from the P-GWAVA-RZ simulation results. Because irrigation was simulated (when needed) at all of the Phase 2 sites, the BFI values used for this analysis included estimates of groundwater withdrawals for irrigation in each location (David Wolock, U.S. Geological Survey, written commun., February 2011), and are referred to herein as irrigated BFI (or iBFI) values, to distinguish them from the BFI values examined during Phase 1 ([fig. 35](#)), which did not include estimates of irrigation.

As with the BFI values for the Phase 1 model simulation results, the recharge rates predicted by the P-GWAVA-RZ simulations were significantly correlated with those estimated using the iBFI method. Statistically significant correlations between the P-GWAVA-RZ predictions and the iBFI values were observed whether the comparisons encompassed all of the sites for which the iBFI estimates were available ($R^2 = 0.15$ [$P \leq 0.0001$]; Spearman $\rho = 0.30$ [$P(\rho) < 0.001$]; 447 sites) or only sites where the average DTW was greater than the 3-m assessment depth ($R^2 = 0.29$ [$P \leq 0.0001$]; Spearman $\rho = 0.39$ [$P(\rho) < 0.001$]; 232 sites). These results indicate that the iBFI accounted for a higher percentage of the overall variability in the recharge values predicted by the P-GWAVA-RZ simulations when the only sites examined were those where the average DTW was greater than the 3-m assessment depth than when all of the sites were included in the analysis. The recharge rates predicted by the P-GWAVA-RZ simulations were lower than the iBFI values at 60 percent of all of the sites, and at 61 percent of the sites with depths to water exceeding 3 m. The recharge rates simulated for all of the 453 Phase 2

sites spanned a range from 0.5 to 33.8 cm/yr, exhibiting a considerable degree of overlap with the range of groundwater recharge values estimated by Fisher and Healy (2008) from the rates of water table fluctuation in four agricultural areas of the Nation (11.9 to 47.5 cm/yr). For reasons that remain unclear, however, no significant correlation was observed between the mean annual recharge values predicted by the P-GWAVA-RZ and P-GWAVA-PR simulations (with both models simulating irrigation in response to soil moisture demand at all sites) for the 146 sites where both models were run and where the DTW was greater than 3 m ($P > 0.05$). This indicates that different combinations of factors may be responsible for influencing the estimates of water flow predicted by PRZM and RZWQM.

Solute Transport

As was the case for water flow, the P-GWAVA-RZ simulations predicted temporal patterns of solute concentrations in the subsurface that also were consistent with those commonly observed in situ. Patterns for the simulated concentrations of atrazine, DEA, and nitrate in water at the 3-m assessment depth over the course of the 7-year simulation period for SSURGO component 21840 in south-central Wisconsin (Marquette County) are shown in [figure 43](#). The time evolution of the *atrazine residue yield* (that is, the mole percentage of applied atrazine represented by the cumulative amount of atrazine and [or] DEA predicted to have passed the assessment depth in the deep seepage since the beginning of a P-GWAVA-RZ simulation) is also displayed ([fig. 43C](#)). For ease of analysis, the hydrographs for deep seepage and runoff, reproduced from [figure 40B](#), are also provided ([fig. 43E](#)).

The chemographs in [figure 43](#) indicate that more than 1 year was required for the initial peak concentrations of the applied compounds predicted by the P-GWAVA-RZ simulations to appear in deep seepage at the 3-m assessment depth at the Wisconsin site. These predictions are consistent with results from other studies that have reported similar delays in the detection of acetochlor (Barbash and others, 1999, 2001) and other pesticides (Barbash and Resek, 1996) in shallow groundwater following their initial application. The chemographs in [figure 43](#) also provide support for the use of the 2-year stabilization period prior to the simulation period when the flow-weighted mean solute concentrations were computed ([table 1](#)). The first nitrate peak appeared earlier than the peaks for atrazine or DEA, consistent with the fact that under the oxic conditions that predominate in the vadose zone, nitrate migrates in water as a conservative solute, whereas the movement of the more hydrophobic atrazine and DEA is slowed by sorption interactions with the soil. The atrazine and DEA peaks appeared at similar times during the simulation, but those for DEA were observed slightly earlier than those for atrazine, as expected from the fact that the K_{oc} value for the degradate is lower than that of its parent compound ([table 14](#)).

Soil texture

[Last day of simulation period: December 31, 2004]

Layer	Maximum depth (centimeters)	Sand (percent)	Silt (percent)	Clay (percent)	Soil texture
1	23	80	17	3	Loamy sand
2	51	80	17	3	Loamy sand
3	66	77	16	7	Sandy loam
4	300	97	1	2	Sand

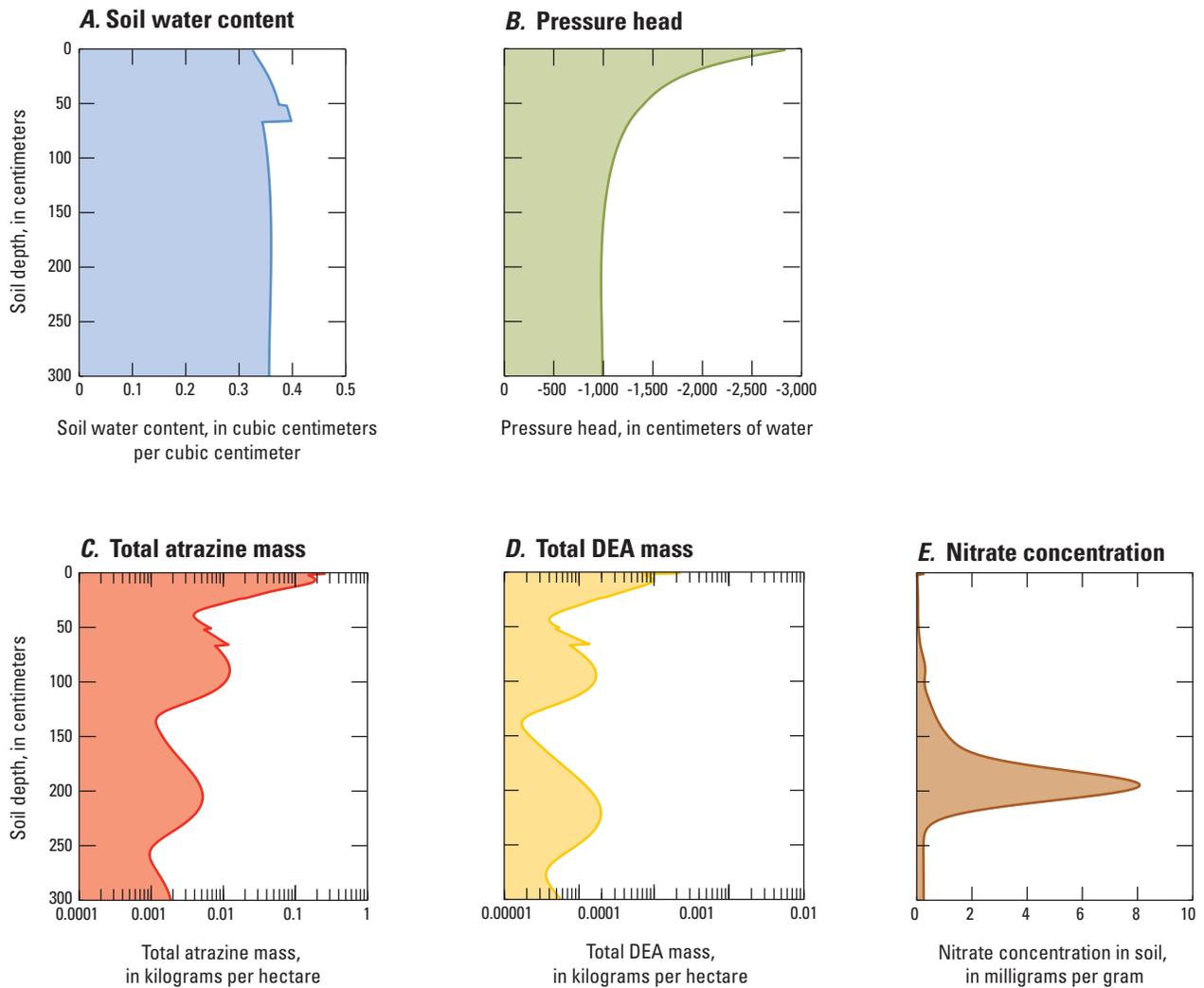


Figure 41. Vertical variations of soil texture (from Soil Survey Geographic database [SSURGO]) and vertical variations of simulated (A) soil water content, (B) pressure head, (C) total atrazine mass, (D) total deethylatrazine (DEA) mass, and (E) nitrate concentration at a site in south-central Wisconsin (SSURGO component 21840; Marquette County) on the last day of the 7-year P-GWAVA-RZ (Phase 2) simulation period (1998–2004).

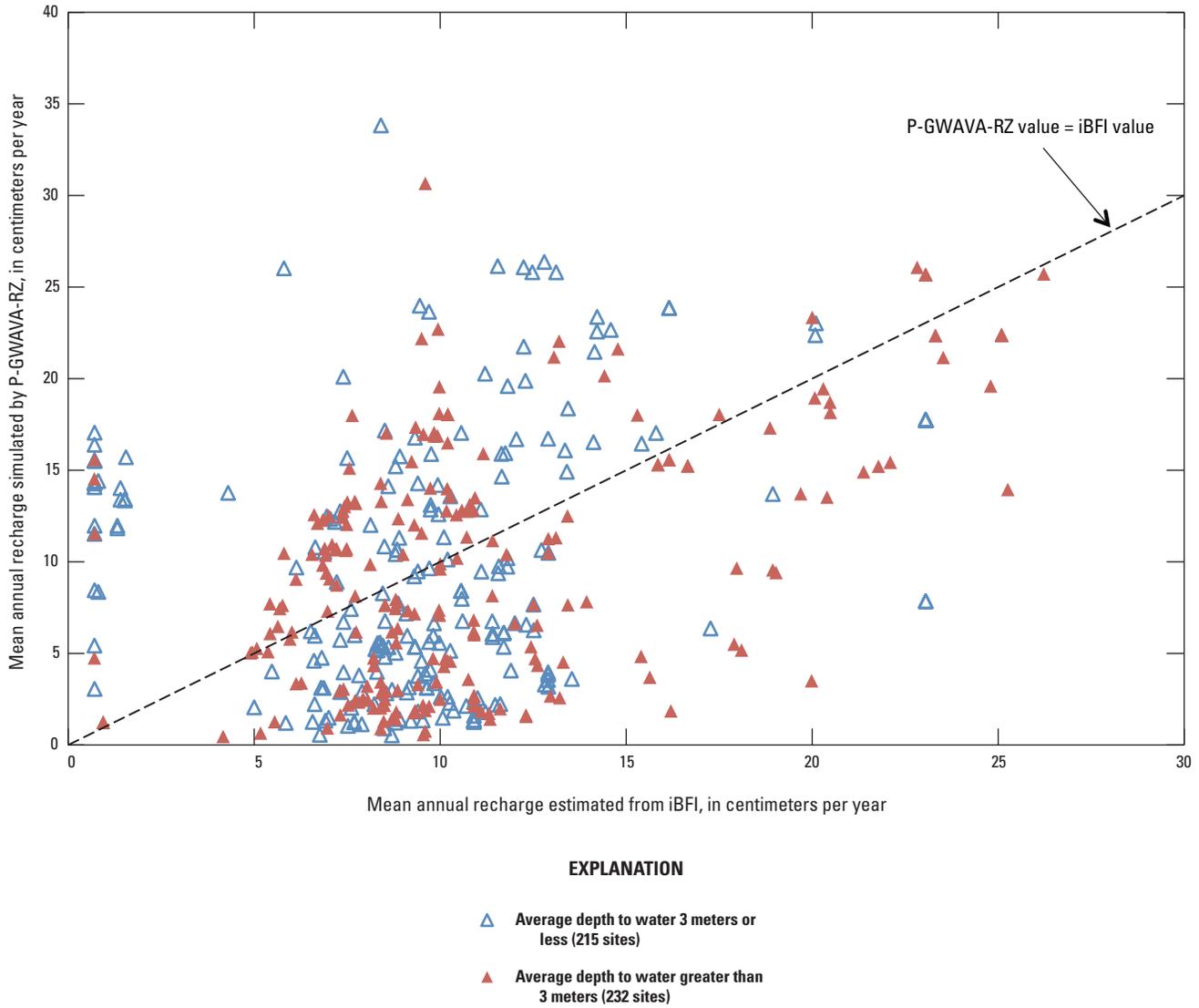


Figure 42. Average annual estimated groundwater recharge rates simulated at the 3-meter assessment depth by the P-GWAVA-RZ (Phase 2) model, and rates estimated from the Base Flow Index method including irrigation withdrawals (iBFI), in 10 contiguous states in the Corn Belt of the United States. Estimates of iBFI are from David Wolock, U.S. Geological Survey (written commun., February 2011).

Comparisons with the hydrograph for deep seepage (fig. 43E) indicate that a major recharge event during summer 1999 may have been largely responsible for the simulated appearance of the initial atrazine and DEA peaks at the assessment depth soon thereafter. This conclusion is consistent with the general observation that major recharge events can lead to the transport of substantial amounts of surface-applied solutes through soil—including hydrophobic compounds—especially if the events occur relatively soon after the solutes are applied (Barbash and Resek, 1996; McGrath and others, 2010). Additionally, the temporal changes in the atrazine residue yield that were simulated in the deep seepage over the course of the 7-year simulation period (fig. 43C) indicate that multiple years may be required before this parameter approaches a semi-stable value, if ever.

Comparisons between the simulated chemographs for atrazine, DEA and nitrate at the Wisconsin site (figs. 43A, B, and D, respectively), and the corresponding profiles for each solute in the soil column at the end of the P-GWAVA-RZ simulation (figs. 41C, D, and E, respectively) illustrate the contrast in the rates at which some solutes may migrate through soil, relative to their rates of movement in water. At least five of the seven concentration peaks expected for atrazine, DEA and nitrate (on the basis of the atrazine and nitrogen application histories) were simulated in deep seepage at the 3-m assessment depth during the 7-year simulation period (figs. 43A, B, and D, respectively), indicating roughly similar rates of movement of all three, relatively water-soluble solutes in the dissolved state. However, whereas three of the concentration peaks for atrazine and DEA still remained in the soil profile at the end of the simulation (figs. 41C and D, respectively), only one of the peaks for nitrate (which does not sorb to most soil surfaces) was still present in the soil at the end of the simulation (fig. 41E). As in figure 43, the soil profiles in figure 41C and D also display the effect of the lower K_{oc} value for DEA, relative to atrazine, with the DEA peaks reaching slightly greater depths in the soil than those for atrazine by the end of the simulation. These predictions reflect the influence of sorption interactions on the rates of movement of even moderately hydrophobic solutes through the subsurface. (Such effects are analogous to the influence of hydrophobicity on the relative rates of analyte migration within the stationary phase of a liquid- or gas-chromatographic column [Grob and Barry, 2004].) Finally, the soil profiles for atrazine and DEA (figs. 41C and D) exhibit a small but abrupt drop in concentration at the bottom of layer 3, reflecting a slightly higher retention of both solutes by the finer-grained sandy loam in that layer, relative to the underlying sand.

Solute Distributions Among Chemical Forms and Environmental Media

Data from the P-GWAVA-RZ simulations at two of the Phase 2 sites were used to examine the predicted distributions of the applied atrazine and nitrogen among different chemical forms and environmental media at the end of the simulation period. Because the simulated annual applications of atrazine to corn were presumed to be the sole source of the herbicide and DEA in the subsurface, a mass-balance approach was used to calculate the percentages of the applied herbicide that were simulated to be present as either the parent compound or DEA in water and soil. By contrast, synthetic fertilizer, applied in irrigation water for the P-GWAVA-RZ simulations (a practice referred to as *fertigation*), represents only one of several potential sources of nitrate in the soil (Komor and Anderson, 1993; Burns and others, 2009; Bartling and others, 2011; fig. 21). Consequently, for the nitrogen species, the model outputs were used solely to examine nitrogen fluxes and shifts (if any) in the distribution of nitrogen among various chemical forms and media between the beginning and the end of the simulations, rather than to account for the fate of all of the applied nitrogen.

Atrazine and Deethylatrazine

The simulated distributions of atrazine and DEA between the sorbed and dissolved states in the subsurface at two Phase 2 sites are shown in figure 44, expressed as mole percentages of the total amount of atrazine applied over the 7 years of simulated annual applications. The amounts of atrazine and DEA in water represent the total amounts that flowed past the 3-m assessment depth (per hectare) over the course of the 7-year simulation period (that is, the numerator in equation 48), whereas those associated with the soil are the amounts present on the last day of the simulation. No specific values are shown for the simulated concentrations of either compound in plant materials because these quantities are not reported by RZWQM.

Consistent with the results from the Phase 1 simulations (fig. 25), substantial proportions of the remaining, unreacted atrazine were predicted to be sorbed to the soil at both sites examined in figure 44. Considerable fractions of the total amount of the DEA formed during the simulations were also associated with the soil, as might have been expected from the similarities of its chemical structure and properties to those of atrazine (fig. 20; table 14). Substantially higher amounts of atrazine and DEA were simulated and measured in the water at the Wisconsin site than at the Indiana site.

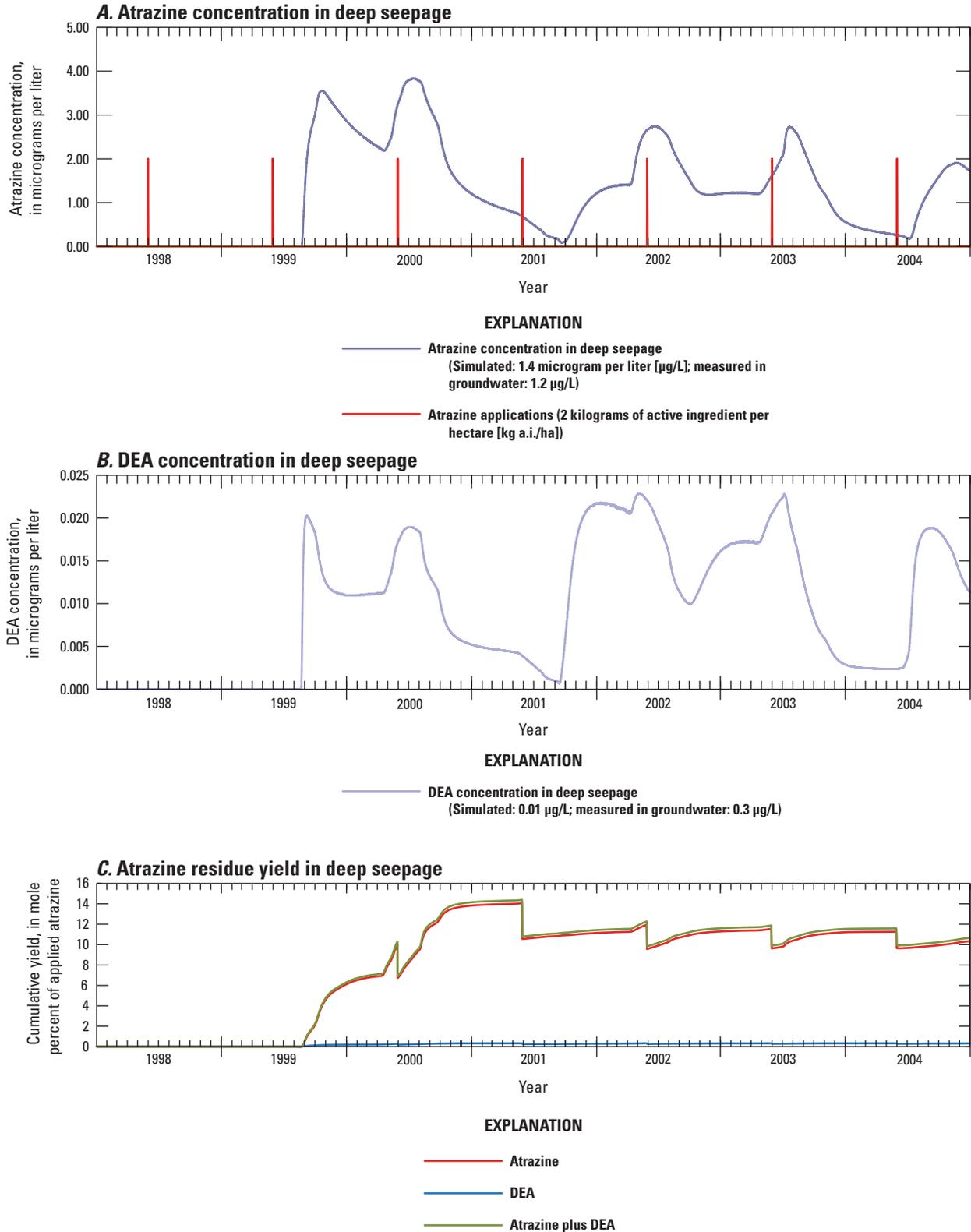
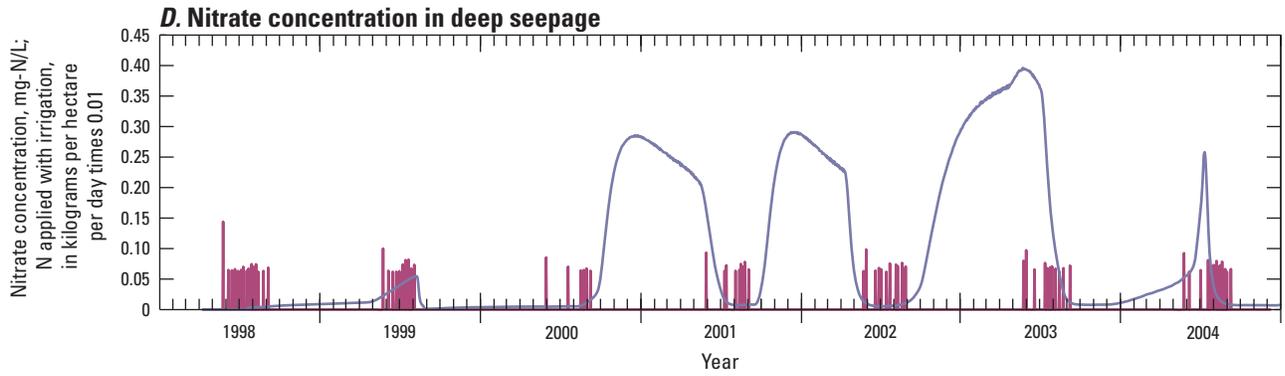
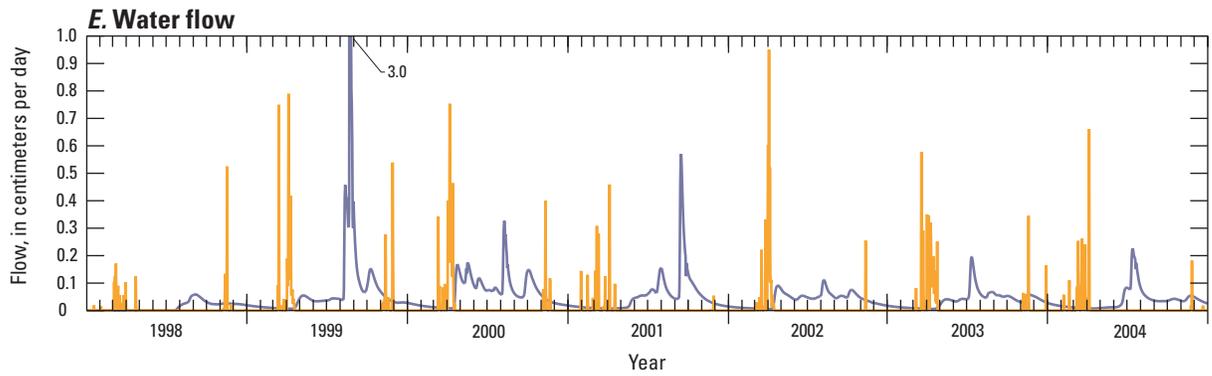


Figure 43. Variations in solute concentrations and water flow simulated at the 3-meter assessment depth by the P-GWAVA-RZ (Phase 2) simulations for (A) atrazine concentration, (B) deethylatrazine (DEA) concentration, (C) atrazine residue yield, (D) nitrate concentration, and (E) deep seepage and runoff (copied from fig. 40B) at Soil Survey Geographic database (SSURGO) site 21840 in south-central Wisconsin (Marquette County) during the 7-year simulation period, 1998–2004. Where applicable, concentrations simulated as flow-weighted means at the assessment depth, or measured in the underlying groundwater, are provided in the figure explanations.



EXPLANATION

- Nitrate concentration in deep seepage
[Simulated: 0.06 milligrams per liter as N (mg-N/L);
measured in groundwater: 11 mg-N/L]
- Nitrogen applications in irrigation water (kilogram per hectare per day x 10²)

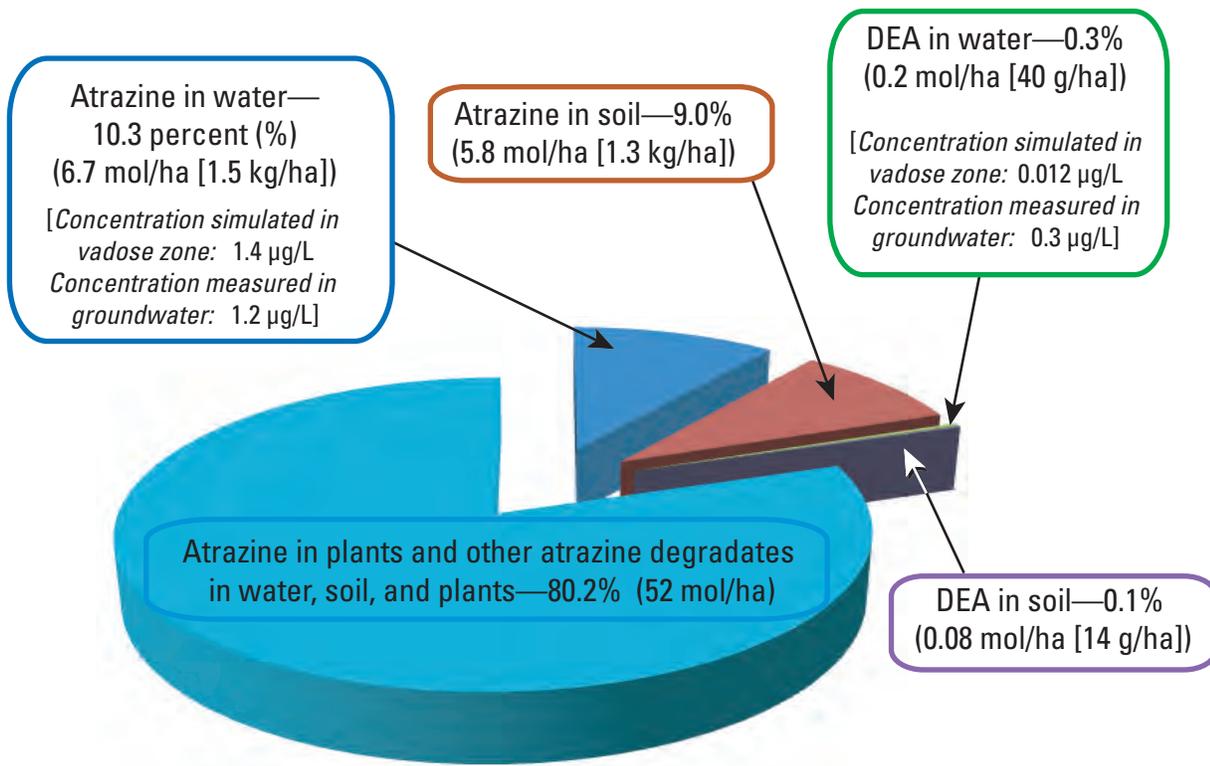


EXPLANATION

- Deep seepage
- Runoff

Figure 43.—Continued

A. South-central Wisconsin (Marquette County; SSURGO component #21840)



B. Southwestern Indiana (Daviness County; SSURGO component #20001)

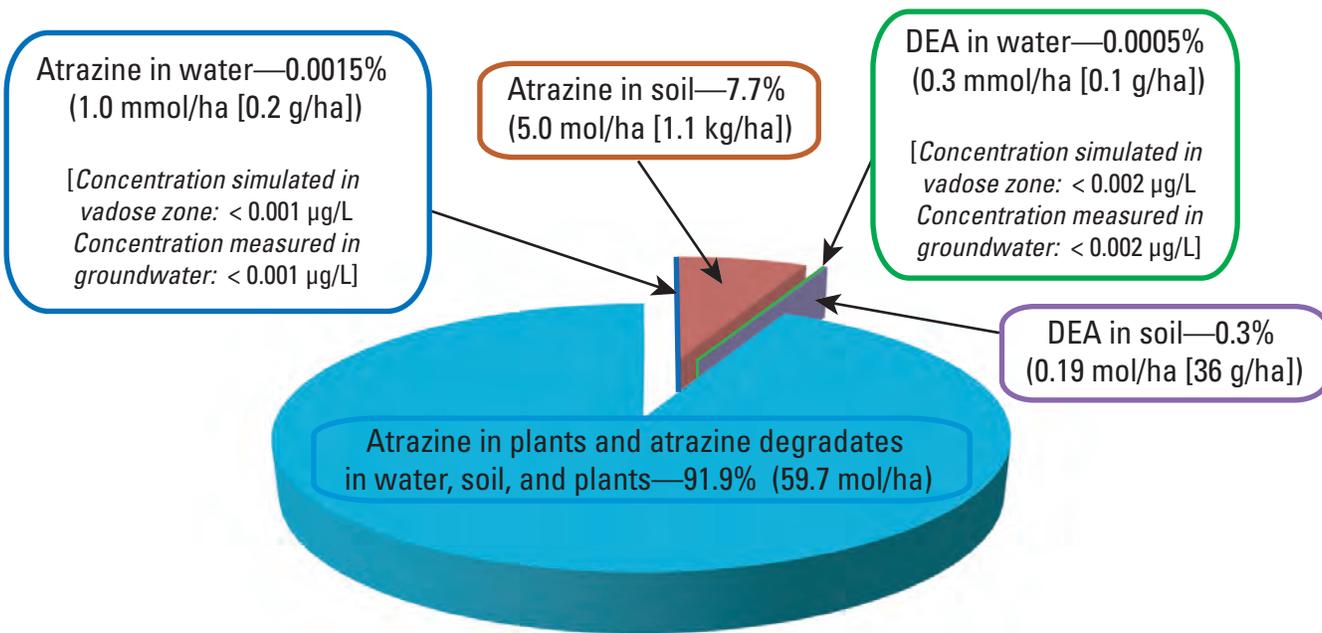


Figure 44. Distributions of atrazine and deethylatrazine (DEA), computed from the P-GWAVA-RZ (Phase 2) simulations, in water, soil, and plants (in mole percentages of the total amount of atrazine applied) after 7 years of simulated annual atrazine applications at a rate of 2 kilograms of active ingredient per hectare per year (kg a.i./ha-yr) to sites in (A) Marquette County, Wisconsin (Soil Survey Geographic database [SSURGO] component number 21840), and (B) Daviness County, Indiana (SSURGO component number 20001). (mol/ha, mole per hectare; kg/ha, kilogram per hectare, µg/L, microgram per liter; mmol/ha, millimole per hectare; g/ha, gram per hectare.)

This may have been partly because the permeability of the soil is between 3 and 30 times higher at the Wisconsin site than at the Indiana site (Natural Resources Conservation Service, 2011a). The simulated concentrations of atrazine and DEA were negligible in the runoff at both locations, so all the remaining mass of applied atrazine not accounted for in soil or water was presumed to have been either present in plant materials, or converted to degradates other than DEA (fig. 20). However, because DEA was the only atrazine degradate for which transport and fate were simulated, the amounts of the other atrazine degradates that may have been present in the dissolved or sorbed states were not estimated individually.

Most field studies that have measured the percentages of applied atrazine in the subsurface following application have detected less than 1 percent of the mass of applied herbicide in vadose-zone water (Barbash and Resek, 1996; Flury, 1996; Ma and Selim, 1996; Bergström and Stenström, 1998; Bayless, 2001; Kördel and others, 2008). The results shown in figure 44 for DEA at the Wisconsin site, and for atrazine and DEA at the Indiana site were consistent with this general pattern, but the amount of applied atrazine predicted to have been leached past the 3-m assessment depth at the Wisconsin site (10.3 percent of the atrazine applied) was considerably higher than those reported by most of these earlier studies. The latter observation may have been partly related to the high permeability of the soil at this site. However, it also may have been a consequence of the fact that the amounts of atrazine and DEA that were predicted to have leached past the 3-m assessment depth at both sites were computed over a time interval that was substantially longer than the time intervals used by most previous studies.

Whereas the percentages of applied atrazine that were simulated to be present as either atrazine or DEA in the dissolved state (fig. 44) were computed over a 7-year interval, nearly all other investigations that have measured pesticide recoveries in water as a percentage of the amount applied have been carried out over periods of less than 2 years (Barbash and Resek, 1996; Flury, 1996). The chemograph displayed in figure 43C, however, indicates that if the P-GWAVA-RZ simulations are accurate, several years may be required for the overall percent recovery of an annually applied, surface-derived contaminant (including its degradates, as well as the unreacted parent compound) to reach a quasi-stable value in deep seepage and shallow groundwater—even for only moderately hydrophobic compounds such as atrazine or DEA at a site with highly permeable soils. The amount of time required for this to occur (about 4 years for atrazine and DEA at the Wisconsin site) is presumed to be the time required for the total mass of the retained compounds to reach a quasi-stable value in the soil column above the assessment depth. Support for this hypothesis is provided by the results from an investigation of atrazine in the vadose zone and groundwater beneath an area of continuous corn cultivation in Nebraska, which led the study authors to estimate that it would take

about 30 years for atrazine concentrations in the groundwater at that site to reach a stable value (Wehtje and others, 1981).

In contrast with the results for the dissolved state, the amounts of atrazine that were predicted to be in the sorbed state at the Wisconsin and Indiana sites (fig. 44) are consistent with results from several previous investigations that have measured the concentrations of the herbicide in soils as percentages of the amounts applied. The results from 11 of these earlier studies, tabulated by Barbash and Resek (1996), indicated that for the 10 measurements made 90 or more days after application, an average of 11 ± 3 percent of the applied atrazine was present in the soil. (As might have been expected for a compound as reactive as atrazine, the percentages of the applied herbicide detected in soils by previous studies were generally lower for measurements made after several months had passed following application; the amounts of atrazine reported to have been recovered within the first 24 hours after application ranged from 46 to 130 percent.)

Because sorption to soil OM typically slows the migration of neutral organic solutes through soils, these observations from previous studies—along with the data displayed in figures 41 and 44—indicate that large proportions of atrazine and its hydrophobic degradates may be retained within the vadose zone for substantially longer periods than the residence times inferred for most of the water. This hypothesis is supported by the results from a combined field and modeling investigation by Bayless (2001) in the White River Basin, Indiana, where atrazine and its degradates were inferred to have been retained in the vadose zone long enough to undergo transformation to other, unknown compounds before reaching the water table. Bayless (2001) suggested that one of the processes that may have contributed to this was ET, which causes upward flow of water toward the land surface, and thus a slowing of the downward migration of any of the solutes that it may contain. McMahan and others (2006) suggested that a similar mechanism has contributed to the accumulation of substantial quantities of atrazine, DEA, nitrate and other agriculturally derived chemicals in the thick vadose zones underlying irrigated corn-growing areas in the High Plains.

Nitrogen

Figures 45A and B illustrate the shifts that were predicted to have occurred in the distributions of nitrogen among the various forms tracked by RZWQM during the 7-year simulation period at the Wisconsin and Indiana sites, respectively. At both sites over the course of the simulation period, the P-GWAVA-RZ model predicted decreases in the percentages of nitrogen in the fast OM pool, small or negligible reductions in the percentages in the medium OM pool, and small increases in the percentages in the slow OM pool. Increases were also observed in the nitrogen content of the microbial populations and the residue pools.

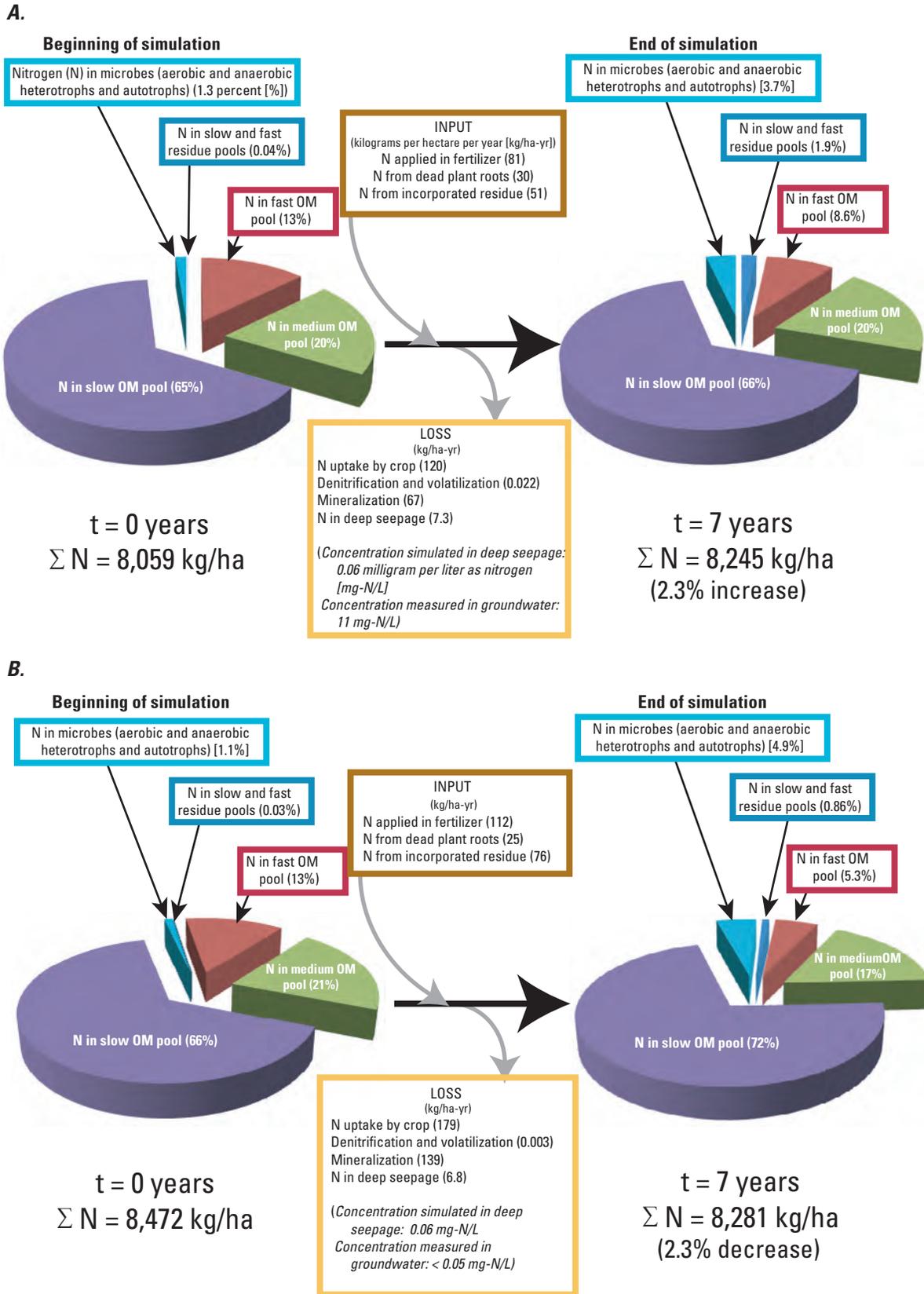


Figure 45. Nitrogen (N) distributions among primary environmental compartments estimated by the P-GWAVA-RZ (Phase 2) simulations before and after 7 years of nitrogen fertilizer applications (fig. 43D), estimated inputs and losses of nitrogen, and nitrate concentrations estimated in the vadose zone and measured in shallow groundwater at study sites in (A) Marquette County, Wisconsin (Soil Survey Geographic database [SSURGO] component 21840) and (B) Daviess County, Indiana (SSURGO component 20001). (OM, organic matter.)

These changes are consistent with an overall transfer of nitrogen from more labile chemical forms to living biomass or more refractory forms, as might be expected to occur during the biological processing of nitrogen in the soil. According to the guidance provided by Hanson and others (1999), the 7-year simulation period used during Phase 2 was likely to have been sufficient for the pools of the more labile forms of nitrogen to stabilize at the sites of interest, but may not have been long enough for the slow OM pools to stabilize.

The rates of nitrate input from fertilizer applications shown in [figure 45](#), as well as the estimates of the total nitrogen inventories stored in the soil column, were within the ranges of these parameters estimated from a series of RZWQM simulations done by Nolan and others (2010) for areas of corn cultivation in California, Maryland, and Nebraska. The nitrogen fluxes of 7.3 and 6.8 kg N/ha/yr predicted by the P-GWAVA-RZ simulations in deep seepage at the Wisconsin and Indiana sites, respectively, were consistent with the interquartile range of nitrate-derived nitrogen fluxes through the vadose zone (0–30 kg NO₃-N/ha/yr) reported at a site in central Indiana by Green and others (2008), but an order of magnitude lower than the nitrogen fluxes of 56–102 kg N/ha-yr simulated by Nolan and others (2010) for their three study areas. Results from a preliminary set of P-GWAVA-RZ model simulations done for this study indicated that among the 349 SSURGO components for which such predictions were examined, changes in the total amount of nitrogen in the upper 3 m of the soil over the 7-year simulation period ranged from a reduction of 4.0 percent to an increase of 4.3 percent.

Model Residuals and Water-Table Depths

Because the accuracy of the P-GWAVA predictions at individual sites was often evaluated by comparing the solute concentrations simulated at a fixed depth in the vadose zone (the assessment depth) with those measured in shallow groundwater, it was necessary to examine the possibility that the extent of agreement between the simulated and measured concentrations may have been influenced by variations in the depth of the water table among different sites. Consequently, a series of statistical analyses were done to examine the degrees of correlation (if any) between the average DTW and the P-GWAVA model residuals for the concentrations of atrazine, DEA, and nitrate, as well as those for the DEA fraction, at the study sites of interest. The results from these analyses are summarized in [table 9](#). The distributions of the P-GWAVA-RZ model residuals for the concentrations of the three solutes and the DEA fraction at the Phase 2 sites, relative to the DTW, are shown in [figure 46](#).

Significant, positive correlations with the DTW were observed for the model residuals for atrazine concentrations for both study phases ([table 9](#)). This pattern was noted regardless of whether or not sites with water tables shallower than the assessment depth were included in the analysis. No significant correlations were observed, however, when the analysis was restricted to sites with water-table depths shallower than the assessment depth. In contrast with the atrazine results, significant negative correlations with the DTW were observed for the model residuals for the DEA and nitrate concentrations. The strength of these correlations varied among the response variables and among the depth ranges examined, but the general trends are consistent with current understanding regarding the influence of redox conditions and vadose-zone residence time on the environmental chemistry of the three solutes.

Atrazine and Deethylatrazine

The results shown in [figure 46](#) and [table 9](#) indicate that the deeper the water table, the greater the extent to which the P-GWAVA-RZ simulations overpredicted the atrazine concentrations—and underpredicted the DEA concentrations—measured in groundwater. Although no statistically significant correlations were observed between DTW and the model residuals for the DEA fraction, the signs of the correlation coefficients were consistent with those observed for the model residuals for the DEA and atrazine concentrations. These patterns are in agreement with the work of Tesoriero and others (2007), who observed more extensive conversion of atrazine to DEA in the subsurface beneath agricultural areas where the thickness of the vadose zone is greater and, by inference, the residence time of the parent compound in the vadose zone is longer.

Microorganisms are ubiquitous in near-surface environments (Ghiorse, 1997; Flynn and others, 2008). Furthermore, the potential for the microbial transformation of atrazine in the subsurface has been demonstrated above and below the water table to depths of at least 25 m below the land surface (for example, Konopka and Turco, 1991; Issa and Wood, 1999). Because they are oxidation reactions, the dealkylation of atrazine to form either DEA, deisopropylatrazine or didealkyl atrazine ([fig. 20](#)) should occur more readily in the presence of higher concentrations of dissolved oxygen. This would explain why atrazine is generally more reactive under oxic conditions than under anoxic conditions (for example, Kaufman and Kearney, 1970; Nair and Schnoor, 1992; Papiernik and Spalding, 1998; Rügge and others, 1999; and Larsen and others, 2000).

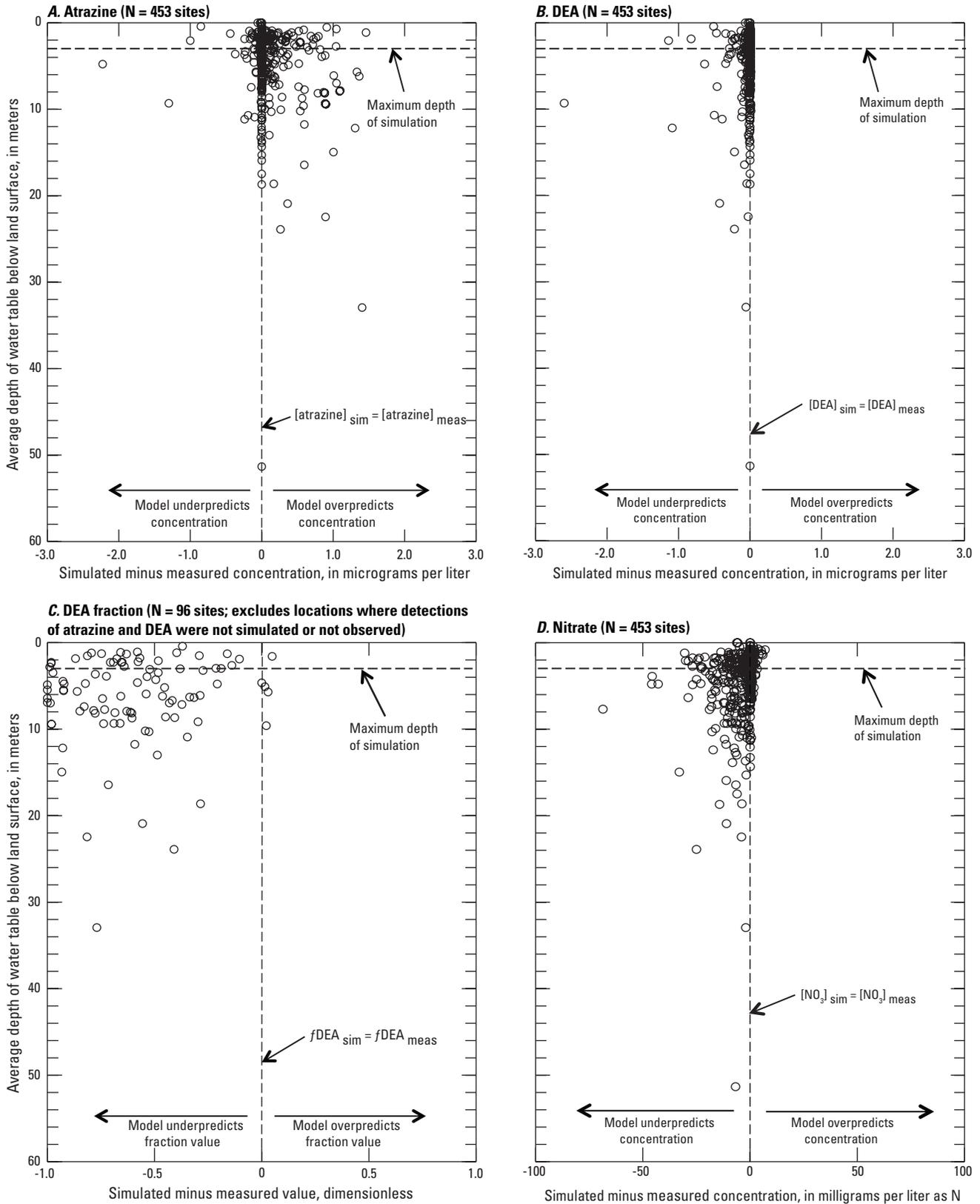


Figure 46. Relations between P-GWAVA-RZ (Phase 2) model residuals for (A) atrazine concentrations, (B) deethylatrazine (DEA) concentrations, (C) DEA fractions, and (D) nitrate concentrations and the average depth of the water table at study sites in the 10 northernmost states of the Corn Belt, 1992–2006.

Table 9. Correlations between average depths to water and P-GWAVA model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations in agricultural areas of the United States.

[P-GWAVA-PR simulations used areally averaged intensities of atrazine application, stochastically distributed irrigation, and atrazine transformation in both the sorbed and dissolved states; P-GWAVA-RZ simulations used a uniform intensity of atrazine application (2 kilograms of active ingredient per hectare) and simulated irrigation (table 4). Other differences between the approaches used for the P-GWAVA-PR and P-GWAVA-RZ simulations are summarized in tables 1, 4, and 14. **Spearman ρ** : Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. **P (ρ)**: Probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the model residuals (each of which represents the value predicted by the P-GWAVA simulations minus the value measured in groundwater) and the average water-table depths. **Abbreviations**: m, meter; <, less than; \leq , less than or equal to]

Response variable for model residuals	Model	Average water-table depth range (m)	Correlations between model residuals and average water-table depth		Number of sites
			Spearman ρ	P (ρ)	
Atrazine concentration	P-GWAVA-PR (Assessment depth: 1 m)	0.25–178.27	0.07	0.012	1,202
		0.25–0.99	0.11	0.35	77
		1.01–178.27	0.08	0.008	1,125
	P-GWAVA-RZ (Assessment depth: 3 m)	0.00–51.33	0.13	0.005	443
		0.00–2.99	0.028	0.69	208
		3.02–51.33	0.21	0.001	236
DEA concentration	P-GWAVA-RZ (Assessment depth: 3 m)	0.00–51.33	-0.096	0.04	443
		0.00–2.99	-0.019	0.79	208
		3.02–51.33	-0.074	0.26	236
DEA fraction ¹	P-GWAVA-RZ (Assessment depth: 3 m)	0.41–32.94	-0.092	0.37	96
		0.41–2.99	-0.081	0.68	28
		3.02–32.94	-0.040	0.74	68
Nitrate concentration	P-GWAVA-RZ (Assessment depth: 3 m)	0.00–51.33	-0.27	\leq 0.0001	443
		0.00–2.99	-0.25	0.0003	208
		3.02–51.33	-0.22	0.0006	236

¹Examined only at sites where detections of atrazine and (or) DEA were simulated or measured. Sites where neither compound was detected—or where the detection of neither compound was simulated—were excluded from the calculations.

Because diffusion rates are considerably higher in air than in water, the dissolved oxygen consumed by the conversion of atrazine to DEA is likely to be replenished more rapidly in the vadose zone than in the saturated zone. In areas with greater depths to water, the longer transit times from the land surface to the water table might therefore be expected to result in more extensive formation of DEA from atrazine than in areas with thinner vadose zones. This, in turn, would lead to the positive

correlation observed between DTW and the model residuals for atrazine concentrations and the negative correlation observed between DTW and the DEA concentration residuals during this study (table 9), as well as the direct relation noted by Tesoriero and others (2007) between vadose-zone thickness and the extent of conversion of atrazine to DEA in the subsurface.

Nitrate

Significant, negative correlations were noted between DTW and the P-GWAVA-RZ model residuals for nitrate concentrations, regardless of the depth range examined (table 9). As with the pattern noted for atrazine and DEA, the negative correlations between the model residuals for nitrate concentrations and DTW also indicate a direct relation between residence time in the vadose zone and the extent of a biochemical reaction that requires oxic conditions. In this case, the reaction involves the formation of nitrate from the oxidation of the more reduced forms in which nitrogen is often applied (fig. 21). As part of a comprehensive analysis of groundwater chemistry in 15 major aquifers across the United States, McMahan and Chapelle (2007) determined that shallow groundwater is more likely to exhibit reducing conditions in areas with relatively thin vadose zones than in areas with greater depths to the water table. A similar pattern was reported on a more localized scale by Landon and others (2011) for groundwater in the San Joaquin Valley, California. Because nitrate is more stable under oxic conditions than when the supply of dissolved oxygen is limited, the results from these earlier studies indicate that, if all other factors are equal, nitrate concentrations in groundwater may be higher in locations with a relatively thick vadose zone than in areas with a relatively thin vadose zone. This expectation is consistent with the significant negative correlations observed between the model residuals for nitrate concentrations and the DTW in the Phase 2 study area (table 9).

Agreement Between Simulated and Observed Solute Concentrations

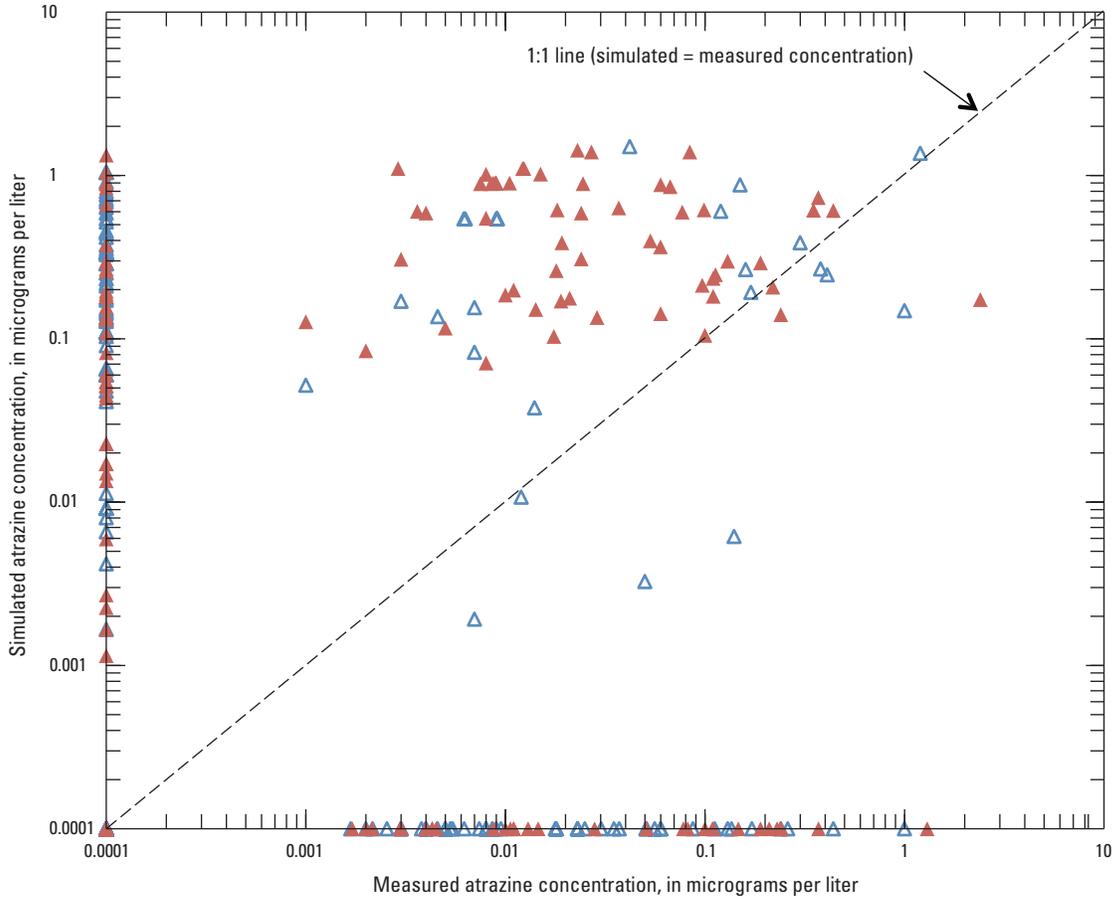
Much of the analysis of the Phase 1 results involved comparing the atrazine concentrations predicted by the P-GWAVA-PR simulations in the vadose zone with those measured in shallow groundwater at the same sites. During Phase 2, concentrations simulated in the vadose zone using the P-GWAVA-RZ model were compared with concentrations measured in groundwater for DEA and nitrate, as well as for atrazine. The inclusion of DEA in the P-GWAVA-RZ simulations also made it possible to compare predicted DEA fractions with DEA fractions measured in groundwater. In addition, the fact that many of the sites examined in the Corn Belt during Phase 2 were also among those examined during Phase 1 provided opportunities to compare the P-GWAVA-PR and P-GWAVA-RZ models with respect to the level of agreement between their simulated atrazine concentrations and the atrazine concentrations measured in groundwater.

Atrazine

Simulated Atrazine Concentrations Compared with Concentrations Measured in Groundwater

As with the P-GWAVA-PR simulations (for example, figs. 26 and 33; table 7), the final set of P-GWAVA-RZ simulations were more likely to overpredict the atrazine concentrations measured in groundwater than to underpredict them. The cumulative distributions of the model residual for the atrazine concentration predicted by the P-GWAVA-RZ simulations (that is, the value simulated at the assessment depth of 3 m in the vadose zone minus the value measured in shallow groundwater in the same location) among all study sites in the Corn Belt for Phase 2 are shown in figure 47. To facilitate an examination of the potential influence of water-table depth on the model residuals, the results are displayed for three subsets of sites: (1) sites where the DTW was less than or equal to 3 m, (2) sites where the DTW was greater than 3 m, and (3) all sites. The extent of agreement between the simulated and measured atrazine concentrations at sites where the water table was deeper than 3 m, as well as at sites where it was shallower than or equal to this depth, is shown in figure 48. Summary statistics describing the degrees of correlation between simulated and measured atrazine concentrations for the two site categories, as well as when all sites are considered, are presented in table 10.

Atrazine concentrations predicted by the P-GWAVA-RZ simulations in the vadose zone showed patterns of correlation with the concentrations measured in groundwater (table 10) that were similar to those observed for the P-GWAVA-PR simulations (table 7). When the analysis was restricted to sites where the average DTW was shallower than the Phase 2 assessment depth (< 3 m), the atrazine concentrations predicted by the P-GWAVA-RZ simulations were not significantly correlated with those measured in groundwater (table 10). However, the simulated atrazine concentrations were positively correlated with those measured in groundwater when all of the Phase 2 sites were examined, or just those where the DTW was greater than the assessment depth ($P[\rho] \leq 0.0001$; Spearman rank correlations). Additionally, the degree of correlation was stronger when the analysis of the P-GWAVA-RZ predictions was restricted to sites with DTW greater than the assessment depth than when all of the sites were examined. As with the Phase 1 results, the lack of a significant correlation between the simulated and measured atrazine concentrations for the sites where DTW was shallower than the assessment depth during Phase 2 may have been partly caused by the narrow depth range examined.



EXPLANATION

- △ Average depth to water less than or equal to 3 meters (217 sites)
- ▲ Average depth to water greater than 3 meters (236 sites)

Figure 48. Atrazine concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4A). Atrazine concentrations (simulated or measured) less than the reporting limit were assigned a value of 0.0001 microgram per liter for the purposes of display. Summary statistics for correlations between simulated and measured atrazine concentrations are presented in table 10.

Table 10. Agreement between atrazine, deethylatrazine (DEA), or nitrate concentrations (or DEA fractions) simulated at the 3-meter assessment depth in the vadose zone by the P-GWAVA-RZ (Phase 2) model and the concentrations (or DEA fractions) measured in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006.

[Concentrations predicted for atrazine and DEA were obtained with P-GWAVA-RZ simulations using the uniform atrazine application intensity (2 kilograms of active ingredient per hectare); predicted nitrate concentrations were obtained with simulations using fertilizer application intensities that varied spatially with soil organic-carbon content (table 14). Irrigation was simulated at all sites. For the purposes of these calculations, non-detections of atrazine and DEA—either measured or simulated—were assigned a concentration of 0.0001 microgram per liter (µg/L); for nitrate, non-detections were assigned a concentration of 0.01 milligram per liter as N (mg-N/L). **Spearman ρ:** Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. **P(ρ):** The probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the simulated and measured values. **Model residuals:** The model residual for a given parameter is equal to the value predicted in the vadose zone by the P-GWAVA-RZ simulation minus the value measured in groundwater at the same site. **95th percentile:** For each case, 95 percent of the model residuals were smaller than the value shown. **Abbreviations:** m, meter]

Parameter	Range of depths to water at the sites (m)	Correlation (if any) between simulated and measured values		Model residuals (simulated minus measured values)		Number of sites
		Spearman ρ	P(ρ)	Median	95th percentile	
Atrazine concentration	<3	0.024	0.73	0.000 µg/L	0.55 µg/L	217
	3.02–51.33	0.42	≤0.0001	0.000 µg/L	0.90 µg/L	236
	All sites	0.25	≤0.0001	0.000 µg/L	0.87 µg/L	453
DEA concentration	<3	0.26	0.0001	0.000 µg/L	0.002 µg/L	217
	3.02–51.33	0.49	≤0.0001	0.000 µg/L	0.004 µg/L	236
	All sites	0.41	≤0.0001	0.000 µg/L	0.003 µg/L	453
DEA fraction ¹	<3	0.072	0.71	-0.64	-0.12	28
	3.02–32.94	-0.17	0.17	-0.61	-0.073	68
	All sites	-0.085	0.41	-0.62	-0.078	96
Nitrate concentration	<3	-0.004	0.96	-0.063 mg-N/L	2.2 mg-N/L	217
	3.02–51.33	0.027	0.68	-2.2 mg-N/L	0.72 mg-N/L	236
	All sites	-0.018	0.71	-0.84 mg-N/L	1.6 mg-N/L	453

¹Examined only at sites where detections of atrazine and DEA were simulated or measured. Sites where neither compound was detected—or where the detection of neither compound was simulated—were excluded from the calculations.

Simulated Frequencies of Atrazine Detection Compared with Measured Values

The frequencies of atrazine detection predicted in the vadose zone by the P-GWAVA-RZ simulations for the NAWQA groundwater sampling networks with 10 or more sites are compared with the measured frequencies of detection in shallow groundwater for these networks in figure 49. As with the Phase 1 results (fig. 37), these comparisons are shown for all the networks with 10 or more sites (all sites; fig. 49A), and for the subset of networks where the depths to water exceeded the 3-m assessment depth at 10 or more sites

(sites with DTW greater than 3 m only; fig. 49B). In contrast with the results from the analysis for Phase 1, statistically significant correlations were observed between the frequencies of atrazine detection predicted by the P-GWAVA-RZ simulations and the measured values (table 11). Consistent with the results from the analysis of the atrazine concentration data (table 10), table 11 indicates that the correlation between the simulated and measured frequencies of atrazine detection for Phase 2 was stronger when sites with depths to water equal to or shallower than the assessment depth were excluded from the analysis than when all of the sites were examined.

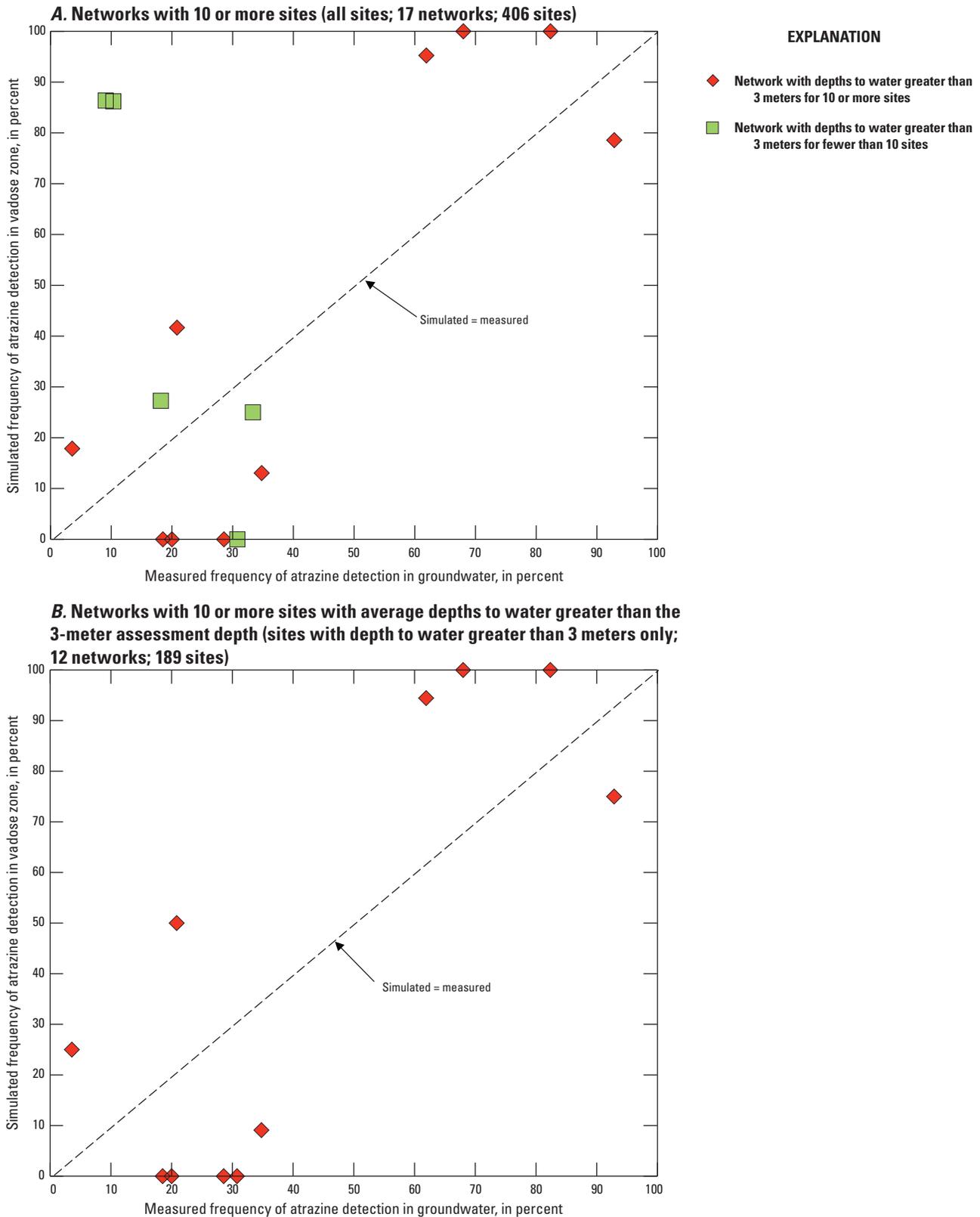


Figure 49. Frequencies of atrazine detection simulated at a depth of 3 meters in the vadose zone using the P-GWAVA-RZ (Phase 2) model and the measured frequencies of atrazine detection in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006. Data are shown for networks consisting of (A) all sites in groundwater networks with 10 or more sites, and (B) sites with depths to water greater than the 3-meter assessment depth in networks with 10 or more such sites. Simulated and measured detections of atrazine were determined using reporting limits that varied over time (fig. 4A). Summary statistics for correlations between simulated and measured detection frequencies are presented in table 11.

Table 11. Correlations between simulated and measured frequencies of detection of atrazine, deethylatrazine, and nitrate in shallow groundwater sampling networks with 10 or more sites.

[Results are shown for Phase 1 (P-GWAVA-PR simulations; conterminous United States, 1992–98; atrazine only) and Phase 2 (P-GWAVA-RZ simulations; 10 northernmost states of the Corn Belt of the United States, 1992–2006; atrazine, deethylatrazine [DEA], and nitrate). The geographic locations of the Phase 1 networks are shown in figure 38; those of the Phase 2 networks are shown in figures 66–68. P-GWAVA-PR simulations used areally averaged intensities of atrazine application, stochastically distributed irrigation, and atrazine transformation in both the sorbed and dissolved states; P-GWAVA-RZ simulations used a uniform intensity of atrazine application (2 kilograms of active ingredient per hectare) and irrigation at all sites (table 4). Detections—either simulated or measured—were determined using a reporting limit of 0.001 microgram per liter (µg/L) for atrazine during Phase 1, and reporting limits that varied over time for atrazine, DEA, and nitrate (fig. 4) during Phase 2. Results from statistically significant ($P < 0.05$) correlations are shown in **boldface**. R^2 : Pearson correlation coefficient. $P(R^2)$: Probability associated with the Pearson correlation coefficient. **Spearman ρ** : Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P(\rho)$) are displayed in **boldface**. $P(\rho)$: The probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the simulated and measured values. **Number of networks**: Number of networks included in each analysis. **Number of sites**: Number of sites included in each analysis. **Abbreviation**: m, meter]

Compound (model)	Depths to water at the sites examined (m)	Correlations between simulated and measured frequencies of detection				Number of networks	Number of sites
		R^2	$P(R^2)$	Spearman ρ	$P(\rho)$		
Atrazine (P-GWAVA-PR)	1.01–178.27	0.025	0.29	0.13	0.38	46	1,051
	All sites	0.036	0.20	0.18	0.24	47	1,149
Atrazine (P-GWAVA-RZ)	3.02–32.94	0.69	0.0009	0.66	0.020	12	189
	All sites	0.24	0.046	0.29	0.26	17	406
DEA	3.02–32.94	0.66	0.0013	0.78	0.0026	12	189
	All sites	0.56	0.0006	0.57	0.018	17	406
Nitrate	3.02–32.94	0.060	0.44	-0.18	0.58	12	189
	All sites	0.061	0.34	-0.076	0.77	17	406

Comparison of Predictions from the P-GWAVA-PR and P-GWAVA-RZ Simulations

For the statistical analyses that included the sites where the DTW exceeded the assessment depth for each model of interest, the atrazine concentrations predicted by the final sets of P-GWAVA simulations were significantly correlated with those measured in shallow groundwater at the same locations for both study phases (tables 7 and 10). However, although significant correlations were noted between the simulated and observed frequencies of atrazine detection for the Phase 2 results ($P < 0.05$), the corresponding relations for the Phase 1 results were not statistically significant (table 11). These disparities in the relative strengths of the correlations between the simulated and observed patterns of atrazine occurrence for the two models may have been partly because the Phase 1 study sites (fig. 1) encompassed a much wider variety of agricultural, hydrogeologic, and climatic settings than the Phase 2 sites (fig. 2).

Because simulations were conducted using both P-GWAVA-PR and P-GWAVA-RZ at many of the study sites in the Corn Belt, opportunities were available to make direct

comparisons between the two models with respect to (1) their simulated atrazine concentrations, and (2) the accuracy with which each model predicted these concentrations in shallow groundwater. To account for the potential effects of irrigation, the comparisons were made using the predictions from the set of P-GWAVA-PR model simulations for which irrigation had been simulated at all sites (as was the case for all the P-GWAVA-RZ simulations), rather than those for which the irrigated sites had been randomly distributed among sites in individual groundwater networks. Except for the manner in which irrigation was assigned to different sites for the P-GWAVA-PR simulations, however, these comparisons were made using the final simulation approaches described in table 4. Three methods were used to compare the predictions from the two models: (1) graphical comparisons of the cumulative distributions of the model residuals, (2) statistical analysis of the correlation between the atrazine concentrations simulated by the two models at individual sites, and (3) statistical analysis of the correlation between the model residuals for atrazine concentrations from the two models at individual sites.

The cumulative distributions of the model residuals for atrazine concentrations for the two models at the 136 sites in the Corn Belt where simulations were done using both models and the depths to water exceeded 3 m (the greater of the assessment depths for the two models) are shown in figure 50. Virtually identical distributions were observed for each model in the corresponding plots (not shown) that included the data from all 268 of the sites in the Corn Belt where both models were run, regardless of water-table depth. The atrazine

concentrations predicted by the P-GWAVA-RZ simulations were generally in closer agreement with the concentrations measured in groundwater than were the concentrations predicted by the P-GWAVA-PR simulations (fig. 50). On the basis of the results shown in figure 31, this pattern may have been partly because the P-GWAVA-PR simulations used soil property data drawn from STATSGO, whereas the P-GWAVA-RZ simulations used soils data obtained from SSURGO.

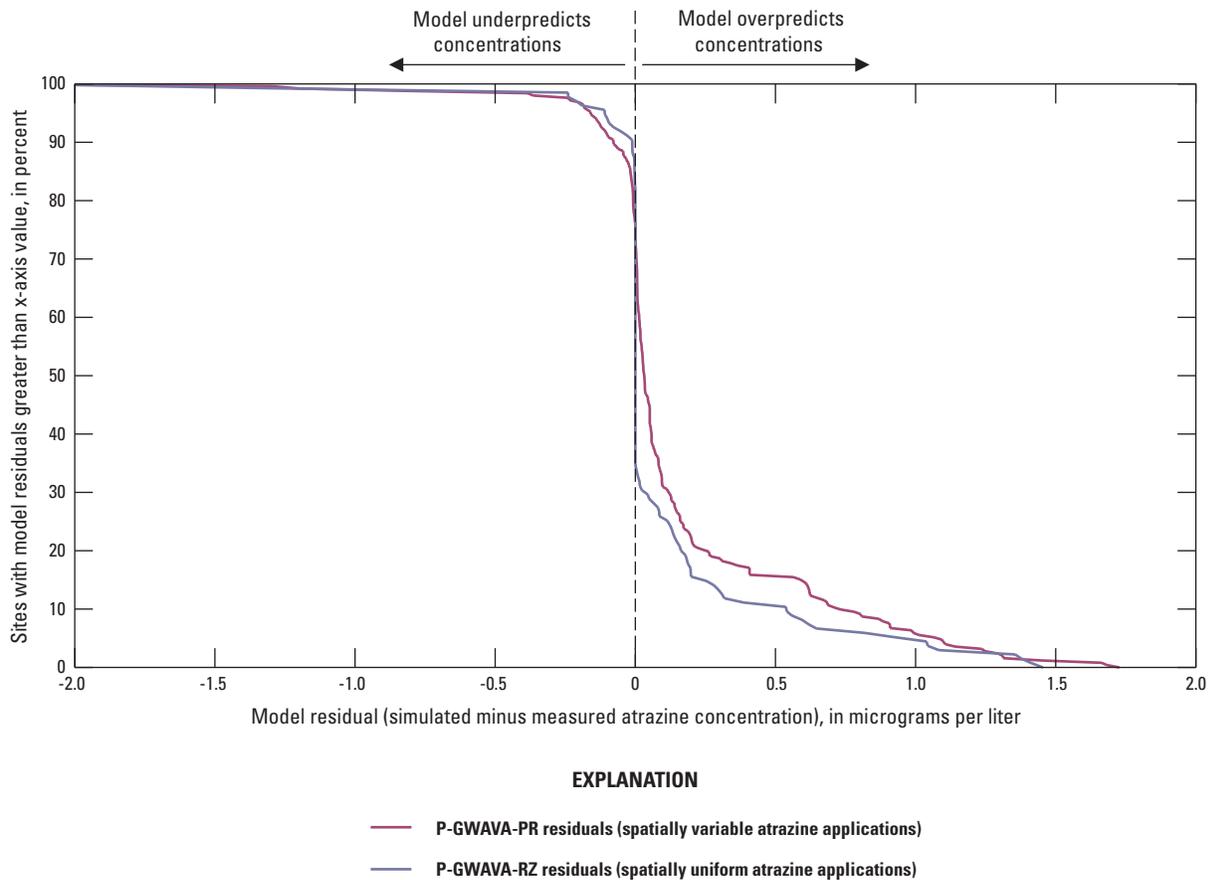


Figure 50. Cumulative distributions of model residuals for atrazine concentrations simulated by P-GWAVA-PR (Phase 1, 1992–98) and P-GWAVA-RZ (Phase 2, 1992–2006) at 136 study sites where simulations were done with both models and the depth to water was greater than 3 meters in agricultural areas of the 10 northernmost states in the Corn Belt. Simulations were carried out as described in table 4, with the exception that irrigation was simulated at all sites with both models. Concentrations were not corrected for temporal variations in analytical recoveries. A uniform reporting limit of 0.001 microgram per liter ($\mu\text{g/L}$) was applied to all simulated concentrations, and all sites with non-detections were assigned a concentration of 0.0001 $\mu\text{g/L}$ for the purposes of the calculations.

Additionally, the atrazine concentrations in shallow groundwater may have been overestimated by the P-GWAVA-PR simulations to a greater extent than by the P-GWAVA-RZ simulations because RZWQM simulates the upward transport of solutes in response to the upward flow of water during ET, whereas PRZM does not. Previous studies (Bayless, 2001; McMahon and others, 2006) have inferred that this process may be responsible for the retention of surface-derived solutes within the root zone for extended periods, long after the water that carried them has moved to greater depths (or transferred to the atmosphere through ET). For compounds like atrazine that react at higher rates within the root zone than at greater depths beneath the land surface, this process could result in lower fluxes of the herbicide to the water table than would occur otherwise, causing the P-GWAVA-PR model to overpredict atrazine concentrations to a greater extent than the P-GWAVA-RZ model (fig. 50).

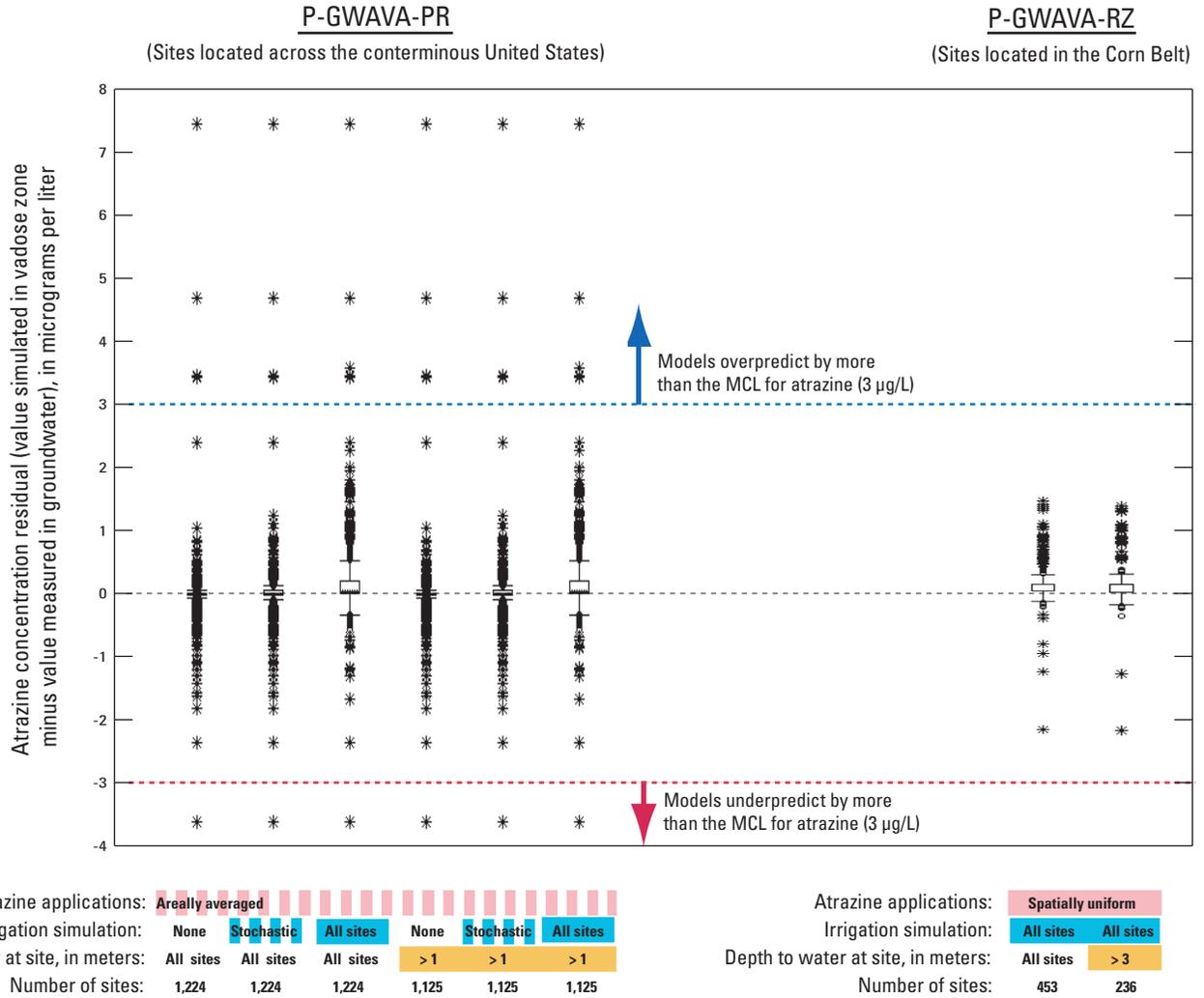
At the 136 Corn Belt sites where the DTW was greater than 3 m and simulations using both models were carried out (with irrigation simulated in all locations), the atrazine concentrations predicted by the two models were negatively correlated (Spearman $\rho = -0.43$; $P[\rho] \leq 0.0001$). Similarly, the residuals for atrazine concentrations derived from the two models at these sites were also negatively correlated (Spearman $\rho = -0.17$; $P[\rho] = 0.04$). Given the considerable differences between the two models, and between the simulation approaches used for the two phases of this study (table 4), the precise reasons for these disparities between the atrazine concentrations simulated by the two models are not clear. However, these observations indicate that different factors likely were responsible for the errors associated with the two models.

Despite these disparities, the data shown in tables 7 and 10, and figures 34 and 47, indicate that the atrazine concentrations simulated by the two models were in relatively close agreement with the values measured in shallow groundwater. In figure 51, the distributions of the model residuals for the atrazine concentrations derived from the P-GWAVA-RZ simulations are compared with the distributions of model residuals from the three P-GWAVA-PR scenarios that showed the closest agreement between the simulated and measured atrazine concentrations among all the Phase 1 sites (namely, the simulations for which the areally averaged intensities of atrazine application were used and where atrazine transformation was simulated in both the sorbed and the dissolved states). These results, presented for two subsets of sites for each model scenario (that is, all sites, and sites where DTW was greater than the assessment depth

for each study phase), indicate that the model residuals for the atrazine concentrations derived from the P-GWAVA-PR simulations spanned a wider range (-3.6 to 7.4 $\mu\text{g/L}$) than the residuals from the P-GWAVA-RZ simulations (-2.2 to 1.5 $\mu\text{g/L}$). This may have been caused, in part, by the fact that the P-GWAVA-PR simulations were carried out over a much larger geographic area.

As with the data shown in tables 7 and 10, figure 51 indicates that for more than 95 percent of the sites of interest, the atrazine concentrations simulated by the two models were in agreement with the measured concentrations by margins that were an order of magnitude less than the MCL of 3 $\mu\text{g/L}$ established by the U.S. Environmental Protection Agency (2003) for atrazine. Additionally, in most locations the atrazine concentrations simulated in the vadose zone by both models were greater than or equal to those measured in the saturated zone (figs. 34, 47, 51; tables 7, 10). This is consistent with the general expectation that the concentrations of any surface-derived solute would tend to be higher in the vadose zone than in the underlying groundwater, owing to the effects of dilution, hydrodynamic dispersion, sorption, and transformation during solute transport toward, and below, the water table.

Results from several previous investigations indicate that pesticide concentrations measured in groundwater tend to be higher for locations or periods with higher recharge rates (Barbash and Resek, 1996). Therefore, differences in precipitation between the Phase 1 and Phase 2 simulation periods may have been one of the factors contributing to the differences in the levels of agreement between the simulated and measured atrazine concentrations during the two study phases (figs. 50 and 51). The P-GWAVA-PR simulations were conducted from 1991–95 (table 1). The P-GWAVA-RZ simulation period was a 5-year window from 2000 through 2004, but used weather data that were generated stochastically by Cligen from historical data gathered between 1949 and 1996. Consequently, actual meteorological data could not be used to make direct comparisons between the precipitation inputs used for the two study phases. However, historical data from 1991 to 2007 for 338 of the agricultural sites in the Corn Belt where simulations were carried out with one or both models provide little evidence of significant shifts in precipitation during this period (fig. 52). Therefore, temporal variations in precipitation alone are not likely responsible for systematic changes in the atrazine concentrations measured in groundwater in the Corn Belt between 1991 and 2004 and, by extension, the contrast in the levels of agreement between the simulated and measured atrazine concentrations or detection frequencies for the two phases of this study.



EXPLANATION

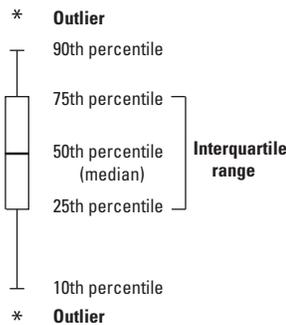


Figure 51. Statistical distributions of model residuals for atrazine concentrations from selected P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) scenarios at agricultural sites in the conterminous United States (Phase 1, 1992–1998) and the 10 northernmost states of the Corn Belt (Phase 2, 1992–2006). Results shown for Phase 1 are from the P-GWAVA-PR simulations where atrazine transformation was assumed to occur in both the sorbed and the dissolved states. For each modeling scenario (for both study phases), simulation results are shown for all sites, as well as for sites with depths to water greater than the assessment depth. A uniform reporting limit of 0.001 microgram per liter (µg/L) was applied to all concentrations (simulated or measured), and no concentrations were corrected for temporal variations in analytical recoveries. All non-detections of atrazine (either simulated or measured) were assigned a concentration of 0.0001 µg/L for the purposes of the calculations. (MCL, maximum contaminant level.)

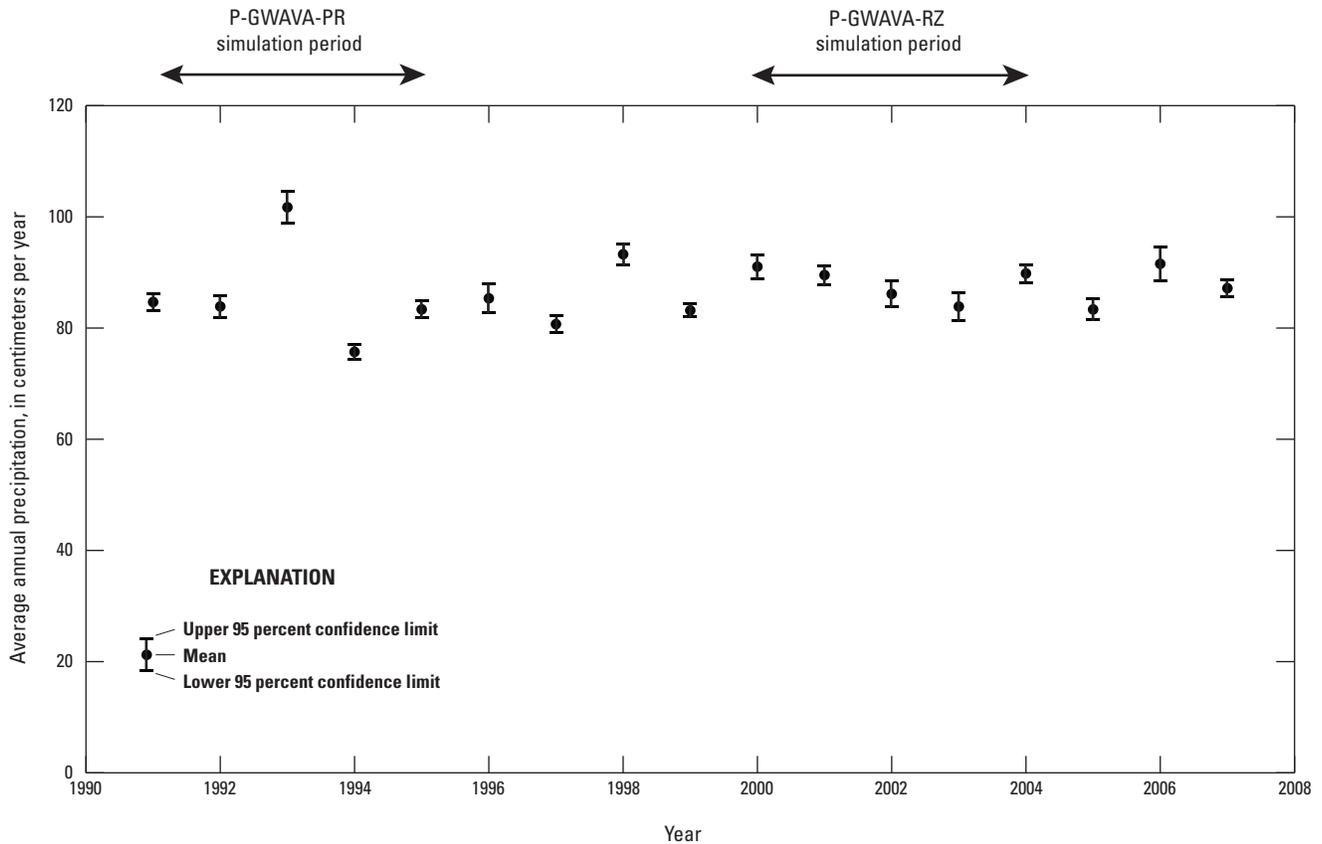


Figure 52. Average annual precipitation at 338 of the agricultural sites examined during one or both phases of this study in the 10 northernmost states of the Corn Belt, 1990–2007. Precipitation data from PRISM Climate Group (2009) and David Wolock, U.S. Geological Survey (written commun., June 2011).

Deethylatrazine

The DEA concentrations predicted by the P-GWAVA-RZ simulations were in relatively close agreement and significantly correlated with the concentrations measured in groundwater, regardless of whether or not sites with depths to water equal to or shallower than the 3-m assessment depth were included in the analysis (table 10; fig. 53). The strongest correlation between the simulated and measured DEA concentrations was detected when the sites with depths to water equal to or shallower than the assessment depth were excluded (also observed for atrazine), and the weakest correlation observed when the analysis was restricted to such sites. Similarly, the frequencies of DEA detection predicted by the P-GWAVA-RZ simulations also were correlated with those measured in groundwater (table 11; fig. 54), with the stronger relation being noted when the sites with depths to water equal to or shallower than the 3-m assessment depth were excluded from the analysis.

The P-GWAVA-RZ model simulated a much narrower range of DEA concentrations (0.002–0.023 $\mu\text{g/L}$) than were measured in the groundwater (0.001–2.6 $\mu\text{g/L}$) (fig. 55). This was in marked contrast with the atrazine results, in which both the simulated and measured concentrations spanned approximately the same range (fig. 48). The results shown in figures 53, 54, and 55 also indicate that most of the disparities between the simulated DEA concentrations (or detection frequencies) and those measured in groundwater were biased toward underprediction. This pattern is consistent with the assumptions that (1) DEA concentrations are likely to increase with residence time in the vadose zone, and (2) atrazine or DEA detected in the saturated zone are likely to have a longer subsurface residence time, and thus reflect a more extensive conversion of the parent compound to the degradate, than the same solutes detected in the overlying vadose zone in the same location.

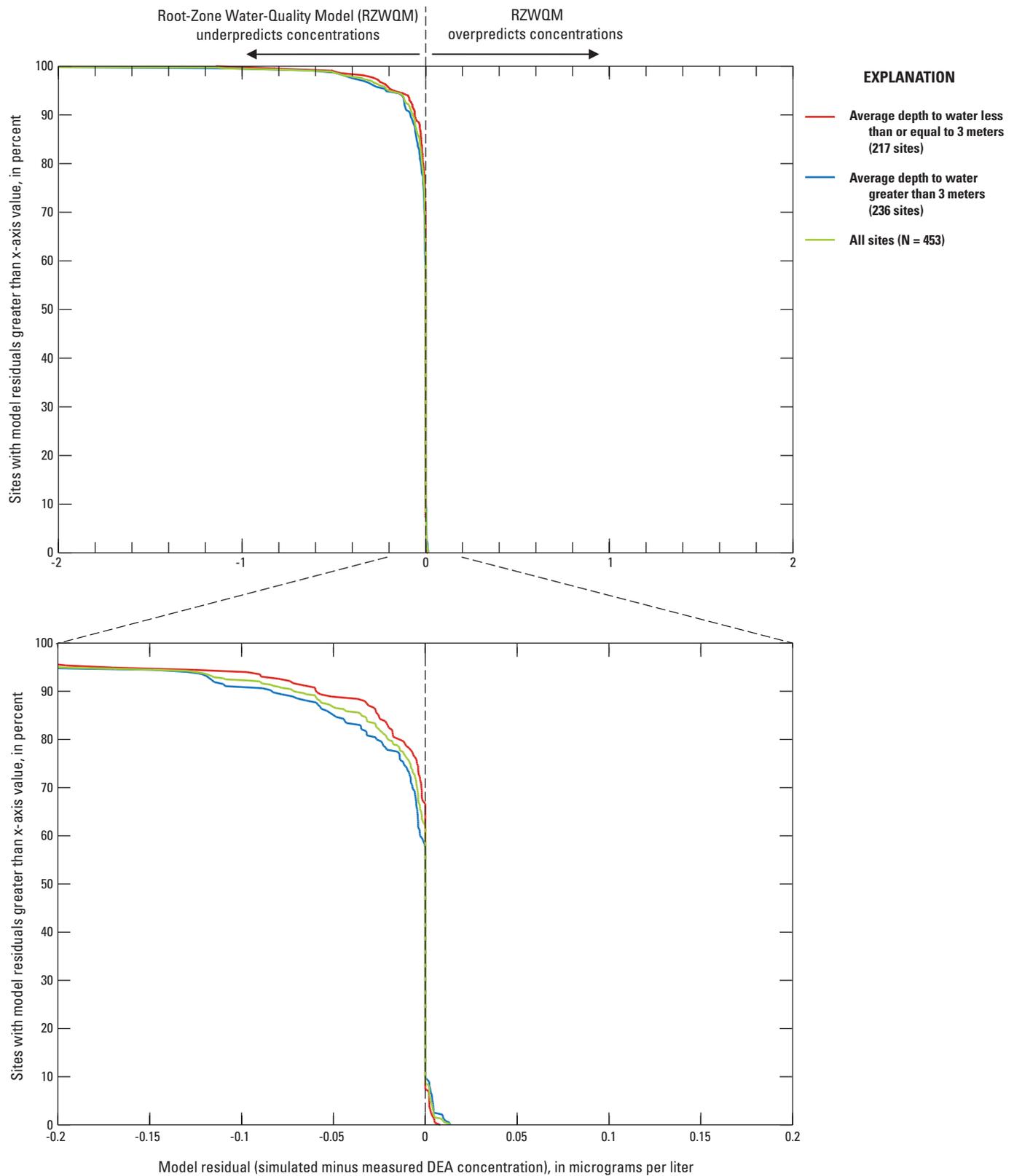


Figure 53. Cumulative distributions of P-GWAVA-RZ (Phase 2) model residuals for deethylatrazine (DEA) concentration (value simulated at the 3-meter assessment depth in the vadose zone minus value measured in shallow groundwater at each site) at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006. Data shown depend on the range of depths to water for each subset of sites. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4B). DEA concentrations (simulated or measured) less than the reporting limit were assigned a value of 0.0001 microgram per liter for the purposes of the calculations. Summary statistics for the model residuals are presented in table 10.

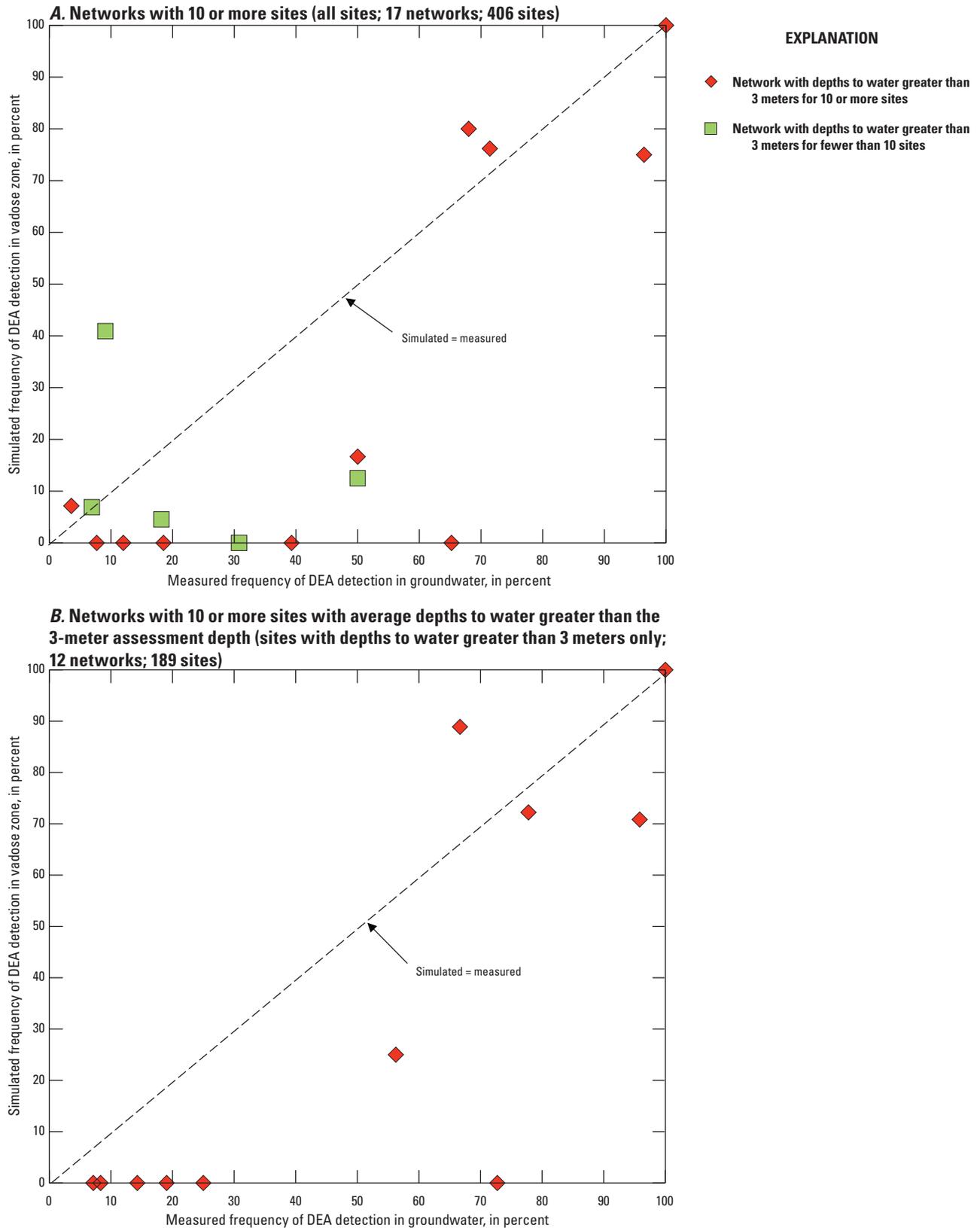
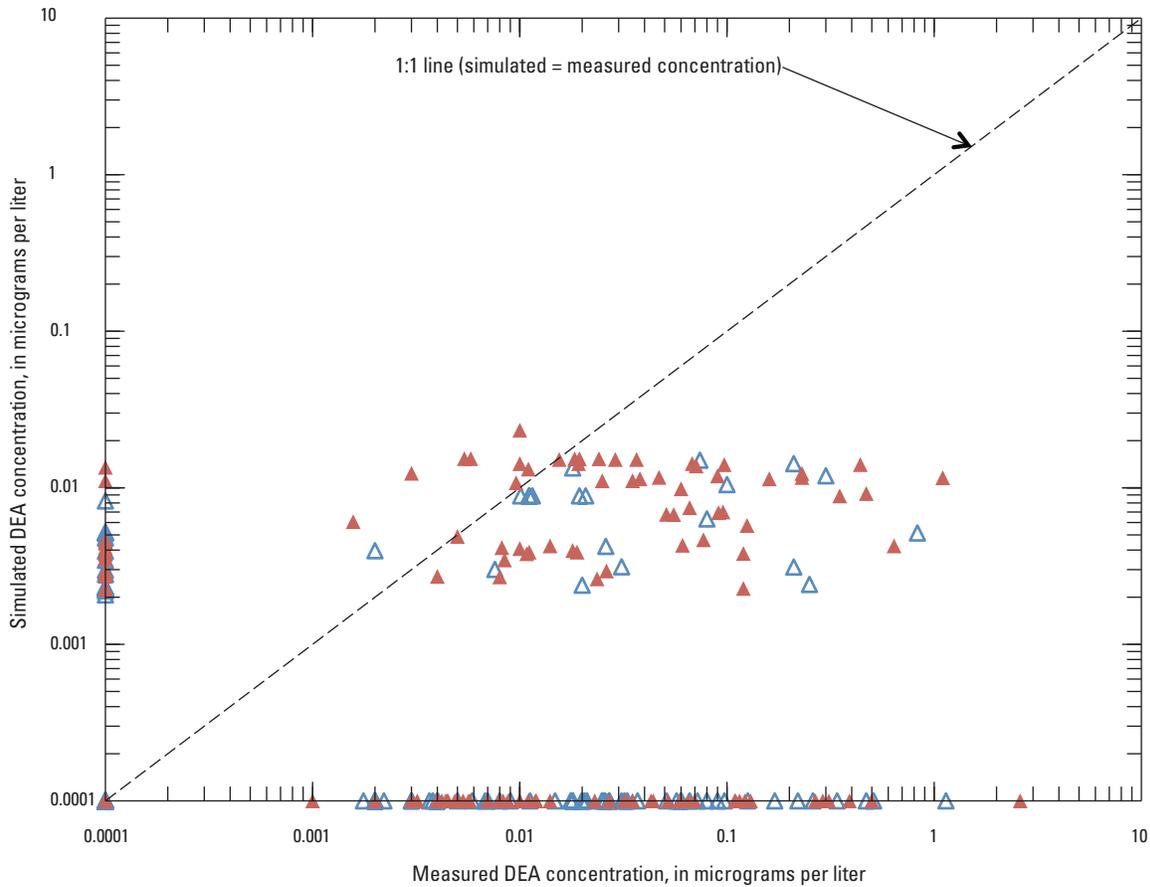


Figure 54. Frequencies of deethylatrazine (DEA) detection simulated at a depth of 3 meters in the vadose zone by the P-GWAVA-RZ (Phase 2) model and the measured frequencies of DEA detection in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006. Data are shown for networks consisting of (A) all sites in groundwater networks with 10 or more sites, and (B) sites with depths to water greater than the 3-meter assessment depth in networks with 10 or more such sites. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4B). Summary statistics for correlations between simulated and measured detection frequencies are presented in table 11.



EXPLANATION

- △ Average depth to water less than or equal to 3 meters (217 sites)
- ▲ Average depth to water greater than 3 meters (236 sites)

Figure 55. Deethylatrazine (DEA) concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4B). DEA concentrations (simulated or measured) less than the reporting limit were assigned a value of 0.0001 microgram per liter for the purposes of display. Summary statistics for correlations between simulated and measured DEA concentrations are presented in table 10.

Comparisons of Atrazine and Deethylatrazine Concentrations Predicted by P-GWAVA-RZ with those from Stackelberg Regression Model

Stackelberg and others (2012) used the NAWQA data to develop two linear Tobit regression models for predicting the sum of the concentrations of atrazine and DEA (computed on a mass basis, rather than a molar basis) in shallow groundwater in the conterminous United States. One model was developed using only national-scale data for the explanatory variables, whereas the other model used more site-specific values for some of the parameters. The sum of the (mass based) atrazine and DEA concentrations simulated by the P-GWAVA-RZ model was compared with the sum of the atrazine and DEA concentrations predicted by the national-scale model of Stackelberg and others (2012) at all 329 Phase 2 sites that were included in both studies. This comparison only could be carried out using the Phase 2 results because the concentrations of DEA were not simulated during Phase 1. Because of the exclusive focus of this study on national-scale sources of input data, the comparison was made with the model of Stackelberg and others (2012) that used only national-scale data. To be consistent with the data from Stackelberg and others (2012), the solute concentrations predicted by the P-GWAVA-RZ simulations were censored using the Stackelberg and others (2012) reporting limits of 0.004 µg/L for atrazine and 0.007 µg/L for DEA. Similarly, the sum of the atrazine and DEA concentrations predicted by the regression model was censored at the sum of these reporting limits for the two compounds (0.011 µg/L). A value of 0.001 µg/L was assigned to all the regression-predicted values less than this threshold for the purposes of the calculations. The sum of the atrazine and DEA concentrations simulated by the P-GWAVA-RZ model exhibited a significant, positive correlation with the concentrations predicted by the national-scale regression model of Stackelberg and others (2012) at the 329 Corn Belt sites ($R^2 = 0.21$ [$P \leq 0.0001$]; Spearman $\rho = 0.37$ [$P(\rho) \leq 0.0001$]).

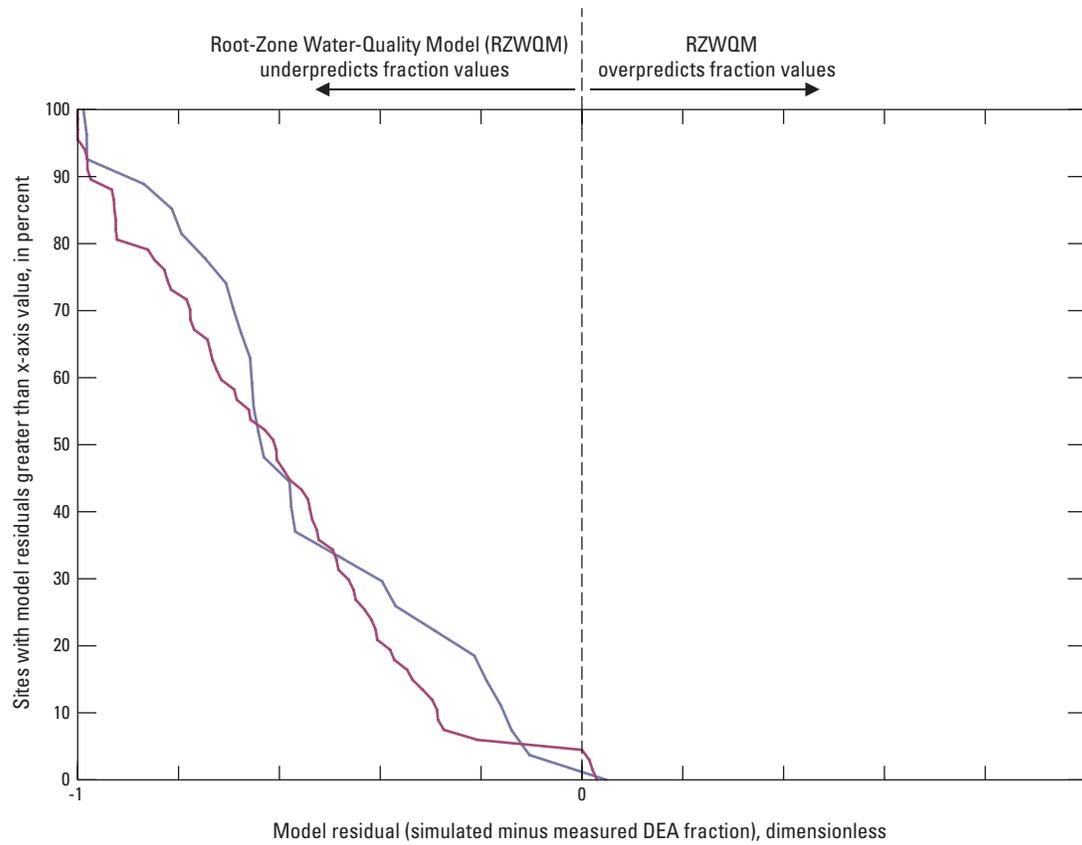
Deethylatrazine Fractions

The DEA fractions predicted by the P-GWAVA-RZ simulations (and calculated using equation 51) exhibited no significant correlations with the values computed from the concentrations of DEA and atrazine measured in groundwater at the same locations (figs. 56 and 57; table 10). This was observed regardless of whether or not sites with DTW less

than or equal to the 3-m assessment depth were included in the analysis. Thus, although the P-GWAVA-RZ simulations predicted concentrations of atrazine and DEA that were significantly correlated with the corresponding values measured in groundwater (table 10), they did not provide reliable predictions of the mole fraction of the applied atrazine that was converted to DEA in the subsurface. For nearly every site where the DEA fraction could be predicted, the model simulation results underpredicted the values measured in groundwater, consistent with the fact that most of the disparities between the simulated and measured DEA concentrations also were underpredictions (figs. 53, 54, and 55). This observation, in turn, is consistent with the expectation that the conversion of atrazine to DEA is likely to have proceeded to a greater extent in the saturated zone than in the overlying vadose zone in the same locations.

Nitrate

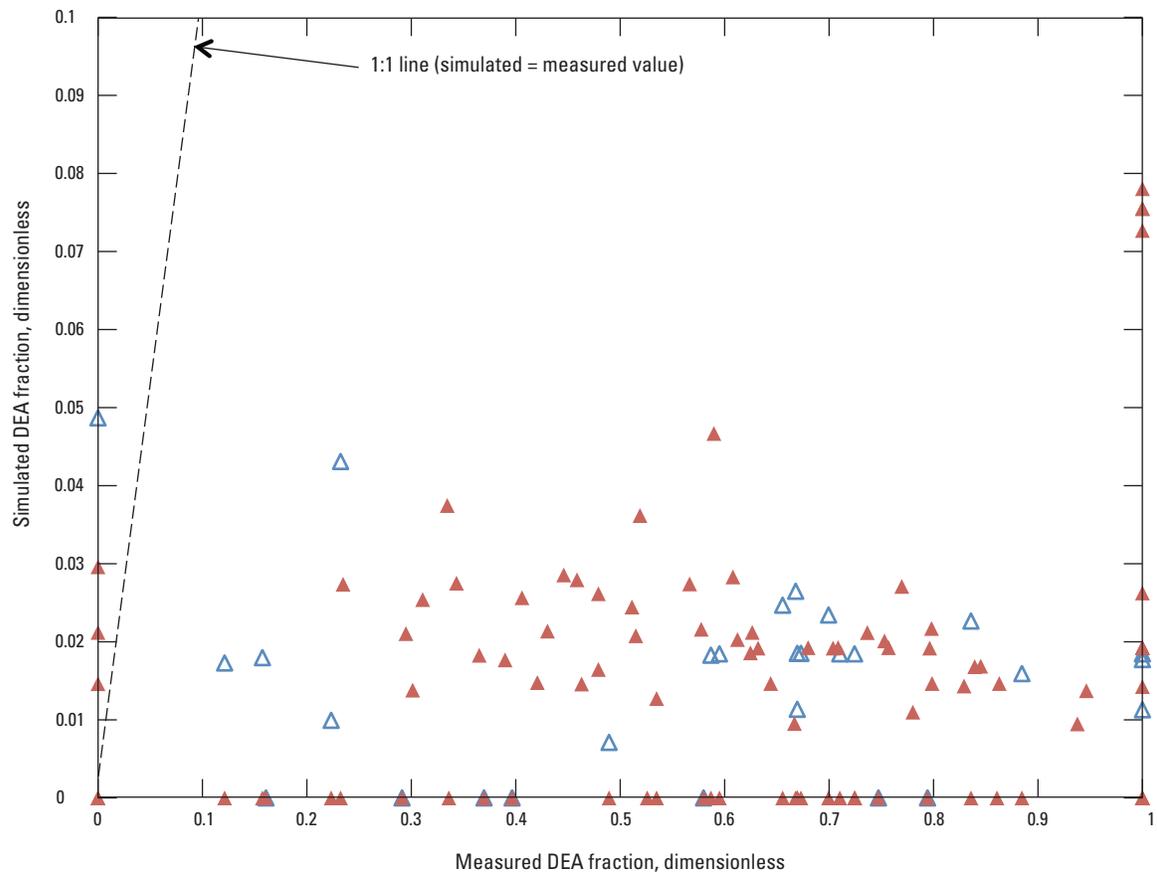
At most of the study sites, the nitrate concentrations simulated by the P-GWAVA-RZ model at the 3-m assessment depth in the vadose zone were less than the concentrations measured in shallow groundwater (figs. 58 and 59). Additionally, the simulated nitrate concentrations were not significantly correlated with the measured values, regardless of whether or not sites with depths to water less than or equal to 3 m were included in the analysis (table 10). The fact that the simulated nitrate concentrations were less than the concentrations measured in groundwater at most of the study sites is consistent with the observation by Nolan and others (2010) that in some settings, especially those where macropore flow is significant, RZWQM tends to underpredict the rate of transport of nitrate and other conservative solutes (such as bromide) in soil macropores. Another possible reason for the underestimation of the nitrate concentrations in groundwater by the P-GWAVA-RZ simulations was that nitrogen inputs were derived from crop requirements (table 14), rather than from known rates of application of fertilizer and manure; therefore, P-GWAVA-RZ may have underestimated the actual nitrogen inputs in many locations. Consistent with the results for the nitrate concentrations, the frequencies of nitrate detection simulated by the P-GWAVA-RZ model in the vadose zone showed no significant correlations with those measured in shallow groundwater, regardless of whether or not sites with depths to water less than or equal to the 3-m assessment depth were included in the analysis (table 11, fig. 60).



EXPLANATION

- Average depth to water less than or equal to 3 meters (28 sites)
- Average depth to water greater than 3 meters (68 sites)

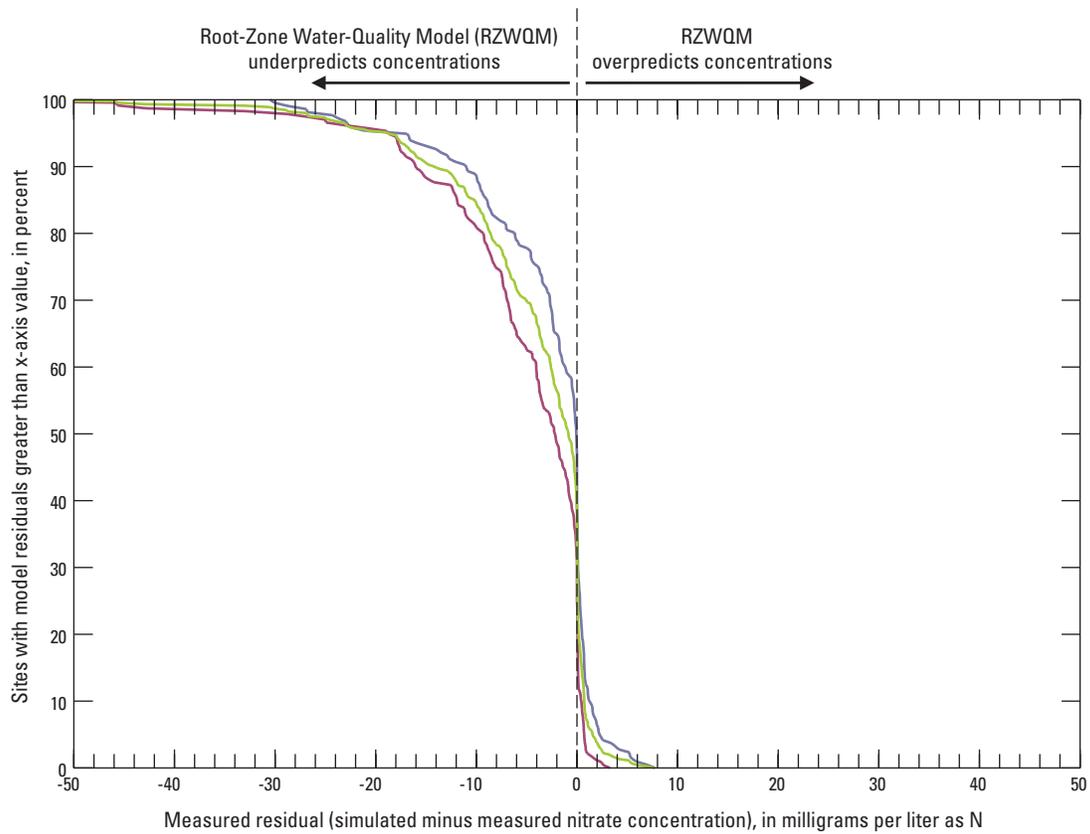
Figure 56. Cumulative distributions of P-GWAVA-RZ (Phase 2) model residual for the deethylatrazine (DEA) fraction (value simulated at the 3-meter assessment depth in the vadose zone minus value measured in shallow groundwater at each site) at agricultural sites in the 10 northernmost states in the Corn Belt, 1992–2006. Data shown depend on the range of depths to water for each subset of sites. Data not shown for sites where simulated concentrations of DEA and atrazine were below their reporting limits, or sites where detections of neither DEA nor atrazine were observed. Simulated and measured detections of DEA and atrazine were determined using reporting limits that varied over time (figs. 4A, 4B). Atrazine or DEA concentrations (simulated or measured) less than their reporting limits were assigned a value of 0 microgram per liter for the purposes of the calculations. Summary statistics for the model residuals are presented in table 10.



EXPLANATION

- △ Average depth to water less than or equal to 3 meters (28 sites)
- ▲ Average depth to water greater than 3 meters (68 sites)

Figure 57. Deethylatrazine (DEA) fractions simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and values measured in shallow groundwater at the same locations in agricultural areas of the 10 northernmost states in the Corn Belt, 1992–2006. Data not shown for sites where simulated concentrations of DEA and atrazine were below their reporting limits, or sites where detections of neither DEA nor atrazine were observed. Simulated and measured detections of DEA and atrazine were determined using reporting limits that varied over time (figs. 4A, 4B). Atrazine or DEA concentrations (simulated or measured) less than their reporting limits were assigned a value of 0 microgram per liter for the purposes of display. Summary statistics for correlations between simulated and measured DEA fractions are presented in table 10.



EXPLANATION

- Average depth to water less than or equal to 3 meters (217 sites)
- Average depth to water greater than 3 meters (236 sites)
- All sites (453)

Figure 58. Cumulative distributions of P-GWAVA-RZ (Phase 2) model residuals for nitrate concentrations (value simulated at the 3-meter assessment depth in the vadose zone minus value measured in shallow groundwater) at agricultural sites in the 10 northernmost states in the Corn Belt, 1992–2006. Data shown depend on the range of depths to water for each subset of sites. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4C). Nitrate concentrations (simulated or measured) less than the reporting limit were assigned a value of 0.01 milligram per liter as nitrogen for the purposes of the calculations. Summary statistics for the model residuals are presented in table 10.

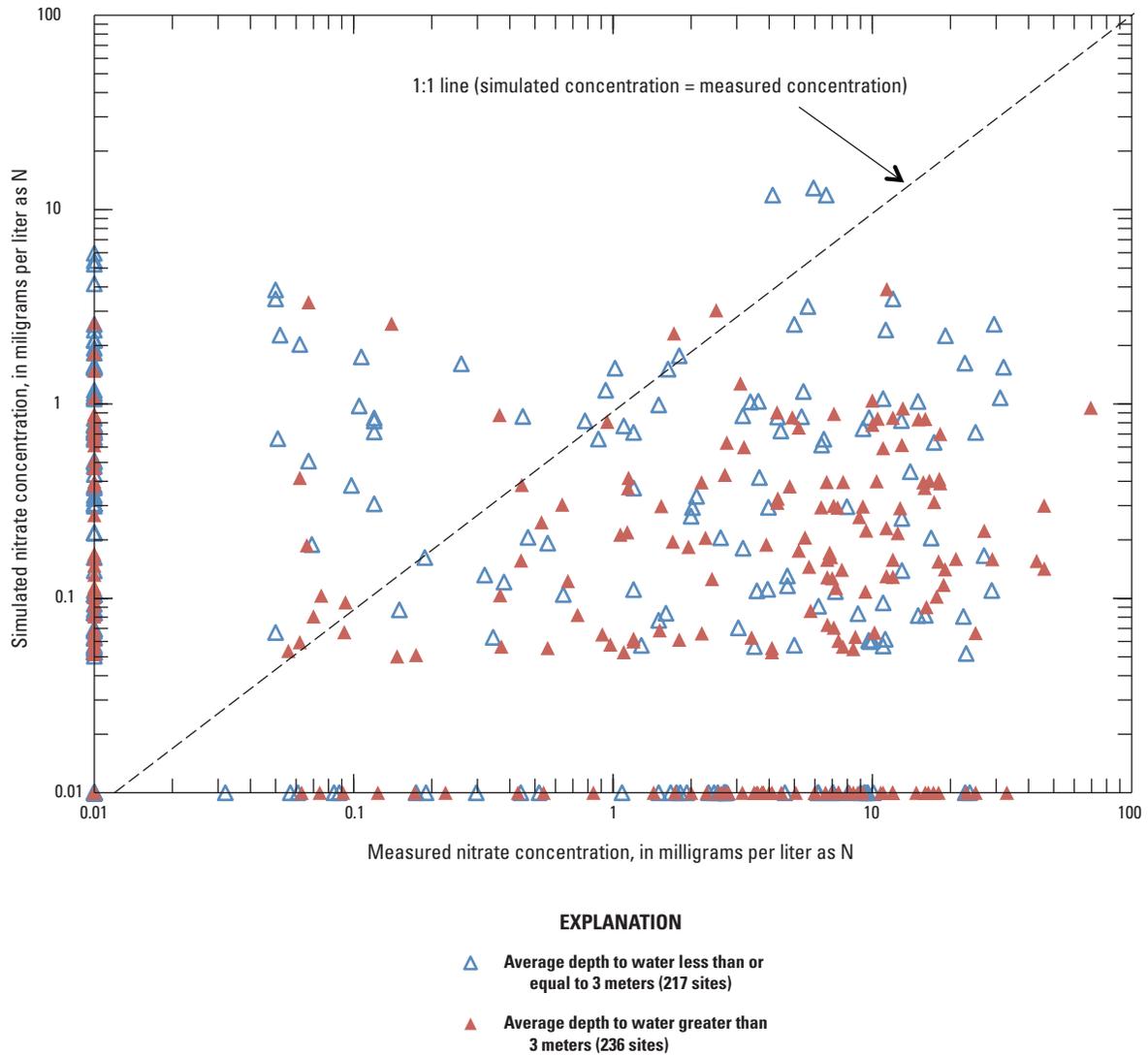


Figure 59. Nitrate concentrations simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and measured concentrations in shallow groundwater at agricultural sites in the 10 northernmost states of the Corn Belt, 1992–2006. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4C). Nitrate concentrations (simulated or measured) less than the reporting limit were assigned a value of 0.01 milligram per liter as nitrogen for the purposes of display. Summary statistics for correlations between simulated and measured nitrate concentrations are presented in table 10.

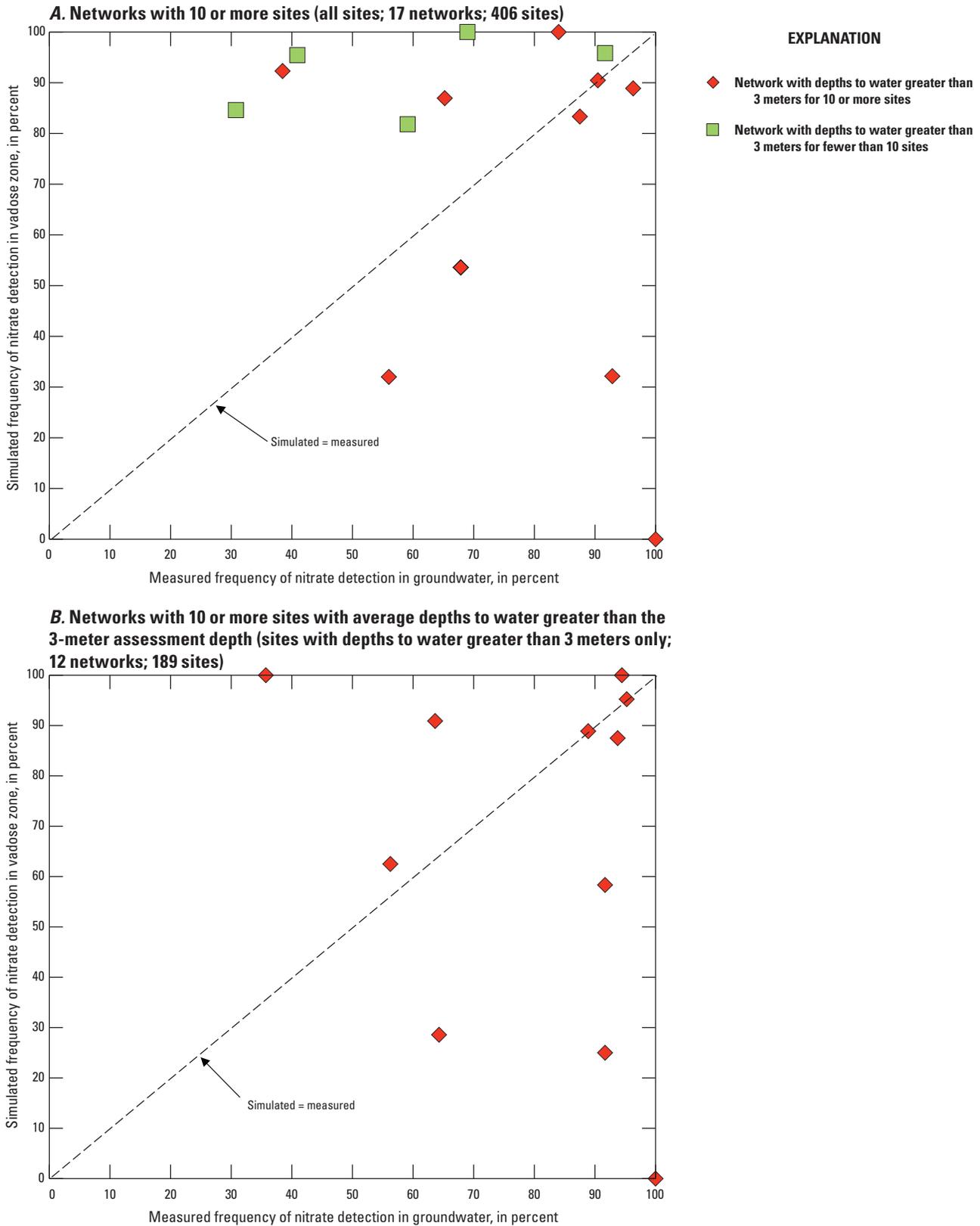


Figure 60. Frequencies of nitrate detection simulated by the P-GWAVA-RZ (Phase 2) model at the 3-meter assessment depth in the vadose zone and frequencies of nitrate detection measured in shallow groundwater networks in agricultural areas of the 10 northernmost states of the Corn Belt, 1992–2006. Data are shown for networks consisting of (A) all sites in groundwater networks with 10 or more sites, and (B) sites with depths to water greater than the 3-meter assessment depth in networks with 10 or more such sites. Simulated and measured detections were determined using reporting limits that varied over time (fig. 4C). Summary statistics for correlations between simulated and measured detection frequencies are presented in table 11.

Influence of Corn-and-Soybean Rotations on Model Residuals

All of the P-GWAVA simulations assumed that corn was grown every year at every study site (table 14), despite the fact that corn is commonly grown in rotation with soybeans, especially in the Corn Belt. Therefore, it was anticipated that the extent of agreement between the solute concentrations (or DEA fraction) simulated in the vadose zone by the P-GWAVA-RZ model and those measured in groundwater may have been influenced by the percentage of corn-and-soybean area in corn cultivation. Significant correlations were observed between the average annual percentage of corn-and-soybean area on which corn was grown each year, relative to soybeans, between 1995 and 2005 (computed using equation 50) and the P-GWAVA-RZ model residuals for the concentrations of atrazine, DEA and nitrate at the Phase 2 sites where the DTW was greater than the 3-m assessment depth (fig. 61; table 12). No significant correlation was observed, however, with the model residuals for the DEA fraction. Among the three solutes, the strongest relation was a positive correlation between the percentage of corn-and-soybean area in corn cultivation and the model residuals for atrazine concentrations, with weaker, negative correlations noted for DEA and nitrate.

Because atrazine is not typically applied to soybeans, the total amounts of the herbicide applied to the land are expected to be higher in areas where corn is grown more frequently, relative to soybeans. Although the rates of atrazine transformation by soil microorganisms might be expected to be higher in areas with more frequent applications of the herbicide because of microbial adaptation (Zablotowicz and others, 2007; Krutz and others, 2008, 2010a, 2010b), this phenomenon was not accounted for in estimating the atrazine reaction rates for the P-GWAVA simulations. The results shown in table 12 and figure 61A indicate that significantly higher degrees of overprediction of the atrazine concentrations occurred in areas with more extensive corn cultivation. This suggests that the atrazine concentrations in the groundwater in the Phase 2 study area were more strongly influenced by the adaptation of the soil microorganisms to repeated atrazine applications than by the total amounts of the herbicide that were applied during the simulation period. The significant, negative correlation between the model residuals for the DEA concentrations and the percentage of corn-and-soybean area under corn cultivation, however, would be consistent with either an increase in atrazine inputs or an increase in atrazine biotransformation rates in response to repeated applications of the herbicide, because both phenomena would be expected to cause increases in DEA production.

Table 12. Correlations between P-GWAVA-RZ model residuals for atrazine concentrations, deethylatrazine (DEA) concentrations, DEA fractions, and nitrate concentrations, 1992–2006, and average annual percentages of corn-and-soybean area in corn cultivation in the surrounding county during 1995–2005 for all Phase 2 sites where the depth to water was greater than the 3-meter assessment depth in the 10 northernmost states of the Corn Belt.

[The average annual percentage of nearby corn-and-soybean area in corn cultivation was estimated using equation 50. **R²**: Pearson correlation coefficient. **P (R²)**: Probability associated with the Pearson correlation coefficient. **Spearman ρ**: Values that were statistically significant (P < 0.05) and their associated probabilities (P (ρ)) are displayed in **boldface**. **P (ρ)**: The probability associated with the Pearson correlation coefficient (R²) for the correlation between the ranks of the simulated and measured values]

Response variable	Correlations between P-GWAVA-RZ model residuals and average annual percentage of nearby corn-and-soybean area in corn cultivation				Number of sites
	R ²	P (R ²)	Spearman ρ	P (ρ)	
Atrazine concentration	0.25	≤0.0001	0.30	≤0.0001	234
DEA concentration	0.055	0.0003	-0.29	≤0.0001	234
DEA fraction	0.036	0.12	-0.16	0.19	67
Nitrate concentration	0.023	0.019	-0.23	0.0004	234

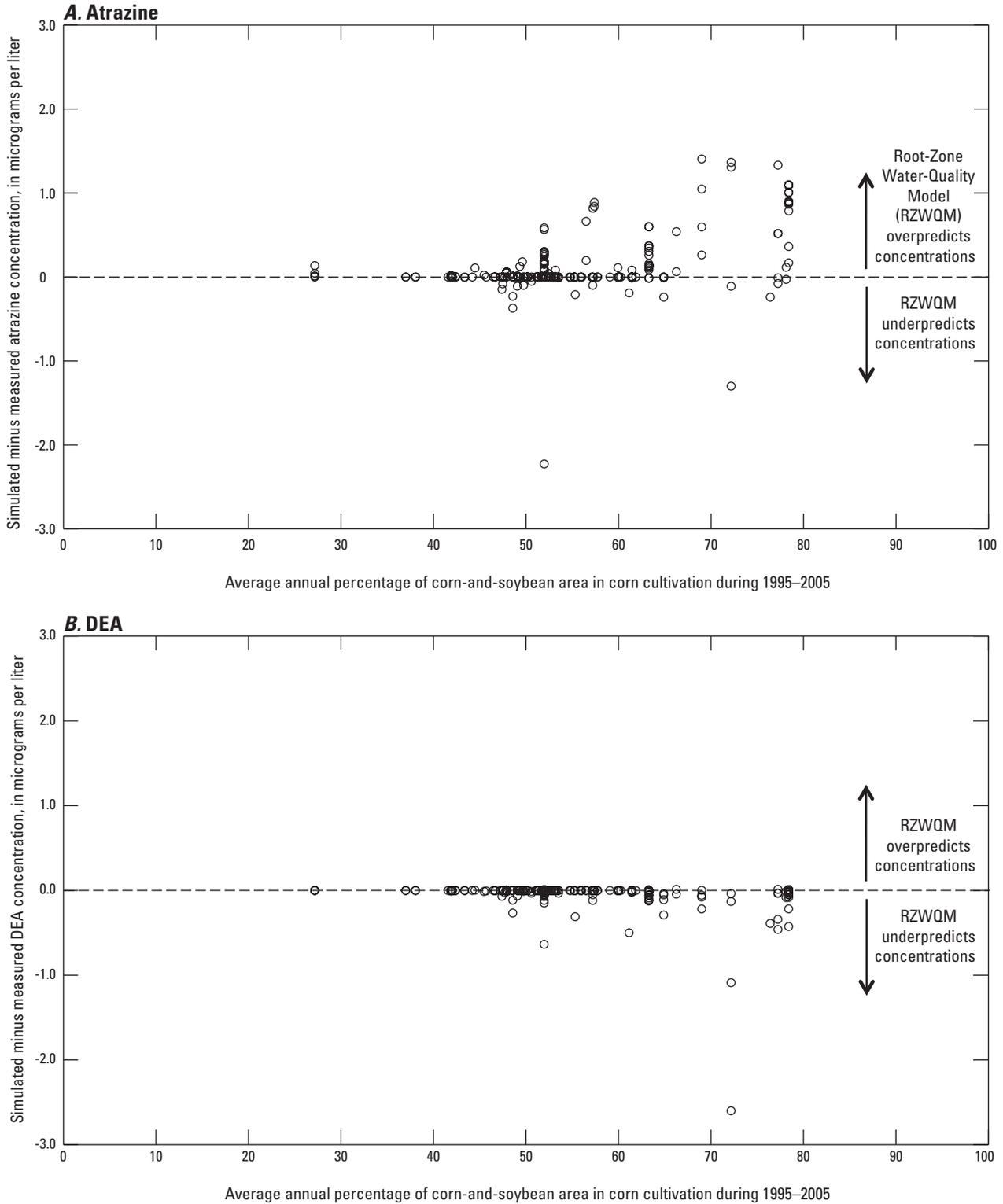


Figure 61. P-GWAVA-RZ model residuals (simulated values minus measured values) for (A) atrazine concentrations, (B) deethylatrazine (DEA) concentrations, (C) DEA fractions, and (D) nitrate concentrations, 1992–2006, and average annual percentage of corn-and-soybean area in corn cultivation in the surrounding county during 1995–2005 (calculated using equation 50), for all Phase 2 sites where the depth to water was greater than the 3-meter assessment depth in the 10 northernmost states of the Corn Belt.

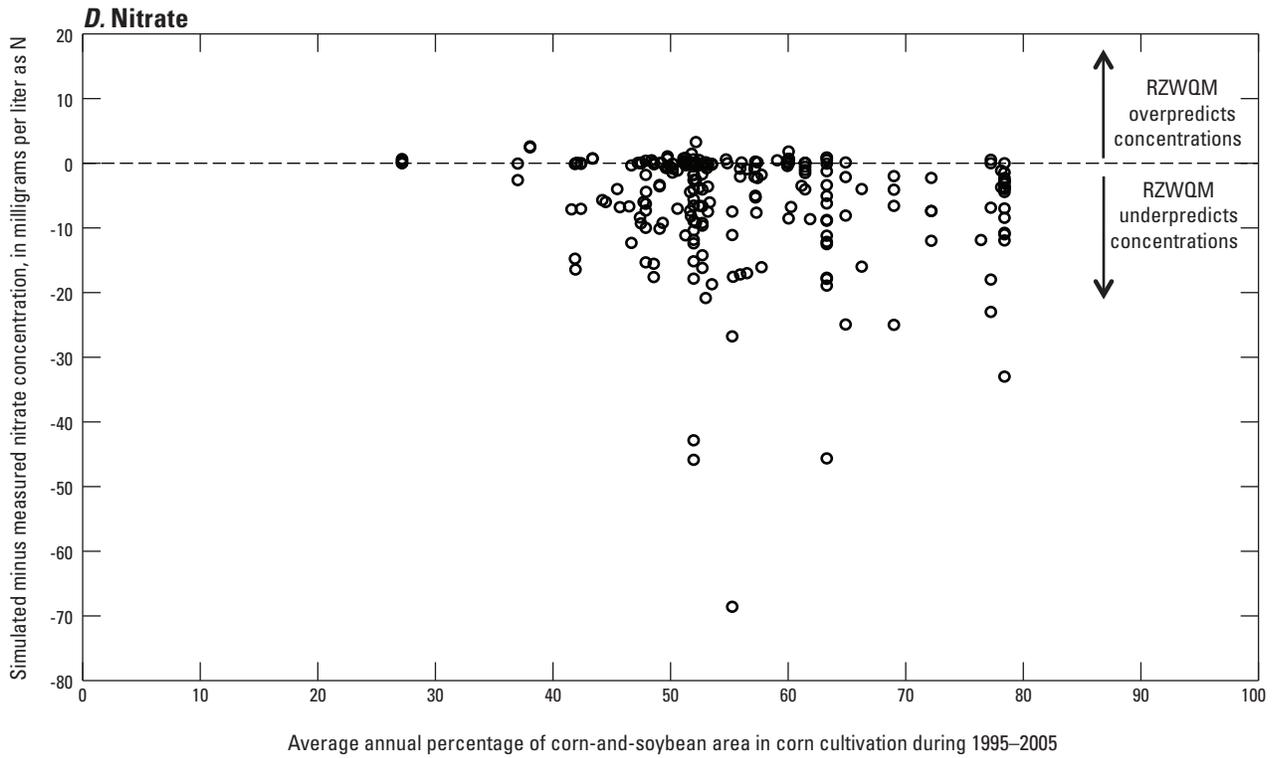
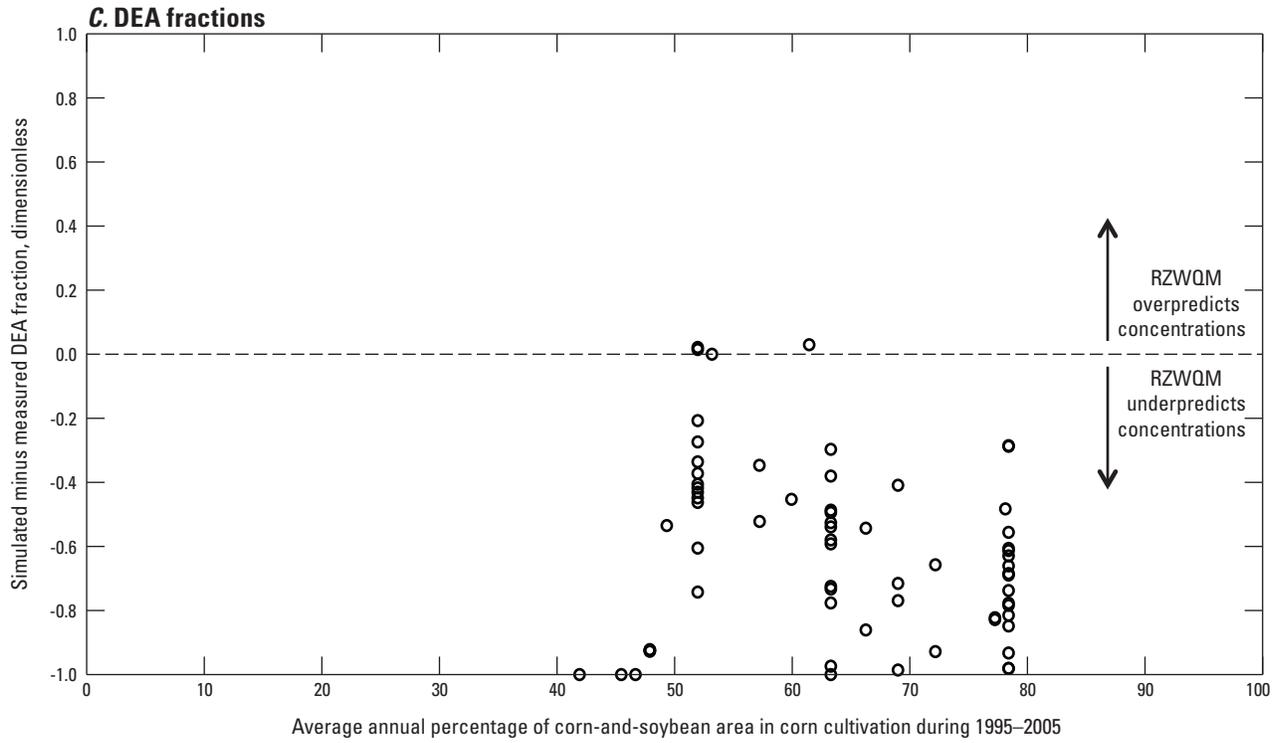


Figure 61.—Continued

In locations where oxic conditions predominate within the vadose zone (as is commonly the case in the permeable soils that are preferred for corn cultivation), most of the nitrate applied to the land, fixed by plants, or formed from the oxidation of more reduced forms of applied nitrogen (fig. 21) and not taken up by plants is likely to pass through to the water table with relatively little additional transformation. The annual amounts of nitrogen fertilizer applied to soybeans in the United States are between 11 and 24 percent of the amounts applied to corn (Economic Research Service, 2011). The significant, negative correlation between the model residuals for the nitrate concentrations and the amount of nearby corn-and-soybean area in corn cultivation (table 12; fig. 61D) indicates that, as anticipated, nitrate behaves conservatively in most of the areas examined in the Corn Belt, with higher amounts reaching the water table in areas where more nitrogen is applied. Although nitrogen fixation by the soybean plants represents another potential source of nitrate in areas where soybeans are grown (in addition to fertilizer applications), this negative correlation also indicates that the amounts of nitrate passing below the root zone under soybean cultivation are still substantially lower than the amounts of nitrate passing below the root zone under continuous corn cultivation. The observation of a significant correlation for nitrate that was opposite to that for atrazine provides further support for the hypothesis that microbial adaptation to repeated atrazine applications exerted a stronger effect on the amounts of atrazine reaching the water table than the total quantities of the herbicide being applied to the land.

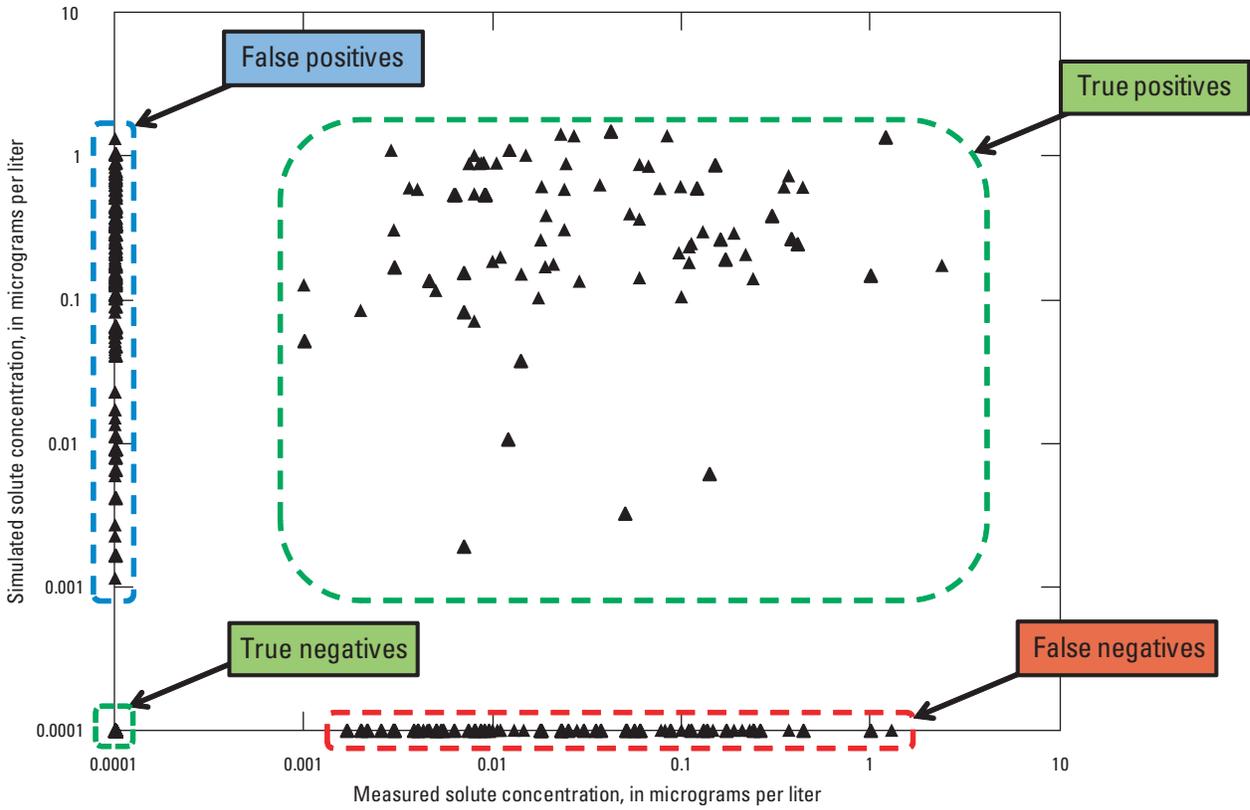
Solute Detection Classifications

The graphical comparisons between the simulated and measured solute concentrations (or DEA fraction) displayed in figures 36, 48, 55, and 59 may be reformulated to convey the accuracy of the final sets of P-GWAVA model predictions in more a generalized, categorical manner by calculating the frequencies with which actual detections or non-detections of a given solute coincided with simulated detections or non-detections of that solute. The concentration relations represented by the four resulting categories of classification are shown in figure 62. *False positives* occur at sites where the detection of the solute was simulated by the model in the vadose zone but the compound was not detected in shallow groundwater; *false negatives* represent the opposite circumstance. *True positives* indicate that the detection of the

solute was both simulated and measured, and *true negatives* indicate that a non-detection was accurately simulated.

For each solute examined, the distributions of true positives, true negatives, false positives, and false negatives resulting from the P-GWAVA simulations are shown in figure 63 for all of the Phase 1 and Phase 2 sites, regardless of water-table depth. To provide a more direct comparison between the predictions of the P-GWAVA-PR and P-GWAVA-RZ models, a separate set of results is also displayed for the 267 sites in the Corn Belt where both models were run—again, regardless of water-table depth (fig. 63B). The P-GWAVA-PR simulations generated more detections (positives) than non-detections (negatives) for atrazine (fig. 63A). By contrast, for the P-GWAVA-RZ simulations, non-detections of atrazine (negatives) were predicted more often than detections (positives) (fig. 63C), with the same pattern being observed for DEA (fig. 63D). The direct comparison between the atrazine results for the 267 sites in the Corn Belt where both models were run (fig. 63B) reflects patterns similar to those observed separately for the two models, with more simulated detections of atrazine than non-detections observed for the P-GWAVA-PR model, and the opposite pattern noted for the P-GWAVA-RZ model. Although figure 58 indicated that the P-GWAVA-RZ model underpredicted nitrate concentrations more often than it overpredicted them, the distribution of detection classifications shown in figure 63E for nitrate was similar to that observed for atrazine during Phase 1, with simulated detections being more common than simulated non-detections.

Figure 63 also presents more generalized summaries of the accuracy of the model predictions for each solute by grouping the true positives and true negatives together as *correct predictions* and grouping the false positives and false negatives together as *incorrect predictions*. Viewed from this perspective, correct and incorrect predictions of atrazine detections by the P-GWAVA-PR model occurred with equal frequencies (50 percent) when all sites were considered (fig. 63A), but with a higher percentage of incorrect predictions (65 percent) when the analysis was restricted to the 267 sites in the Corn Belt where simulations were carried out with both models (fig. 63B). By contrast, the P-GWAVA-RZ simulations produced correct predictions more frequently than incorrect predictions for all three solutes, with the highest rate of correct predictions for DEA (70 percent, fig. 63D), the lowest rate for nitrate (56 percent, fig. 63E), and a rate of 62 percent for atrazine (fig. 63C).



(Non-detections assigned a concentration of 0.0001 micrograms per liter)

Figure 62. Relations between solute detection classifications and different combinations of simulated and measured detections and non-detections for a hypothetical solute. For the purposes of display, simulated or measured concentrations below the reporting limit were assigned a value of 0.0001 microgram per liter.

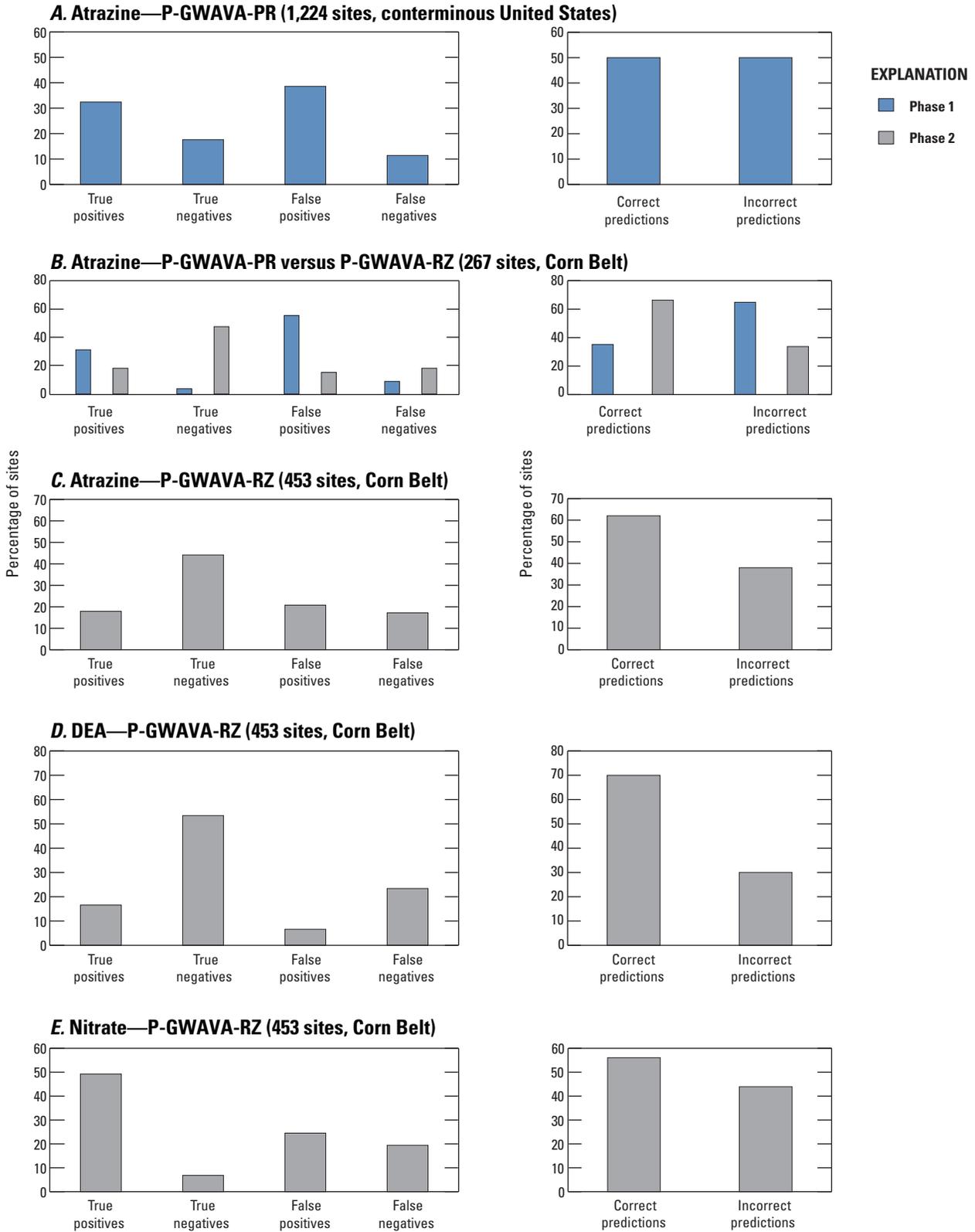


Figure 63. Accuracy of solute detection classifications from the Phase 1 (P-GWAVA-PR) simulations for the conterminous United States, 1991–95 and the Phase 2 (P-GWAVA-RZ) simulations for the 10 northernmost states in the Corn Belt, 2000–2004. Results are shown, regardless of depth to water, for (A) atrazine at sites in the conterminous United States; (B) atrazine at sites in the 10 northernmost states of the Corn Belt where simulations were done with both models; (C) atrazine at all sites in the Corn Belt where simulations were done with the P-GWAVA-RZ model; (D) deethylatrazine (DEA) at all sites in the Corn Belt where simulations were done with the P-GWAVA-RZ model; and (E) nitrate at all sites in the Corn Belt where simulations were done with the P-GWAVA-RZ model. Solute detections (both simulated and measured) determined using a fixed reporting limit of 0.001 microgram per liter for the Phase 1 results, and temporally varying reporting limits (fig. 4) for the Phase 2 results.

Overall Frequencies of Simulated and Measured Solute Detection

For each of the three solutes of interest, figures 64 and 65 compare the overall detection frequencies predicted in the vadose zone by the final sets of P-GWAVA simulations with the overall frequencies of detection in shallow groundwater among the study sites in the conterminous United States (Phase 1) or in the Corn Belt (Phase 2). Whereas the atrazine detection frequencies computed for Phase 1 (both simulated and measured) were obtained using a fixed reporting limit (0.001 µg/L), the frequencies of detection of the three solutes of interest during Phase 2 (simulated and measured) are displayed in these figures using either temporally varying reporting limits (fig. 64) or uniform reporting limits (fig. 65). In both figures, the pattern of agreement between the simulated and measured detection frequencies when all the sites were examined (fig. 64A and fig. 65A) was similar to the pattern noted when only sites with DTW greater than the model assessment depths were included in the analyses (fig. 64B and fig. 65B). The detection frequencies calculated from the P-GWAVA-RZ simulations for atrazine (39 percent) and DEA (23 percent) using the temporally varying reporting limits (fig. 64) were consistent with the results from several other large-scale sampling studies in the United States that, like the NAWQA program (Barbash and others, 1999; Kolpin and others, 2000; Gilliom and others, 2006), also observed the frequency of DEA detection to be similar to that of atrazine in shallow groundwater beneath agricultural areas (Kolpin and others, 1993; Barbash and Resek, 1996).

The reporting limit used to compute the simulated and measured detection frequencies shown in figure 65 for each solute examined during Phase 2 was the highest value used for each compound (fig. 4). As a result, all the detection frequencies computed using these reporting limits were less than the corresponding values obtained with temporally variable reporting limits (fig. 64). The most pronounced illustration of this effect was for DEA, for which the simulated frequency of detection using the fixed reporting limit was zero, even when all Phase 2 sites were included in the calculation. Using the temporally varying reporting limits, the overall frequencies of DEA detection simulated by the P-GWAVA-RZ model were 23 percent when all sites were examined, and 30 percent when the sites with DTW less than or equal to 3 m were excluded. For nitrate, however, the simulated and measured overall frequencies of detection were in close agreement when the fixed reporting limit was used (fig. 65), as well as when the temporally varied reporting limits were used (fig. 64). The fact that the level of agreement between simulated and measured detection frequencies was substantially less affected by the approach

used for quantifying detections for nitrate than for atrazine or DEA is likely because the simulated and measured nitrate concentrations were generally much larger, relative to their reporting limit, than for atrazine or DEA. This is consistent with the general observation that detections of environmental contaminants tend to be considerably more intermittent when their concentrations are close to their reporting limits than at higher concentrations (Barbash and Resek, 1996). Temporally varying reporting limits were used to determine solute detections for Phase 2 (figs. 49, 54, 60 and 64) because this approach retains more information than does the use of uniform reporting limits.

When calculated using the temporally varying reporting limits (fig. 64), the overall frequencies of atrazine detection predicted by the P-GWAVA-RZ simulations were in closer agreement with those measured in shallow groundwater than were the concentrations predicted by the P-GWAVA-PR simulations. Although the substantially larger geographic area covered during Phase 1 may have contributed to this disparity, other factors may have been involved. The results presented in figures 50 and 63 indicate that even when the predictions from the two models were compared directly with one another in the same locations, the atrazine concentrations predicted by the P-GWAVA-RZ simulations were still in closer agreement with those measured in groundwater than were the concentrations predicted by the P-GWAVA-PR simulations.

Among the three solutes examined during Phase 2, the overall frequencies of detection simulated by the P-GWAVA-RZ model for the entire study area were in substantially closer agreement with those measured in shallow groundwater for nitrate and atrazine than for DEA (fig. 64). The fact that the simulations overpredicted the overall detection frequency for atrazine, but underpredicted the overall frequency for DEA, was consistent with the patterns of agreement for the concentrations of the two solutes (figs. 47 and 53, respectively). The close agreement displayed in figure 64 between the simulated and measured overall frequencies of detection for nitrate in the Phase 2 study area, however, is in marked contrast with the lack of any significant correlations between the simulated and measured concentrations (fig. 58, table 10) or network-based detection frequencies (fig. 60, table 11) for this solute. Applied in the manner used for this study, the P-GWAVA-RZ model thus provided a relatively accurate simulation of the presence or absence of nitrate in shallow groundwater, but only at the coarsest scale examined, that is, the entire study area. Significant correlations between simulated and measured concentrations (table 10) or detection frequencies (table 11) in groundwater at finer spatial scales during Phase 2 were observed only for atrazine and DEA.

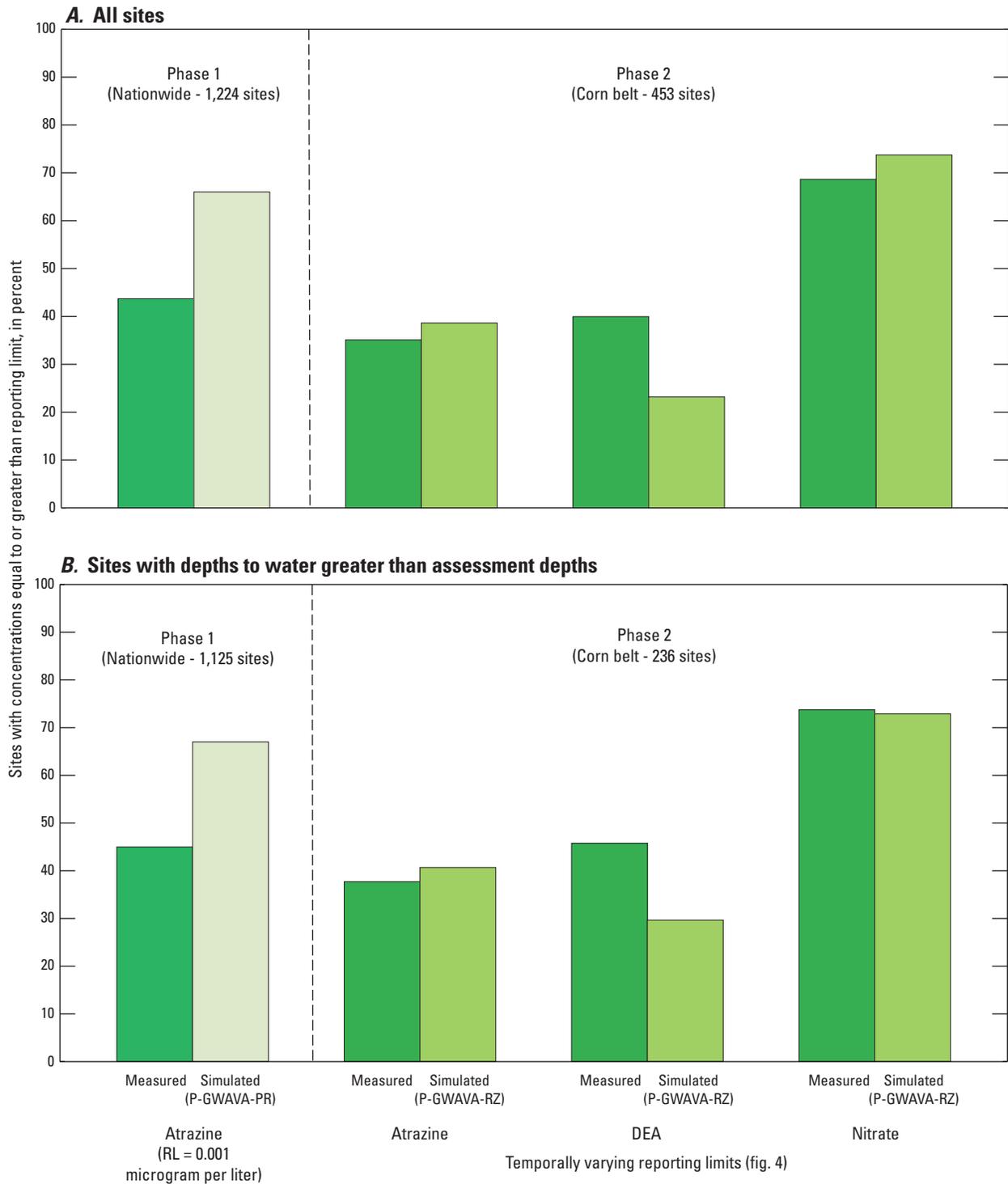


Figure 64. Overall frequencies of atrazine, deethylatrazine (DEA), and nitrate detection predicted in the vadose zone by the final set of P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) simulations and measured in shallow groundwater in agricultural areas of the conterminous United States (Phase 1, 1992–1998) or the 10 northernmost states of the Corn Belt (Phase 2, 1992–2006), using a fixed reporting limit for the Phase 1 results and temporally varying reporting limits for the Phase 2 results. Results are shown for (A) all sites and (B) sites where the depth to water was greater than the assessment depth for each model. Detections (simulated and measured) were determined using a fixed reporting limit (RL) of 0.001 microgram per liter for the Phase 1 results, and temporally varying reporting limits (fig. 4) for the Phase 2 results. Assessment depths were 1 meter for the P-GWAVA-PR simulations and 3 meters for the P-GWAVA-RZ simulations. Simulation approaches used for each of the two models are summarized in tables 1, 4, and 14.

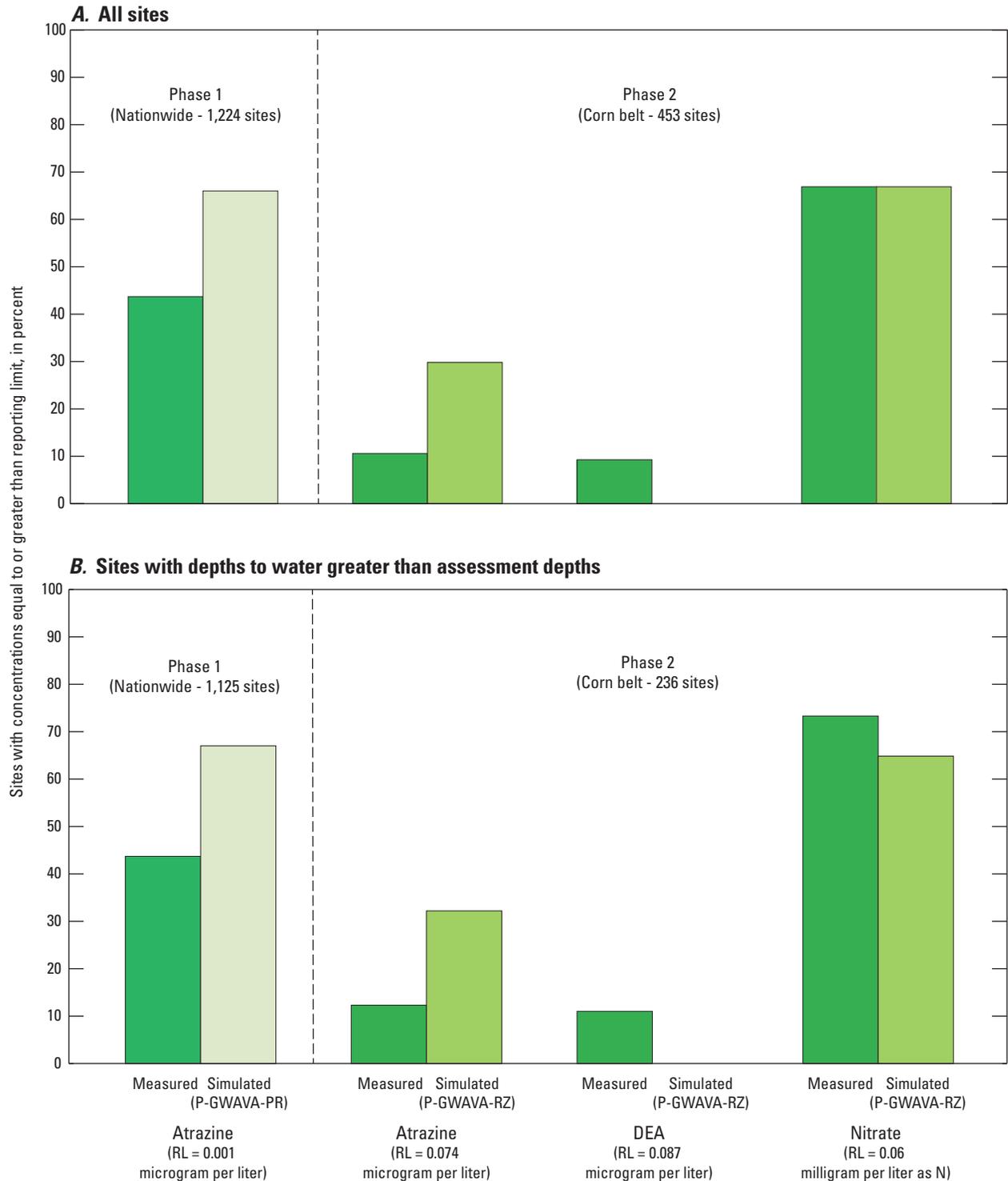


Figure 65. Overall frequencies of atrazine, deethylatrazine (DEA), and nitrate detection predicted in the vadose zone by the final set of P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) simulations and measured in shallow groundwater in agricultural areas of the conterminous United States (Phase 1, 1992–1998) or the 10 northernmost states of the Corn Belt (Phase 2, 1992–2006), using fixed reporting limits for the results from both phases. Results are shown for (A) all sites and (B) sites where the depth to water was greater than the assessment depth for each model. Detections (simulated and measured) were determined using fixed reporting limits (RLs) in all cases. Assessment depths were 1 meter for the P-GWAVA-PR simulations and 3 meters for the P-GWAVA-RZ simulations. Simulation approaches used for each of the two models are summarized in tables 1, 4, and 14.

Geographic Patterns of Agreement Between Simulated and Measured Frequencies of Detection

The geographic distributions of P-GWAVA-RZ model residuals (simulated minus measured values) for the frequencies of detection of atrazine, DEA, and nitrate for the 17 sampling networks with 10 or more wells in the Phase 2

study area are shown in figures 66, 67, and 68, respectively. To maximize the geographic coverage of the data, and to examine the accuracy of the model predictions when information on water-table depth is not available (as is likely to be the case in most study locations), the results shown in these figures included the data from all Phase 2 sites, regardless of DTW. All detections, predicted and observed, were determined using the temporally varying reporting limits (fig. 4).

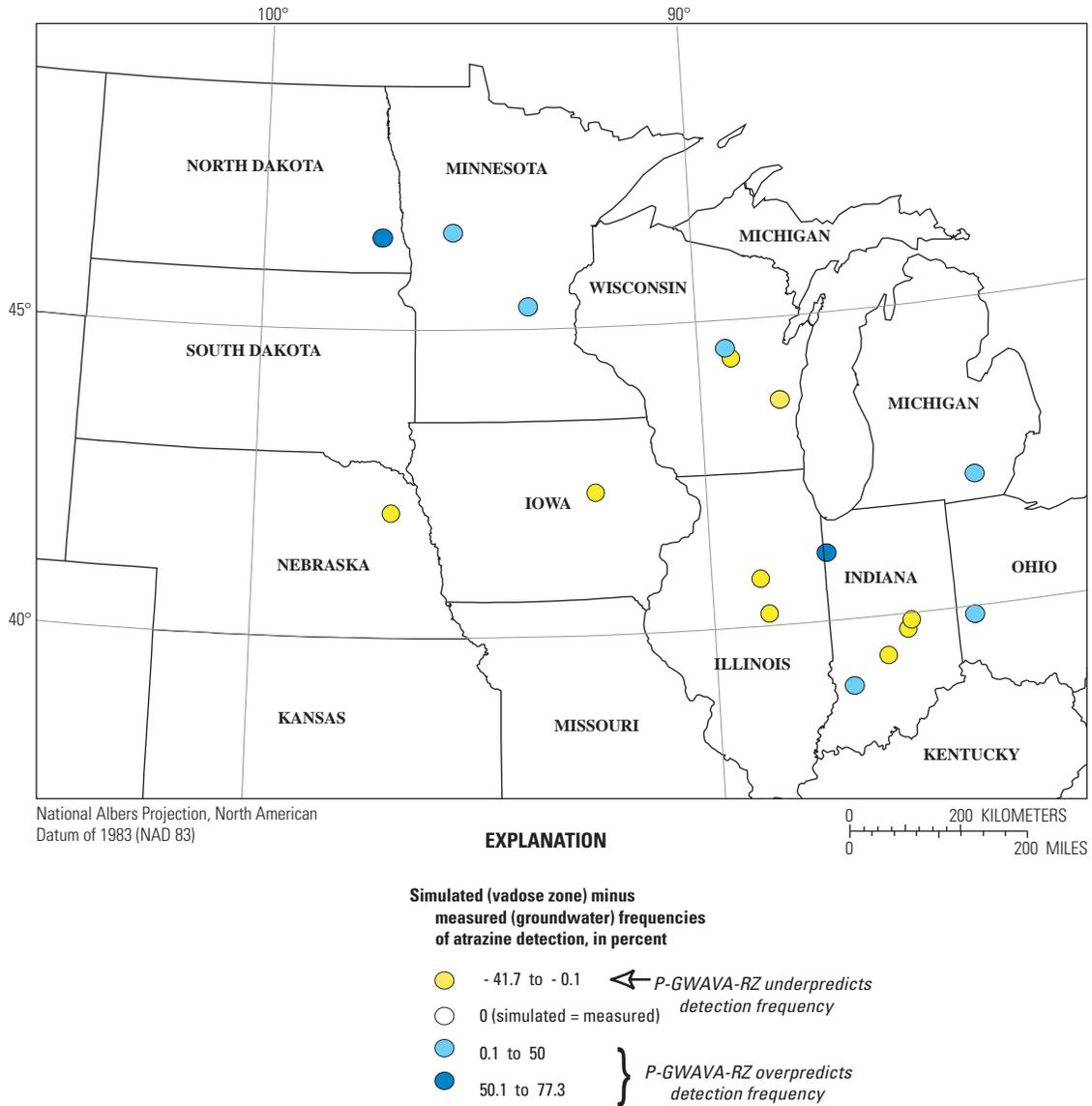


Figure 66. Model residuals for the frequencies of atrazine detection (simulated minus measured values) calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006. All sites were included regardless of water-table depth. All simulated detections accounted for temporal variations in reporting limits (fig. 4A).

Atrazine (fig. 66) and DEA (fig. 67) detection frequencies exhibited similar geographic patterns of over- and underprediction across the Phase 2 study area, with most of the underpredicted frequencies of detection of either solute occurring in the southern part of the study area and central Wisconsin. The similarity in the spatial distributions of occurrence for atrazine and DEA is consistent with the

fact that they share a common source. For nitrate, the most pronounced underpredictions of detection frequencies also were in central Wisconsin, with other areas of underprediction scattered across the southern part of the study area (fig. 68). For all three solutes, detection frequencies were overpredicted in North Dakota and Minnesota, and underpredicted in Nebraska and Illinois.

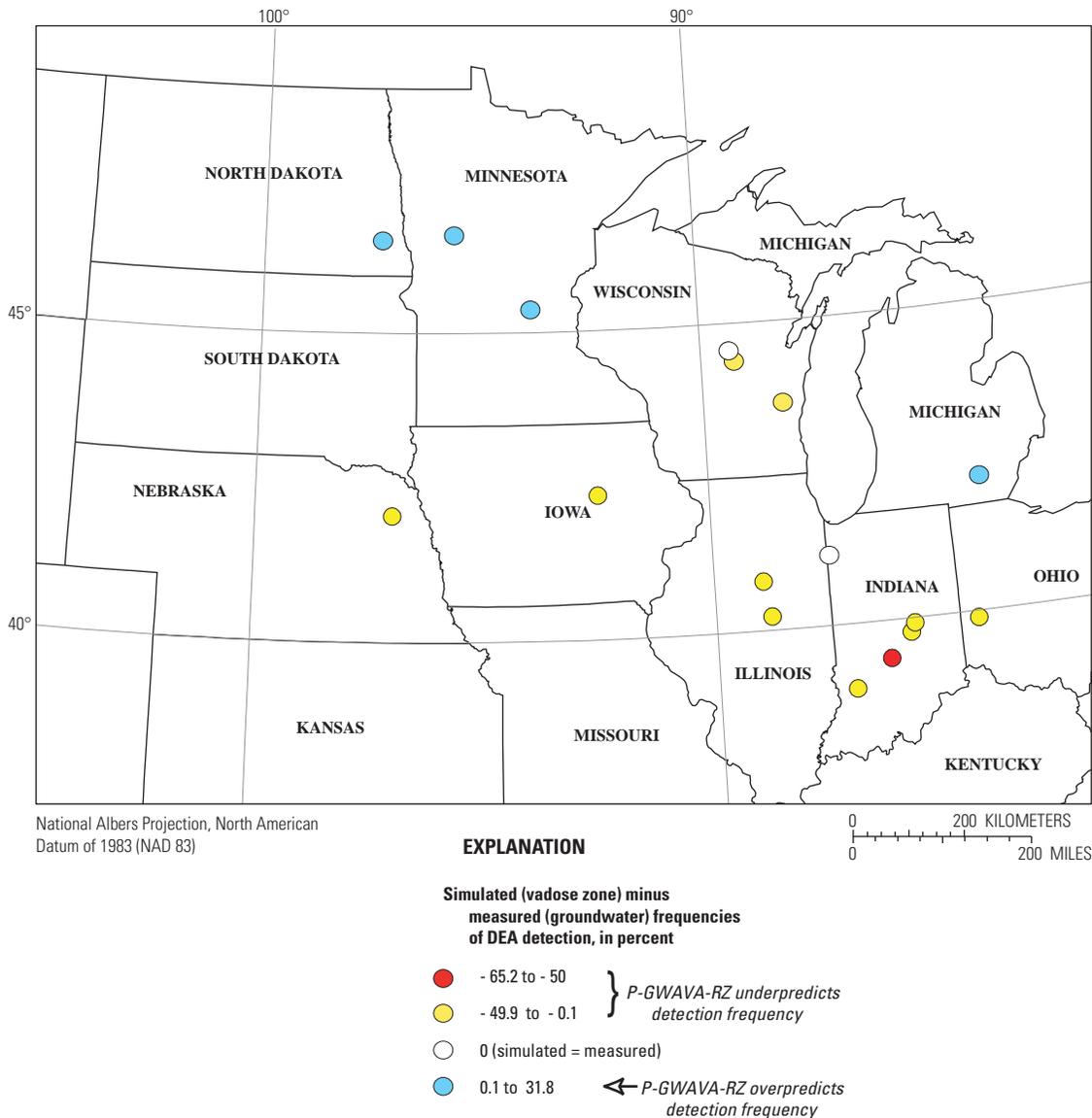


Figure 67. Model residuals for the frequencies of deethylatrazine (DEA) detection (simulated minus measured values) calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006. All sites were included regardless of water-table depth. All simulated detections accounted for temporal variations in reporting limits (fig. 4B).

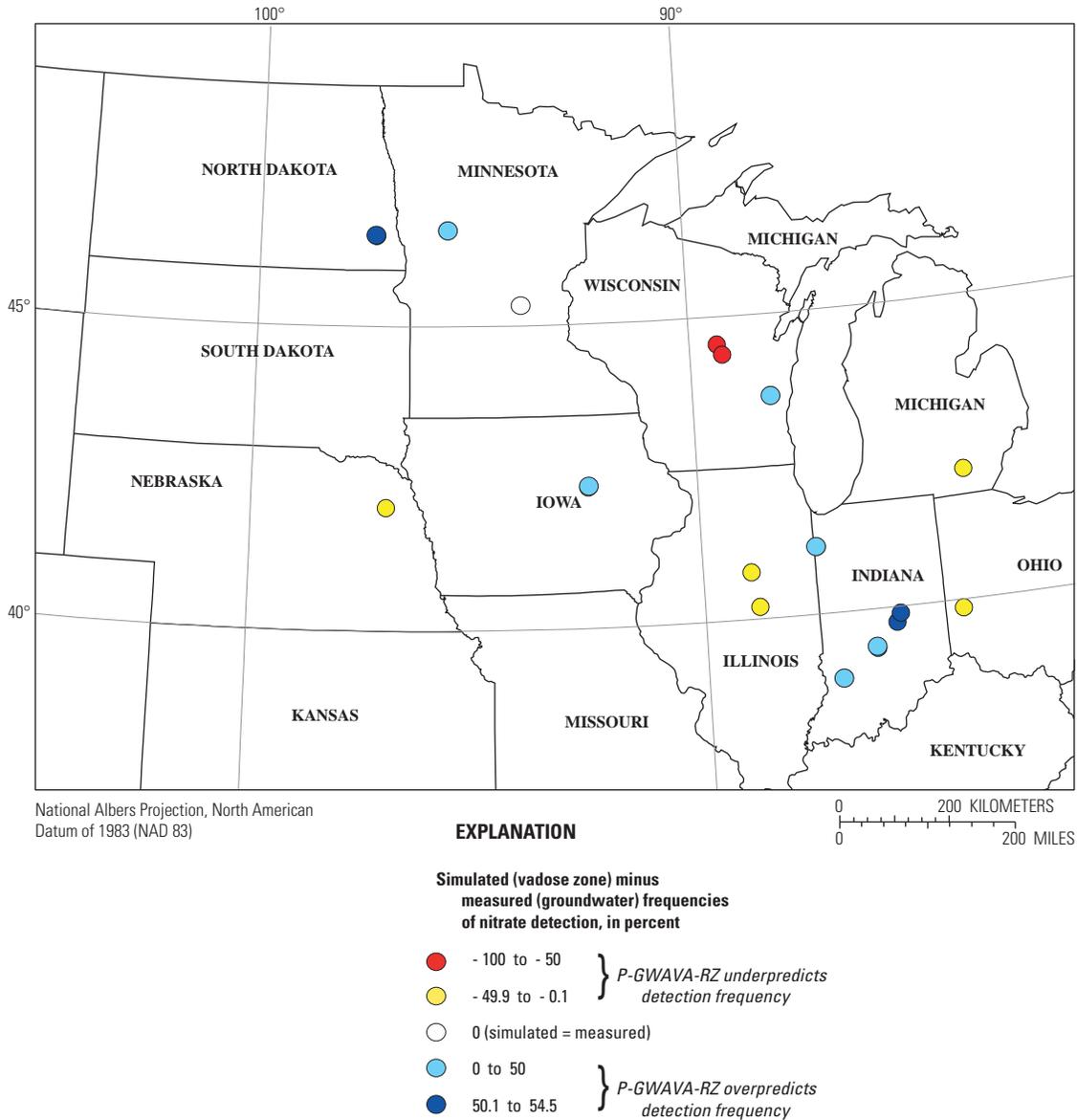


Figure 68. Model residuals for the frequencies of nitrate detection (simulated minus measured values) calculated from the P-GWAVA-RZ (Phase 2) model simulations and sampling results for the 17 groundwater sampling networks with 10 or more sites in the 10 northernmost states of the Corn Belt of the United States, 1992–2006. All sites were included regardless of water-table depth. All simulated detections accounted for temporal variations in reporting limits (fig. 4C).

Statistical Correlations with Site Characteristics

To identify factors that may have contributed to the disparities between the simulated and the measured detection frequencies for atrazine, DEA, and nitrate during Phase 2, a series of statistical comparisons was made between the P-GWAVA-RZ model residuals for the solute detection frequencies and network-averaged values of a variety of explanatory parameters (table 13). This analysis was similar to the one conducted for Phase 1 (table 8), but used different sources of data for the explanatory variables. Most of the comparisons involving soil-related parameters used depth- and component-weighted averages (fig. 7) computed for two depth intervals: the entire 3-m assessment depth and the uppermost 50 cm. However, for all of the parameters examined in this manner, the statistically significant relations observed using the data computed for the uppermost 50 cm of the soil column always exhibited higher Pearson R^2 values than those observed when data for all 3 m were used (data not shown). This is consistent with the expectation that processes and site characteristics close to the land surface tend to exert a predominant level of control over the transport and fate of surface-derived solutes in the vadose zone. Consequently, for the comparisons involving these variables, this analysis focused only on the results obtained using the parameter values computed for the uppermost 50 cm of the soil column.

The results shown in table 13 reveal statistically significant relations with several of the explanatory variables for atrazine and DEA ($P < 0.05$; Pearson and Spearman [rank] correlations), but none for nitrate. Consistent with the similarity between the geographic distributions of their model residuals (figs. 66 and 67), the patterns of correlation for atrazine and DEA were also similar. However, when significant correlations with the same explanatory parameter were noted for both solutes, the strength of the relation was usually greater for atrazine than for DEA. The two exceptions to this pattern were the correlations with the areally averaged intensities of atrazine use and the percentage of sites receiving annual precipitation of less than 60 cm (“dry sites”).

Model residuals computed for the frequencies of atrazine detection from the P-GWAVA-RZ simulations were not significantly correlated with the intensity of atrazine use (table 13). As with the results from the P-GWAVA-PR simulations (table 8), this observation indicates that the intensity of atrazine use was less important than other site factors in controlling the concentrations (and thus the frequencies of detection) of atrazine in the subsurface. However, the significant, negative correlation between the model residuals for the frequencies of DEA detection and atrazine use intensity (as well as the negative, albeit non-significant Spearman ρ value for atrazine) may have been caused by the use of the spatially uniform intensity of atrazine application for the Phase 2 simulations. All other

factors remaining constant, if the simulations at all of the sites assumed a spatially uniform intensity of use, areas where the intensity of atrazine use was, in fact, higher than in other locations might have higher frequencies of detection of DEA and atrazine in groundwater, resulting in smaller model residuals for both compounds. However, because the atrazine use intensity was not correlated with the model residuals for atrazine detection frequencies during either study phase, and only weakly correlated with those for DEA during Phase 2, the spatial patterns of atrazine use appeared to have been largely accounted for by the model simulations.

The statistical results summarized in table 13 indicate that factors controlling the rates of water movement through the subsurface tended to exert a greater influence over the extent to which the model overpredicted the observed frequencies of atrazine or DEA detection in shallow groundwater than factors related to climate. For both atrazine and DEA, the degree of overprediction was negatively correlated with available water capacity (AWC), clay content, and silt content, and positively correlated with sand content (expressed either as the weight percent of sand present, or as the percentage of sites containing more than 95 percent sand in one or more layers) and vertical permeability. Thus, whereas the P-GWAVA-PR simulations underpredicted the effects of hydraulic conductivity on atrazine movement through the soil (table 8), the P-GWAVA-RZ simulations tended to exaggerate the effects of soil properties (AWC, texture, and permeability) on the rates of water flow. No significant correlations with either bulk density or soil OM were noted for atrazine or DEA, which may reflect the less direct connection between these soil properties and hydraulic conductivity, relative to the other soil parameters examined.

No significant correlation was noted between the percentage of sites receiving 60 cm or less of precipitation per year and the model residuals for atrazine detection frequencies, and only a moderate positive correlation was noted between these variables for DEA (table 13). Additionally, no significant correlations were observed between the average air temperature in May and the model residuals for either the atrazine or DEA detection frequencies. As with the results for the parameters related to soil permeability, these Phase 2 results for atrazine contrast with the pattern of correlation observed for the P-GWAVA-PR simulations (table 8). The P-GWAVA-RZ simulations appear to have accounted for the effects of spatial variations in precipitation and temperature on the likelihood of detecting atrazine in shallow groundwater more accurately than did the P-GWAVA-PR simulations. The contrast in the relations with temperature for the two study phases is consistent with the hypothesis that the activation energy used to estimate atrazine transformation rates for Phase 1 was too low, and that the higher value used for Phase 2 (table 14) may have been more appropriate.

Table 13. Correlations between model residuals for the detection frequencies of atrazine, deethylatrazine, and nitrate in shallow groundwater simulated by the P-GWAVA-RZ (Phase 2) model and selected site characteristics in the 10 northernmost states of the Corn Belt, 1992–2006.

[Geographic locations of the groundwater networks are shown in figures 66–68. Data were computed for all sites in groundwater networks with 10 or more wells for which the required ancillary data were available, regardless of water-table depth. The P-GWAVA-RZ simulations used irrigation and a spatially uniform intensity of atrazine application (2 kg a.i./ha) at all sites (table 4). Detections—either simulated or measured—were determined using reporting limits that varied over time for atrazine, deethylatrazine (DEA), and nitrate (fig. 4). Areally averaged atrazine use intensities were computed using equation 10. All data related to soil properties were derived from the SSURGO database (Natural Resources Conservation Service, 2011a); precipitation and air temperature data were obtained from Cligen (Agricultural Research Service, 2009). Results from statistically significant correlations ($P < 0.05$) are shown in **boldface**. R^2 : Pearson correlation coefficient. $P (R^2)$: Probability associated with the Pearson correlation coefficient. **Spearman ρ** : Values that were statistically significant ($P < 0.05$) and their associated probabilities ($P (p)$) are displayed in **boldface**. $P (p)$: The probability associated with the Pearson correlation coefficient (R^2) for the correlation between the ranks of the simulated and measured values. **Number of networks/sites**: Some of the ancillary data were not available for some sites. **Abbreviations**: cm, centimeter; °C, degrees Celsius; dwcw, computed to the specified depth for each site as a depth- and component-weighted average value for the SSURGO map unit in which it was located (fig. 7) and obtained as a network-averaged value among all of the sites for which the ancillary data were available in each network; g/cm³, gram per cubic centimeter; in/hr, inch per hour; kg a.i./ha, kilograms of active ingredient per hectare]

Solute	Site feature	Correlations between model residuals and site feature				Number of networks	Number of sites
		R^2	$P (R^2)$	Spearman ρ	$P (p)$		
Atrazine	Atrazine use intensity, 1997, areally averaged (kg a.i./ha)	0.098	0.22	-0.44	0.078	17	402
	Available water capacity—uppermost 50 cm (dwcw), volume percent	0.52	0.0037	-0.69	0.0070	14	321
	Bulk density—uppermost 50 cm (dwcw), g/cm ³	0	0.95	0.040	0.84	14	321
	Soil organic matter content—uppermost 50 cm (dwcw), weight percent	0	0.95	0.19	0.53	14	321
	Clay content—uppermost 50 cm (dwcw), weight percent	0.41	0.014	-0.58	0.029	14	321
	Silt content—uppermost 50 cm (dwcw), weight percent	0.55	0.0023	-0.78	0.0010	14	321
	Sand content—uppermost 50 cm (dwcw), weight percent	0.53	0.0032	0.67	0.0094	14	321
	Sandy sites ¹ (percent)	0.35	0.012	0.58	0.015	17	406
	Dry sites ² (percent)	0.20	0.076	0.48	0.053	17	406
	Vertical permeability—uppermost 50 cm (dwcw), in/hr	0.51	0.0041	0.61	0.020	14	321
Average air temperature in May (T_{May}), °C	0.071	0.36	-0.32	0.26	14	314	
DEA	Atrazine use intensity, 1997, areally averaged (kg a.i./ha)	0.26	0.039	-0.48	0.051	17	402
	Available water capacity—uppermost 50 cm (dwcw), volume percent	0.42	0.013	-0.68	0.0090	14	321
	Bulk density—uppermost 50 cm (dwcw), g/cm ³	0.008	0.76	0.21	0.47	14	321
	Soil organic matter content—uppermost 50 cm (dwcw), weight percent	0.009	0.75	0.022	0.97	14	321
	Clay content—uppermost 50 cm (dwcw), weight percent	0.28	0.050	-0.55	0.041	14	321
	Silt content—uppermost 50 cm (dwcw), weight percent	0.41	0.014	-0.64	0.019	14	321
	Sand content—uppermost 50 cm (dwcw), weight percent	0.38	0.018	0.60	0.027	14	321
	Sandy sites ¹ (percent)	0.34	0.015	0.50	0.041	17	406
	Dry sites ² (percent)	0.28	0.030	0.56	0.020	17	406
	Vertical permeability—uppermost 50 cm (dwcw), in/hr	0.39	0.018	0.43	0.12	14	321
Average air temperature in May (T_{May}), °C	0.24	0.075	-0.47	0.088	14	314	
Nitrate	Available water capacity—uppermost 50 cm (dwcw), volume percent	0.002	0.88	-0.16	0.56	14	321
	Bulk density—uppermost 50 cm (dwcw), g/cm ³	0.06	0.40	-0.19	0.51	14	321
	Soil organic matter content—uppermost 50 cm (dwcw), weight percent	0	0.99	-0.13	0.71	14	321
	Clay content—uppermost 50 cm (dwcw), weight percent	0.005	0.81	-0.32	0.25	14	321
	Silt content—uppermost 50 cm (dwcw), weight percent	0.008	0.77	-0.13	0.60	14	321
	Sand content—uppermost 50 cm (dwcw), weight percent	0.007	0.78	0.19	0.48	14	321
	Sandy sites ¹ (percent)	0.017	0.62	0.11	0.67	17	406
	Dry sites ² (percent)	0.056	0.36	0.32	0.21	17	406
	Vertical permeability—uppermost 50 cm (dwcw), in/hr	0.017	0.66	0.22	0.43	14	321
	Average air temperature in May (T_{May}), °C	0.009	0.75	0.11	0.71	14	314

¹Percentage of sites in each network with at least one horizon containing more than 95 percent sand.²Percentage of sites in each network receiving less than 60 centimeters of precipitation per year.

Suggestions for Future Work

Because the RZWQM model is sufficiently comprehensive and flexible to simulate most of the physical, hydrologic, chemical, and biological processes and agricultural management practices known to affect the transport and fate of water and solutes in the subsurface (especially preferential transport), future work with the P-GWAVA system will focus on P-GWAVA-RZ, rather than P-GWAVA-PR. The findings from this investigation, however, have revealed several ways that future efforts might improve and expand on the current version of P-GWAVA-RZ. These include the following:

1. Using simulated weather data from the Cligen station closest to each site, even if the station is in an adjacent Cligen grid cell;
2. Using measured, rather than simulated historical data for all weather parameters (if available on a nationwide basis), especially those related to the intensities and timing of storms;
3. Incorporating nationally available data on management practices and cropping patterns, to account for the influence of geographic variations in tillage (Baker, 2011), irrigation (National Agricultural Statistics Service, 2010a), artificial drainage (Jaynes and James, 2007), crop rotations (Kipka and others, 2013) and other agricultural activities on the transport and fate of water and agrichemicals in the subsurface;
4. Automating the procedure for adjusting the RZWQM grid-cell thicknesses to align their boundaries with the boundaries between the soil horizons specified by the SSURGO data;
5. Modifying RZWQM to simulate agrichemical transport and fate under inundated agriculture, especially for growing rice;
6. Calibrating the crop simulation parameters in RZWQM using county-scale crop yields across the United States (National Agricultural Statistics Service, 2011a);
7. Explicitly accounting for the applications of both manure and fertilizer as potential sources of nitrogen in agricultural areas across the Nation;
8. Using a degree-day approach (Jackson, 2003) to account for the effects of diurnal temperature variations on solute transformation rates, water-air partitioning and other temperature-sensitive processes;
9. Incorporating an option in RZWQM for simulating water and solute movement through water films along macropore walls (Nimmo, 2012), rather than requiring that macropores be filled before movement can occur;
10. Activating the non-linear sorption module in RZWQM (Ahuja and others, 2000);
11. Modifying the Rosetta database (Schaap and others, 2001) to provide Brooks-Corey parameter values that are consistent with their known ranges for all soil textures;
12. Developing a series of compound-specific variants of the modified Fenner-Borsuk relation to predict the reaction rates of other contaminants and transformation products from soil properties and other site-specific parameters, using data from previous laboratory studies;
13. Using P-GWAVA-RZ to simulate the transport and fate of water and solutes to the water table—as demonstrated with RZWQM2 on a local scale by Nolan and others (2010)—throughout the conterminous United States using nationwide depth-to-water estimates such as those provided by Fan and others (2007, 2013); and
14. Developing a module for estimating the values of selected input parameters, subject to the constraints imposed by the range of values in the published literature, using inverse modeling and other techniques used by Nolan and others (2010).

Future applications of the P-GWAVA-RZ model might include the development of metamodels to generate large-scale maps of simulated concentrations of selected compounds with the methods used by Nolan and others (2012) for nitrate in the Corn Belt. Other work might involve manipulation of the appropriate P-GWAVA-RZ input parameters to simulate the concentrations of surface-derived contaminants in the vadose zone beneath non-agricultural land-use settings across the United States, including lawns, gardens, golf courses, roads, railroads, utility rights-of-way, septic-system drainfields, herbicide-treated forestlands, and areas irrigated with chlorinated water.

Summary and Conclusions

Numerous studies over the past three decades have used a variety of approaches to predict the likelihood of detecting surface-derived contaminants in groundwater. However, in many cases, these predictions have not been compared with measured contaminant concentrations in groundwater in the locations of interest—especially at regional to national scales. Additionally, most methods introduced by these earlier studies have been predominantly empirical (that is, based on regressions, neural networks, or other statistical relations) or dependent upon the use of semi-arbitrary index or scoring systems. Relatively few studies have used established, quantitative representations of the physical, hydrologic, chemical, and biological processes known to control chemical transport and fate in the subsurface to

simulate the concentrations of surface-derived contaminants in groundwater. As a result, most of the existing approaches are either limited to the specific areas, conditions, and contaminants for which they were derived (for the methods that are based on statistical correlations and [or] the measured concentrations of indicator solutes), or lack an up-to-date underpinning of quantitative process understanding (for the methods that depend on simple overlay, index, or scoring methods).

To address these limitations, a process-based groundwater vulnerability assessment (P-GWAVA) system was constructed and tested that uses numerical simulations of a broad range of well-known physical, hydrologic, chemical, and biological processes and agricultural management practices to predict the concentrations of surface-derived agrichemicals in the vadose zone. To ensure consistency among the predictions for locations across the conterminous United States, the P-GWAVA simulations drew exclusively on national-scale sources of model input data at the finest spatial resolution available for each parameter. The study also made extensive use of published techniques to estimate a variety of model input parameters from basic soil property data at each site. These input parameters include surface albedo, surface crust permeability, soil water retention parameters, Brooks-Corey parameters, saturated hydraulic conductivity, macroporosity and the sizes of microbial populations, as well as solute partition coefficients, reaction rates, and meso-micropore diffusion rates. To assess the accuracy of the model predictions, the simulations were done in agricultural areas across the United States where shallow groundwater was sampled for the target compounds by the U.S. Geological Survey, and the simulated concentrations or detection frequencies compared with the values measured in groundwater.

This study was done in two phases. During Phase 1, a single-porosity, tipping-bucket model, the Pesticide Root-Zone Model (PRZM), was used in the P-GWAVA system (thereby designated as P-GWAVA-PR) to simulate concentrations of atrazine at an assessment depth of 1 meter in the vadose zone beneath 1,224 agricultural sites across the United States. For Phase 2, PRZM was replaced with the Root-Zone Water-Quality Model (RZWQM), a dual-porosity model that simulates the transport and fate of solutes in macropores, as well as in the soil matrix, within the vadose zone. Through its use of RZWQM during Phase 2, the P-GWAVA system (designated as P-GWAVA-RZ) simulated the preferential transport of water and solutes in the subsurface, a phenomenon that has been known for more than three decades to exert substantial effects on solute transport through porous media in many hydrogeologic settings. The P-GWAVA-RZ model was used to simulate the concentrations of atrazine, deethylatrazine (DEA, an atrazine transformation product), and nitrate at an assessment depth of 3 meters in the vadose zone beneath 453 agricultural sites in the 10 northernmost states of the United States Corn Belt.

This study built directly upon the results from a previous investigation that assessed the accuracy with which simulations done without calibration using seven existing solute transport-and-fate models—including PRZM and RZWQM—predicted moisture contents, matric potentials, and the concentrations of surface-derived contaminants in the subsurface beneath two agricultural sites. To facilitate their execution at large numbers of sites, the P-GWAVA-PR and P-GWAVA-RZ simulations for the present study were also conducted without calibration. However, several global adjustments to the modeling approach were implemented to improve the fit between the solute concentrations simulated in the vadose zone and the concentrations measured in shallow groundwater. These adjustments consisted of (1) increasing the size of the P-GWAVA-PR model grid cells to 30 centimeters for the depth interval between 10 and 100 centimeters; (2) reducing the K_{oc} values for atrazine and DEA during Phase 2 while remaining consistent with the ranges of the published values; (3) varying the amounts of organic matter that are metabolized by soil microorganisms at rapid and intermediate rates during Phase 2; and (4) selecting specific approaches from among multiple options for simulating material inputs and processes during both study phases. The last of these adjustments involved comparing simulated and measured contaminant concentrations (or frequencies of detection) to determine the most appropriate approaches for specifying (1) the spatial heterogeneity of irrigation and atrazine applications (for both study phases); (2) whether atrazine transformation in the soil took place in the dissolved state, the sorbed state, both or neither (Phase 1); and (3) the methods used to estimate values for selected soil hydraulic parameters (both study phases) and solute reaction rates (Phase 2). No adjustments were made to any input parameters at any of the individual sites, however, in obedience to the study objective of evaluating the utility of the P-GWAVA-PR and P-GWAVA-RZ models for regional- to national-scale groundwater vulnerability assessments, for which such site-based adjustments would be impractical.

The P-GWAVA-PR and the P-GWAVA-RZ simulations produced chemographs (that is, time series of solute concentrations) that were qualitatively similar to those reported by previous field and laboratory studies. This indicates that solute dispersion in the subsurface can be realistically mimicked using mathematical representations of partial piston displacement, molecular diffusion, sorption, and the exchange of water and solutes between macropores and the soil matrix (the methods used by RZWQM), or by invoking the more empirical approach of using numerical dispersion to simulate hydrodynamic dispersion (the method used with PRZM).

For many of the study sites, the average depth to water (DTW) was shallower than the model assessment depths, which were the depths in the vadose zone where the model simulations estimated water fluxes and solute concentrations (1 meter for Phase 1; 3 meters for Phase 2). In most cases where statistically significant correlations were observed

(P less than [$<$] 0.05) between simulated and measured solute concentrations (or detection frequencies), or the level of agreement was significantly correlated with another explanatory variable, the strength of the correlation was greater among the sites with DTW greater than the assessment depth than for the sites where the water table was shallower than the assessment depth. In many such cases, however, the strength of the correlation observed when all sites were included in the analysis was similar to that observed when sites with DTW shallower than the assessment depth were excluded. This suggests that the value of the P-GWAVA model simulation results in most locations may not be substantially compromised by a lack of knowledge of water-table depth.

The levels of correlation between the P-GWAVA simulation results and the field measurements, or between the model residuals (that is, simulated minus measured values) and other site-based explanatory variables, differed between the two study phases, and among different output parameters (recharge rates, solute concentrations, and solute detection frequencies). Significant correlations were noted between the simulated recharge rates and the base-flow index (an estimate of groundwater recharge that is calculated from streamflow during base-flow periods), both for the P-GWAVA-PR simulations (Spearman $\rho = 0.30$; ($P[\rho]$ less than or equal to [\leq] 0.0001); 676 sites) and the P-GWAVA-RZ simulations (Spearman $\rho = 0.30$; $P[\rho] < 0.001$; 447 sites). Significant correlations were also noted between the simulated and measured concentrations of atrazine for both the P-GWAVA-PR (Spearman $\rho = 0.14$; $P[\rho] \leq 0.0001$; 1,224 sites) and the P-GWAVA-RZ simulations (Spearman $\rho = 0.25$; $P[\rho] \leq 0.0001$; 453 sites). Somewhat stronger correlations were observed between the DEA concentrations predicted by the P-GWAVA-RZ simulations and the measured values (Spearman $\rho = 0.41$; $P[\rho] \leq 0.0001$; 453 sites). No statistically significant correlations were observed, however, between the P-GWAVA-RZ model simulations and the measured values for the nitrate concentrations or the DEA fractions ($P[\rho] > 0.05$; Spearman rank correlations). (The DEA fraction represents the molar percentage of atrazine-derived compounds, including atrazine itself, which is present in the form of DEA.) Agreement between the simulated and measured atrazine concentrations was relatively close for both models, with 95th percentile values for the model residuals of 0.39 microgram per liter ($\mu\text{g/L}$) for the P-GWAVA-PR simulations (1,224 sites) and 0.87 $\mu\text{g/L}$ for the P-GWAVA-RZ simulations (453 sites). These values were an order of magnitude less than the Maximum Contaminant Level of 3 $\mu\text{g/L}$ established by the U.S. Environmental Protection Agency for atrazine. The DEA concentrations simulated by the P-GWAVA-RZ model in the Corn Belt also were in relatively close agreement with the measured values, exhibiting model residuals with a 95th percentile value of 0.003 $\mu\text{g/L}$ among the 453 sites examined. For reasons that remain unclear, however, the atrazine concentration residuals for the two models were negatively correlated with one another among the 136 sites in the Corn Belt where simulations were done during both study

phases and where the DTW was greater than the larger of the two assessment depths (Spearman $\rho = -0.17$; $P[\rho] = 0.04$). This indicates that different factors may have been responsible for the errors associated with the two models.

The concentrations of atrazine and DEA predicted by the P-GWAVA-RZ simulations were combined to examine their level of agreement with the predictions of a Tobit regression model. The Tobit regression model was created by an earlier study to predict the sum of atrazine and DEA concentrations in shallow groundwater beneath agricultural areas of the conterminous United States. The sum of the atrazine and DEA concentrations predicted by the P-GWAVA-RZ simulations at 329 Phase 2 sites was significantly correlated with the values predicted at the same sites by the Tobit regression model (Spearman $\rho = 0.37$; $P[\rho] \leq 0.0001$).

Statistically significant correlations between simulated and measured frequencies of detection (for the 12 sampling networks with 10 or more wells exhibiting average DTW greater than the assessment depths) were noted only during Phase 2 of this study, and only for atrazine (Spearman $\rho = 0.66$; $P[\rho] = 0.020$) and DEA (Spearman $\rho = 0.78$; $P[\rho] = 0.0026$). No significant correlations were noted for such networks for atrazine during Phase 1 or nitrate during Phase 2. As noted for the solute concentrations, the correlations involving the detection frequencies for Phase 2 were stronger when the sites with DTW equal to or shallower than 3 meters were excluded from the analysis.

At the broadest spatial scale, the overall frequency of atrazine detection derived from the P-GWAVA-RZ simulations for all of the sites in the Phase 2 study area (computed using the same temporally varying reporting limits that were applied to the measured concentration values) matched the measured detection frequency more closely than the atrazine detection frequency computed from the P-GWAVA-PR simulations matched the measured value for the conterminous United States during Phase 1 (using a fixed reporting limit). This was the case regardless of whether or not sites with average DTW shallower than the assessment depths were included in the analysis. The P-GWAVA-PR simulations generated correct predictions with regard to atrazine detections (true positives plus true negatives) at 50 percent of the Phase 1 sites examined throughout the conterminous United States, and the P-GWAVA-RZ simulations produced correct predictions for atrazine at 62 percent of the Phase 2 sites. These disparities between the two study phases with respect to the levels of agreement between simulated and measured values for the atrazine results may have been a consequence, in part, of the fact that the P-GWAVA-PR simulations were used to predict the concentrations of the herbicide over a much larger geographic area—and thus a wider range of climatic, hydrogeologic, and land-use settings—than was the case for the P-GWAVA-RZ simulations. However, direct comparisons between the predictions at the 136 sites in the Corn Belt where both models were run, and the DTW was greater than 3 meters, indicated that the atrazine concentrations simulated by the P-GWAVA-RZ model agreed more closely

with those measured in groundwater than was the case for the P-GWAVA-PR simulations in the same locations. Among all of the sites examined during Phase 2, the simulated and measured overall frequencies of detection showed substantially closer agreement with one another for atrazine and nitrate than for DEA. The solute exhibiting the highest rate of correct predictions during the two study phases, however, was DEA, for which the P-GWAVA-RZ simulations predicted a correct result (either a true positive or a true negative) at 70 percent of the Phase 2 sites.

During Phase 2 of this study, the simulated solute concentrations were adjusted to account for temporal variations in analytical recoveries, and the temporally varying reporting limits used for the chemical analyses were also used to designate simulated concentrations as either detections or non-detections. Because this approach has not been commonly implemented by previous investigations, the levels of agreement between the simulated and measured detection frequencies for atrazine, DEA, and nitrate during Phase 2 were also evaluated using the more conventional approach of applying uniform reporting limits to identify detections (both simulated and measured). To include all sites in the analysis, the highest reporting limit for all of the samples analyzed for Phase 2 was used for each solute. As expected, the simulated and measured frequencies of detection for all three solutes were lower using the fixed reporting limits than when the temporally varying reporting limits were used. Use of the fixed reporting limits, however, also led to poorer agreement between the simulated and measured overall frequencies of detection of atrazine and DEA than did the use of the temporally varying reporting limits. For nitrate, however, the simulated and measured overall frequencies of detection were in close agreement when using both the fixed and the temporally varying reporting limits. The similarity of the results for the temporally varying and fixed reporting limits for nitrate likely was because the simulated and measured nitrate concentrations generally were much larger, relative to their reporting limit, than was the case for either atrazine or DEA.

In addition to assessing the levels of agreement between the simulated and measured patterns of solute detection, the extent to which the observed disparities between the simulated and measured concentrations or detection frequencies were related to various system characteristics and assessment approaches was also examined. Comparisons among the results for six sites in Wisconsin indicated that when the most detailed soil property data available (obtained from the Soil Survey Geographic database, or SSURGO) were used, the atrazine concentrations simulated by the P-GWAVA-PR model were in substantially closer agreement with the atrazine concentrations measured in groundwater than when the soil property data from the State Soil Geographic database (STATSGO, which represent spatial aggregations of the SSURGO data) were used. This lent support to the use of the soil property data from SSURGO, rather than those from STATSGO, for the Phase 2 simulations. These results

also indicated that the use of the soils data from SSURGO, rather than the STATSGO data, may have been one reason the atrazine concentrations simulated by the P-GWAVA-RZ model were in closer agreement with those observed in shallow groundwater than the concentrations simulated by the P-GWAVA-PR model.

Statistically significant correlations noted between the DTW and model residuals for atrazine, DEA, and nitrate concentrations during Phase 2 were consistent with anticipated relations between the thickness of the vadose zone and the progress of aerobic reactions in the subsurface. A positive relation with DTW for atrazine and a negative relation for DEA were in agreement with observations from previous research indicating that the extent of conversion of atrazine to DEA in the subsurface—an aerobic process—tends to be higher in areas with thicker vadose zones. Similarly, a negative relation for nitrate indicated that the formation of nitrate from the oxidation of the more reduced forms of nitrogen that are commonly applied as fertilizer—also an aerobic process—is likely to occur to a greater extent in locations with a deep water table than in locations with a shallower water table.

Given the absence of detailed, national-scale data on cropping patterns at the time of this study, all of the model simulations assumed that corn was the only crop grown, and that atrazine and nitrogen fertilizer were applied, during every year of each simulation. Model residuals for the concentrations of all three solutes examined during Phase 2, however, were significantly correlated with the average percentage of nearby corn-and-soybean area in corn cultivation (relative to soybeans, the crop grown most commonly in rotation with corn in the Corn Belt) during the simulation period. Because atrazine is not applied to soybeans, the positive correlation with the percentage of corn observed for atrazine and the negative correlation for DEA provide evidence (consistent with previous studies) suggesting that the rates at which soil microorganisms convert atrazine to DEA may increase with repeated applications of the herbicide—a well-documented process known as microbial adaptation. These results indicate that in areas where atrazine is applied repeatedly over several years (as is common where corn is grown), microbial adaptation may exert more substantial control over the atrazine concentrations in the subsurface than the total amounts of the herbicide applied over time.

A significant negative correlation between the model residuals for nitrate concentrations and the percentage of corn grown nearby was consistent with expectation, given that nitrogen fertilizers are applied more heavily to corn than to soybeans, and that nitrate behaves as an essentially conservative solute as it migrates through the well-aerated soils in which corn is commonly grown. This correlation also indicated that the amounts of nitrate added to the soil by nitrogen fixation in soybean plants are substantially smaller than the additional quantities of nitrogen fertilizer that are typically used to grow corn. The contrast in the directions of correlation for nitrate and atrazine also provided further

support for the hypothesis that microbial adaptation to repeated atrazine applications may be more important than the total amounts of atrazine applied in determining the subsurface concentrations of the herbicide beneath areas of intensive corn cultivation.

The model residuals for the solute detection frequencies exhibited geographic variations that provided clues regarding the influence of soil and climatic factors on the levels of agreement between the simulation results and the observed occurrence of the solutes in shallow groundwater. To test hypotheses regarding the potential reasons for these variations, correlations were examined between the model residuals for the frequencies of detection of the three solutes of interest and various parameters associated with soil properties, climate and, for atrazine and DEA, the intensity of atrazine use. Although no statistically significant relations with any of the explanatory variables were observed for nitrate, several relations examined for atrazine and DEA were significant. The nature of these correlations indicated that the P-GWAVA-PR simulations tended to underemphasize the effect of hydraulic conductivity on atrazine transport to the water table (as reflected in relations to clay content and vertical permeability), but exaggerate the effect of recharge (as reflected in relations to runoff and annual precipitation). By contrast, the P-GWAVA-RZ simulations tended to exaggerate the effects of soil properties (available water content and vertical permeability, as well as clay, silt, and sand content) on the transport of atrazine and DEA to the water table. Whereas there was a statistically significant, positive correlation of the mean annual air temperature with the model residuals for atrazine detection frequencies from the P-GWAVA-PR simulations, no significant correlations were noted between the average air temperature in May and the model residuals for atrazine or DEA detection frequencies from the P-GWAVA-RZ simulations. These results suggest that the activation energy value used for atrazine transformation during Phase 1 may have been inappropriately low, but that the higher value used for atrazine and DEA during Phase 2 adequately accounted for the effect of temperature on the rates of disappearance of both solutes. Together, these disparities between the two models regarding the manner in which the accuracy of their predictions was correlated with different soil- and climate-related parameters may help explain why the predictions from the two models were in such poor agreement.

Correlations also were examined between the areally averaged intensities of atrazine use and the model residuals for the frequencies of atrazine and DEA detection. The model residuals were not significantly correlated with the intensity of atrazine use for atrazine during either study phase, and only weakly correlated for DEA. These patterns of correlation indicate that the intensity of atrazine use may be less important in controlling the concentrations of atrazine (and by extension, DEA) in the subsurface than other site factors, especially factors that control the rates of water flow.

This study has demonstrated the feasibility of constructing and testing a modeling system that uses current understanding of processes and factors controlling the transport and fate of surface-derived contaminants in the subsurface, in conjunction with nationwide sources of ancillary data, to simulate the concentrations of these compounds in the vadose zone anywhere in the conterminous United States. This system was shown to simulate concentrations and frequencies of detection of atrazine and DEA in the vadose zone that are significantly correlated with those measured in shallow groundwater over large geographic areas. Several large-scale sampling studies have reported frequencies of atrazine and DEA detection in groundwater in the United States that are similar to one another over regional to national scales. The results from this study represent the first time that process-based simulations have reproduced this pattern on a regional scale.

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Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.

[**Abbreviations:** Cligen, climate simulator provided by RZWQM; DEA, deethylatrazine; EPA, Environmental Protection Agency; ET, evapotranspiration; FAO, Food and Agriculture Organization of the United Nations; f_{oc} , weight fraction of organic carbon in soil; f_{org} , weight fraction of organic matter in soil; FWM, flow-weighted mean; HPLC, high-performance liquid chromatography; LUS, National Water-Quality Assessment (NAWQA) land-use study; NRCS, Natural Resources Conservation Service (USDA); NRI, Natural Resources Inventory (NRCS); P-GWAVA, process-based groundwater vulnerability assessment system; P-GWAVA-PR, P-GWAVA system using PRZM to simulate solute and water behavior in the vadose zone (fig. 5); P-GWAVA-RZ, P-GWAVA system using RZWQM to simulate solute and water behavior in the vadose zone (fig. 6); PET, potential evapotranspiration; PRZM, Pesticide Root-Zone Model (EPA); PTFs, pedotransfer functions (statistical relations used to predict soil hydraulic parameter values from other soil properties); QMRR, quantitative medium-reactivity relation; QMPR, quantitative medium-property relation; QPPR, quantitative property-property relation; QSPR, quantitative structure-property relation; QSRR, quantitative structure-reactivity relation; RZWQM, Root-Zone Water-Quality Model (USDA); SSURGO, Soil Survey Geographic Database (NRCS); STATSGO, State Soil Geographic database (NRCS); T_{air} , average air temperature in May; TPAW, total plant available water (Barling and others, 2011); USDA, U.S. Department of Agriculture; °C, degrees Celsius; µg C/g, microgram of carbon per gram of soil; cm, centimeter; cm³/d, centimeter per day; cm/h, centimeter per hour; cm³/g, cubic centimeter per gram of soil; d⁻¹, per day; h⁻¹, per hour; ha, hectare; in/hr, inch per hour; kg a.i./ha, kilograms of active ingredient per hectare; m, meter; kJ/mol, kilojoules per mole; mL/g, milliliter per gram; mm, millimeter; mm⁻³, per millimeter; %om, percentage of soil organic matter; ≥, greater than or equal to; >, greater than; <, less than; →, process not simulated or information not needed]

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Elevation, aspect and slope of map unit surface	Obtained from STATSGO	<ul style="list-style-type: none"> STATSGO data obtained from Natural Resources Conservation Service (2011a) Data processed by David Wolock, U.S. Geological Survey, (written commun., March 23, 2000) 	<ul style="list-style-type: none"> Obtained from SSURGO or digital elevation model Aspect assumed to be zero (true North) if data missing 	Natural Resource Conservation Service (2011a)
Maximum and minimum air temperature (T_{max} and T_{min} , respectively) (°C)	<ul style="list-style-type: none"> Daily values 327 stations located near study sites (4,953 stations nationwide) Values from station nearest to each site assigned using Thiessen polygons 	<p>Weather</p> <ul style="list-style-type: none"> Data source: National Climatic Data Center (2002b) Missing values filled in using method of Eischeid and others (2000) Processed data provided by David Wolock, U.S. Geological Survey (written commun., December 5, 2002) 	<ul style="list-style-type: none"> Daily values Data obtained from 87 meteorological stations Values for each site obtained from weather station located within the same Cligen grid cell as the site or, if no weather stations were available in the same cell, from the nearest station outside of the cell (4 sites) 	Cligen (Agricultural Research Service, 2009)
Average air temperature in May (T_{May}) (°C)	Computed for each site as the arithmetic average of monthly averages of T_{max} and T_{min} for May from 1971 to 2000, using the PRISM data	PRISM Climate Group (2009)	Computed for each site as the arithmetic average of monthly averages of T_{max} and T_{min} for May from 1971 to 2000, using the PRISM data	PRISM Climate Group (2009)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Weather—Continued				
Solar radiation	Estimated from latitude using the Penman-Monteith equation for calculation of PET	Allen and others (1998)	Daily values of short-wave radiation obtained from the same locations as those for T_{max} and T_{min}	Cligen (Agricultural Research Service, 2009)
Sunshine fraction	—	—	<ul style="list-style-type: none"> Defined as the average annual fraction of daytime hours without clouds (Food and Agriculture Organization of the United Nations, 2011a; Liwang Ma, U.S. Department of Agriculture, Agricultural Research Service, written commun., November 20, 2011) Value set at 0.6 for all sites, estimated for the northern Corn Belt from worldwide map provided by the Food and Agriculture Organization of the United Nations (2011b) 	—
Wind speed	Monthly values	<ul style="list-style-type: none"> Data source: National Climatic Data Center (1998) Processed data provided by David Wolock, U.S. Geological Survey (written commun., December 5, 2002) 	<ul style="list-style-type: none"> Daily values, obtained from the same locations as those for T_{max} and T_{min} Measured from a height of 10 m 	<ul style="list-style-type: none"> Cligen (Agricultural Research Service, 2009) Measurement height provided by Burns and others (2007)
Pan evaporation (cm/d)	Estimated using the Penman Monteith equation	Allen and others (1998)	Not used	—
Relative humidity (percent)	—	—	Daily values, obtained from the same locations as those for T_{max} and T_{min}	Cligen (Agricultural Research Service, 2009)
Precipitation	Daily values	<ul style="list-style-type: none"> Data source: National Climatic Data Center (2002a) Processed data provided by David Wolock, U.S. Geological Survey (written commun., December 11, 2002) 	<ul style="list-style-type: none"> Hourly data on storms required in order to generate macropore flow Storm data generated stochastically, using information from the same locations as those for T_{max} and T_{min} 	Cligen (Agricultural Research Service, 2009)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Irrigation	<ul style="list-style-type: none"> Sites selected at random for irrigation in each LUS, based on NRI percentages (fig. 17; eq. 8) Carried out only during the growing season (May 1–September 30) Triggered when fraction of available water capacity ($AWC \equiv \theta_{FC} - \theta_{wp}$) dropped below 0.4 Irrigation rates: <ul style="list-style-type: none"> Initial value: 1.0 in/hr (midrange of rates given by Carsel and others [1998] for sprinkler irrigation) Reduced to 0.1 in/hr to avoid generating excessive runoff 	–	<ul style="list-style-type: none"> Simulated as furrow irrigation Carried out only during growing season (May 30–September 7) Triggered when fraction of Total Plant Available Water in the active rooting zone ($TPAW \equiv \theta_{33} - \theta_{500}$) dropped below the following thresholds ($TPAW_{min}$): <ul style="list-style-type: none"> First 15 days after planting: $TPAW_{min} = 0.5$ 73 days or more after planting: $TPAW_{min} = 0.3$ Each irrigation event continued until a specified maximum value of TPAW ($TPAW_{max}$) was reached in the active rooting zone: <ul style="list-style-type: none"> First 15 days after planting: $TPAW_{max} = 0.75$ 73 days after planting: $TPAW_{max} = 0.5$ Minimum number of days between successive irrigation events: 3 	<ul style="list-style-type: none"> Furrow irrigation commonly used on corn in the United States (Christensen, 2002) Corn sensitivity to water stress increases at silking stage, which typically occurs approximately 63–68 days after emergence (McWilliams and others, 1999)
Runoff	<ul style="list-style-type: none"> Curve number method, utilizing two soil properties: <ul style="list-style-type: none"> Predominant soil hydrologic group Surface condition of soil (fallow, crop, or residue) 	<ul style="list-style-type: none"> Soil hydrologic groups from STATSGO (Natural Resources Conservation Service, 2011a) Curve numbers from Carsel and others (1998) 	<ul style="list-style-type: none"> Generated only when rate of water input exceeded infiltration Rate estimated as the difference between rate of water delivery to land surface (from precipitation and [or] irrigation) and the rate of infiltration (Ahuja and others, 2000) 	–
Vertical infiltration into the soil	Computed as difference between rate of precipitation (rainfall plus snowmelt) and the sum of runoff and evaporation	Carsel and others (1998)	Computed from K_{sat} and other parameters using the Green-Ampt equation (Ahuja and others, 2000)	–
Lateral infiltration from macropores into the soil matrix	Not simulated	–	Computed from macropore radius, wetted radius, K_{sat} and radial infiltration rate reduction factor, using the Green Ampt equation (Ahuja and others, 2000)	–

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Soil drainage	Water movement at or below land surface—Continued			
	<ul style="list-style-type: none"> Free drainage for all soils Redistribution simulated to occur within 1 day 	–	<ul style="list-style-type: none"> Water flow through soil matrix (redistribution) simulated using Richards' equation Water flow through macropores simulated using Poiseuille's law 	Ahuja and others (2000); Malone and others (2003)
Rate of evapotranspiration (ET)	<ul style="list-style-type: none"> Computed daily, from potential evapotranspiration (PET), wilting point and soil water content PET estimated as function of T_{min}, T_{max}, wind speed, solar radiation and saturation water vapor pressure, using the Penman-Monteith method, recommended by FAO (Allen and others, 1996) No distinction made between evaporation and transpiration (Carsel and others, 1998) 	<ul style="list-style-type: none"> See entries for water content at wilting point, T_{min}, T_{max}, wind speed and solar radiation. Saturation water vapor pressure estimated from T_{min} and T_{max} 	<ul style="list-style-type: none"> Computed daily as function of T_{min}, T_{max}, wind speed, solar radiation, saturation water vapor pressure and the surface albedo of dry soil, using the extended Shuttleworth-Wallace model (Ahuja and others, 2000) Saturation water vapor pressure estimated from T_{min} and T_{max} 	See entries for T_{min} , T_{max} , wind speed, solar radiation, and surface albedo of dry soil.
Maximum depth of evaporation	<ul style="list-style-type: none"> Values taken from map in Carsel and others (1998) Fallow, dormant conditions assumed 	–	Not needed	Ahuja and others (2000)
Surface boundary condition ($z=0$)	Not applicable (tipping-bucket algorithm)	–	<ul style="list-style-type: none"> Evaporative flux specified when $h [z=0] > -20$ bar ($\approx \theta_{wp}$) Constant head specified ($h [z=0] \equiv -20$ bar) when evaporative flux can no longer be sustained 	Ahuja and others (2000)
Bottom boundary condition	Not applicable (tipping-bucket algorithm)	–	Unit gradient boundary	–
Hydraulic gradient during infiltration	Not applicable (tipping-bucket algorithm)	–	Unit gradient	–
Depth, size and spacing of tile drains	Tile drainage not simulated	Insufficient information available on prevalence of tile drains across the United States	Tile drainage not simulated	Insufficient information available on prevalence of tile drains across the United States

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Soil erosion	Physical, chemical, and hydraulic properties of soils			
Soil texture (weight percentages)	Neglected	–	Neglected	–
<ul style="list-style-type: none"> • Percent sand • Percent silt • Percent clay • Soil organic matter content (%om) 	<p>Values for all soil components combined as spatial averages, weighted vertically (by horizon thicknesses) and horizontally (by percentage of map unit area occupied by each component), as illustrated in figure 7 for soil organic matter</p>	<ul style="list-style-type: none"> • Original data from STATSGO • Averages computed by David Wolock, U.S. Geological Survey (written commun., March 23, 2000) 	<ul style="list-style-type: none"> • Fractions for individual soil constituents for each horizon obtained from SSURGO, as a weight percent of the <2 mm size fraction (Natural Resources Conservation Service, 2007a) • For soil horizons for which SSURGO did not provide percent organic matter (%om) data, values were scaled from the value in the uppermost horizon (for which SSURGO data were always available) according to the average %om values for deeper horizons, using equation 2 • Sites with soil horizons for which %om ≥ 20 percent were considered anomalous (for an agricultural area) and eliminated from consideration 	SSURGO (Natural Resources Conservation Service, 2011a)
Number, depth, thickness, and texture class for individual soil horizons	One uniform layer only (table 1)	–	<ul style="list-style-type: none"> • Data assembled from SSURGO for all soil horizons in each component satisfying minimum data criteria (see section entitled “Characteristics and Use of SSURGO Data”) • Texture class determined by RZWQM from percent sand, silt and clay • Texture for soil horizons with multiple texture designations determined from percent sand, silt and clay, using soil texture triangle program embedded within RZWQM (Brady, 1990) or available online (Gerakis and Baer, 2011) 	SSURGO (Natural Resources Conservation Service, 2011a)
Organic carbon content (f_{oc}), as mass fraction	Computed from mass fraction of soil organic matter ($f_{om} = \%om/100\%$) using equation 15	See entry for soil texture (which includes %om)	Same as for Phase 1	SSURGO (Natural Resources Conservation Service, 2011a)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)																											
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)																										
Surface albedo of soil, as fraction of incident light	<p>Physical, chemical, and hydraulic properties of soils—Continued</p> <ul style="list-style-type: none"> Specified on a monthly basis Value depends upon soil texture, wetness, surface cover, and angle of solar incidence 	<p>Carsel and others (1998, table 5-21)</p>	<ul style="list-style-type: none"> Defined as the fraction of incident short-wave solar radiation reflected by the <2 mm fraction of air-dried surface soil (Natural Resources Conservation Service, 2007a) Values for dry soil (A_d) obtained from SSURGO for uppermost horizon of each component of interest Sites with missing values of A_d assigned average value among all SSURGO values from surficial horizons in the same texture class within the Phase 2 study area, that is: <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Soil texture class</th> <th>A_d</th> </tr> </thead> <tbody> <tr><td>Clay</td><td>¹0.26</td></tr> <tr><td>Clay loam</td><td>0.19</td></tr> <tr><td>Loam</td><td>0.25</td></tr> <tr><td>Loamy sand</td><td>0.21</td></tr> <tr><td>Sand</td><td>0.28</td></tr> <tr><td>Sandy clay</td><td>²0.24</td></tr> <tr><td>Sandy clay loam</td><td>0.23</td></tr> <tr><td>Sandy loam</td><td>0.24</td></tr> <tr><td>Silt</td><td>0.08</td></tr> <tr><td>Silty clay</td><td>0.11</td></tr> <tr><td>Silty clay loam</td><td>0.10</td></tr> <tr><td>Silty loam</td><td>0.26</td></tr> </tbody> </table> 	Soil texture class	A_d	Clay	¹ 0.26	Clay loam	0.19	Loam	0.25	Loamy sand	0.21	Sand	0.28	Sandy clay	² 0.24	Sandy clay loam	0.23	Sandy loam	0.24	Silt	0.08	Silty clay	0.11	Silty clay loam	0.10	Silty loam	0.26	<p>SSURGO (Natural Resources Conservation Service, 2011a)</p>
Soil texture class	A_d																													
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			<p>¹Average among subsurface values only. ²No data available among Phase 2 sites. Intermediate value selected between those for texture classes on either side of sandy clay on the soil texture triangle (Gerakis and Baer, 2011), that is, clay and sandy clay loam.</p> <ul style="list-style-type: none"> Values for wet soils (A_w) estimated from A_d (from SSURGO) using the following relation from Berge (1986): $A_w = 0.5 A_d$ 																											

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Physical, chemical, and hydraulic properties of soils—Continued				
Dry volume heat capacity ($J - mm^3 K^{-1}$)	–	–	Value of 0.002120 $J - mm^{-3} K^{-1}$ used for all soil horizons	Suggested RZWQM default value (Pat Bartling, U.S. Department of Agriculture, written commun., December 17, 2007)
Particle density (specific gravity of solids, ρ_s), in mass per unit volume	–	–	Obtained from SSURGO	SSURGO (Natural Resources Conservation Service, 2011a)
Bulk density (ρ_b), in mass per unit volume	Averaged vertically and horizontally, as illustrated in figure 7 for soil organic matter	STATSGO (Natural Resources Conservation Service, 2011a)	Obtained from SSURGO or, where necessary, estimated from specific gravity of solids (ρ_s) and porosity (n) using the following equation, rearranged from Freeze and Cherry (1979): $\rho_b = \rho_s (1 - n)$	SSURGO (Natural Resources Conservation Service, 2011a)
Porosity (n)	–	–	Set equal to saturated water content (fig. 11)	–
Saturated water content (θ_s), in percent by volume	–	–	Defined as the volumetric water content of soil at or near zero bar tension (Natural Resources Conservation Service, 2007a)	SSURGO (Natural Resources Conservation Service, 2011a)
Saturation fraction (actual saturated water content, as a fraction of θ_s)	–	–	<ul style="list-style-type: none"> Defined as the maximum degree of saturation that can be achieved above the water table. Accounts primarily for the influence of entrapped air (Liwang Ma, U.S. Department of Agriculture, written commun., November 20, 2011). Value of 0.9 used for all sites (that is, 90 percent of θ_s) 	Previous work suggests that this fraction typically ranges between 0.8 and 0.9 (Agricultural Research Service, 2010)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Soil water content at field capacity (θ_{fc}), as a fraction by volume	Physical, chemical, and hydraulic properties of soils—Continued <ul style="list-style-type: none"> Presumed to be equal to the water content at 33 kPa tension (θ_{33}) (Carsel and others, 1998) Estimated from soil texture using Rosetta 	Schaap and others, 2001 (Rosetta)	<ul style="list-style-type: none"> Presumed to be equal to the water content at 33 kPa tension (θ_{33}) θ_{33} obtained directly from SSURGO or, if missing, approximated using values from adjacent horizons To avoid computational difficulties, value set to 6 percent for soil horizons for which θ_{33} was lower than 6 percent Used as the initial condition of water content for all soil horizons 	SSURGO (Natural Resources Conservation Service, 2011a)
Soil water content at wilting point (θ_{wpl}), as a fraction by volume	<ul style="list-style-type: none"> Presumed to be equal to the water content at 1,500 kPa tension (θ_{1500}) (Carsel and others, 1998) Estimated from soil texture using Rosetta 	Schaap and others, 2001 (Rosetta)	<ul style="list-style-type: none"> Presumed to be equal to the water content at 1,500 kPa tension (θ_{1500}) θ_{1500} obtained directly from SSURGO 	SSURGO (Natural Resources Conservation Service, 2011a)
Saturated hydraulic conductivity (K_{sat}), in cm/h	Not applicable (tipping-bucket algorithm)	—	Estimated for each soil horizon from weight percentages of sand and clay using an online program (Nelson, 2012) employing the PTF from Saxton and others (1986)	Weight percentages of sand and clay obtained from SSURGO (Natural Resources Conservation Service, 2011a)
Lateral saturated hydraulic conductivity (K_{lat}), in cm/h	Not applicable (tipping-bucket algorithm)	—	$K_{lat} = 1.5 (K_{sat})$	See entry for K_{sat}
Hydraulic conductivity of surface soil crust (K_{cr}), in cm/h	Not characterized	—	Estimated as follows: $K_{cr} = K_{sat} CF$ where CF is crust factor, that is, the ratio of hydraulic conductivity of the surface soil crust to that of the bulk soil (K_{cr}/K_{sat})	<ul style="list-style-type: none"> Surface crusts, commonly formed from raindrop impacts on both tilled and undisturbed soils (for example, Rawls and others, 1990), presumed to be present at all sites See entries for K_{sat} and CF

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)																											
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)																										
Crust factor (<i>CF</i>), that is, the ratio of hydraulic conductivity of surface soil crust to that of the bulk soil (K_{cr}/K_{sat})	Not characterized	–	Physical, chemical, and hydraulic properties of soils—Continued <i>CF</i> values for each of 12 soil texture classes, computed using data and methods provided by Rawls and others (1990), as described in text: <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Soil texture class</th> <th><i>CF</i></th> </tr> </thead> <tbody> <tr><td>Clay</td><td>0.27</td></tr> <tr><td>Clay loam</td><td>0.32</td></tr> <tr><td>Loam</td><td>0.34</td></tr> <tr><td>Loamy sand</td><td>0.56</td></tr> <tr><td>Sand</td><td>0.65</td></tr> <tr><td>Sandy clay</td><td>0.36</td></tr> <tr><td>Sandy clay loam</td><td>0.43</td></tr> <tr><td>Sandy loam</td><td>0.39</td></tr> <tr><td>Silt</td><td>0.25</td></tr> <tr><td>Silty clay</td><td>0.23</td></tr> <tr><td>Silty clay loam</td><td>0.25</td></tr> <tr><td>Silty loam</td><td>0.27</td></tr> </tbody> </table>	Soil texture class	<i>CF</i>	Clay	0.27	Clay loam	0.32	Loam	0.34	Loamy sand	0.56	Sand	0.65	Sandy clay	0.36	Sandy clay loam	0.43	Sandy loam	0.39	Silt	0.25	Silty clay	0.23	Silty clay loam	0.25	Silty loam	0.27	–
Soil texture class	<i>CF</i>																													
Clay	0.27																													
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Silty clay loam	0.25																													
Silty loam	0.27																													
Brooks-Corey parameters (used to describe dependence of hydraulic conductivity and soil water content on matric suction in the vadose zone)	Not applicable (tipping-bucket algorithm)	–	Estimated by RZWQM from soil texture, using the PTFs from Rawls and others (1982) (see section entitled “ Water Movement Through the Subsurface ”)	<ul style="list-style-type: none"> Ahuja and others (2000) Bartling and others (2011) 																										
Microporosity	Not characterized	–	<ul style="list-style-type: none"> 1 percent for uppermost horizon at each site 10 percent for all deeper horizons 	<ul style="list-style-type: none"> Value for uppermost horizon represented minimum value in range recommended by RZWQM (Agricultural Research Service, 2010), consistent with results reported by Ahuja and others (1995) for wet initial conditions Value for deeper horizons obtained from example provided by RZWQM (Agricultural Research Service, 2010) 																										

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Physical, chemical, and hydraulic properties of soils—Continued				
Radial infiltration rate reduction factor (accounts for the influence of compaction and [or] soil organic matter on lateral water flow into macropores)	Not characterized	–	0.1 (used for all sites)	Value used by Ahuja and others (1995), Malone and others (2003), and Fox and others (2004)
Wetting thickness for lateral infiltration	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • For radial holes: 0.6 cm • For cracks and columns: 0.6 cm 	<ul style="list-style-type: none"> • Value for radial holes suggested by Malone and others (2003) • Same value presumed to be appropriate for cracks and columns
Total macroporosity	Not characterized	–	Estimated for each soil horizon using flow chart (fig. 10) derived from approach of Jarvis and others (2007b)	See figure 10.
Average radius of cylindrical macropores	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • Top horizon: 0.1 cm • All other horizons: 0 cm (assumed by RZWQM to be closed [Agricultural Research Service, 2010]) 	Top horizon value: Jaynes and Miller (1999)
Width of rectangular cracks	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • Top horizon: 0 cm (assumed by RZWQM to be closed [Agricultural Research Service, 2010]) • All other horizons: 0.05 cm 	Value for lower horizons: Jaynes and Miller (1999)
Length of rectangular cracks	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • Top horizon: 0 cm (assumed by RZWQM to be closed [Agricultural Research Service, 2010]) • All other horizons: 10 cm 	Value for lower horizons obtained from example provided by RZWQM (Agricultural Research Service, 2010)
Average length of soil aggregates	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • Top horizon: 0 cm (aggregates assumed to be absent from the soil surface) • All other horizons: 10 cm 	Values obtained from example provided by RZWQM (Agricultural Research Service, 2010)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
	Physical, chemical, and hydraulic properties of soils—Continued			
Number of macropores per unit area	Not characterized	–	Computed by RZWQM from total macroporosity and macropore radii	–
Length of cracks per unit area	Not characterized	–	Computed by RZWQM from total macroporosity, crack lengths, and crack widths	–
Fraction of pore volume in dead-end pores	Not characterized	–	Values used at all sites: <ul style="list-style-type: none"> • Top horizon: 0.001 • All other horizons: 0.5 	Default values, obtained from example provided by RZWQM (Agricultural Research Service, 2010) <ul style="list-style-type: none"> • Caused primarily by the actions of earthworms and other soil organisms • Value provided by Bartling and others (2011)
Percentage of crop residue incorporated into soil each year through bioturbation	Not characterized	–	0.6 percent	
Soil management				
Tillage method	Conventional	Common practice	Conventional	Common practice
Land surface management	Conditions used for all sites: <ul style="list-style-type: none"> • Initial condition: Fallow • During crop growth: Cropping • After harvest: Residue 	Common practice	Conditions used for all sites: <ul style="list-style-type: none"> • 3 metric tons of 100-day-old corn residue (as dry mass) per hectare on soil surface • Average depth of residue layer: 3.0 cm • C:N ratio of predominant (corn) residue material: 50:1 • All residue presumed to lie flat 	RZWQM default values (Agricultural Research Service, 2010)
Crop characteristics and management				
Crop type	Corn	<ul style="list-style-type: none"> • Corn represented 84 percent of atrazine use nationwide in 1997 (U.S. Geological Survey, 2014) • Continuous corn, rather than corn-and-soybean rotations, used for the sake of model simplicity 	<ul style="list-style-type: none"> • Corn, simulated using the “generic plant model” in RZWQM • Potential effect of continuous corn on model predictions, relative to corn-and-soybean rotations, also investigated, using equation 50 	Same reasoning as for Phase 1
Cropping frequency	One cropping period per year (“continuous corn”)	Common practice	One cropping period per year (“continuous corn”)	Common practice

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Timing of events	<p>Crop characteristics and management—Continued</p> <p>Uniform dates for all sites:</p> <ul style="list-style-type: none"> Planting: May 1 Emergence: May 15 Maturation: September 15 Harvest: September 30 	<p>Midrange values from U.S. Department of Agriculture/ National Agricultural Statistics Service data for 17 states</p>	<p>Uniform dates for all sites:</p> <ul style="list-style-type: none"> Planted: May 30 Harvest: September 7 	<ul style="list-style-type: none"> Planting date selected to minimize encounters with killing frosts Harvest date set at 100 days after planting (corn assumed to be fully developed by then) Initial choice of harvest date (September 17) moved 10 days earlier to bring amounts of applied irrigation water in closer agreement with those required to grow corn
Planting population (P_{pop})	—	—	<ul style="list-style-type: none"> Required for computing nitrogen fertilizer inputs $P_{pop} = 85,000$ seeds / ha 	<ul style="list-style-type: none"> Source: Hoskins (2008) Recommended value
Rooting depth	Increases over time to 90 cm	Midpoint of range given for corn by Carsel and others (1998, table 5-9)	Increases over time to 200 cm	Value specified by Generic Crop Growth model in RZWQM for corn (Bartling and others, 2011)
Maximum plant height	200 cm	Midpoint of range given for corn by Carsel and others (1998, table 5-16)	170 cm	Default value specified by RZWQM for corn (Agricultural Research Service, 2010)
Maximum coverage	Increases over time to 100 percent	Carsel and others (1998)	Computed as exponential function of Leaf Area Index	Default parameter values specified by RZWQM for corn (Bartling and others, 2011)
Albedo of mature crop and fresh residue	Values obtained from Carsel and others (1998)	Carsel and others (1998, table 5-21)	Values used for all sites:	Pat Bartling, U.S. Department of Agriculture, Agricultural Research Service (written commun., September 2, 2011)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Crop characteristics and management—Continued				
Percentage of crop residue incorporated naturally into soil each year by bioturbation.	Not characterized	–	0.6 percent	<ul style="list-style-type: none"> Caused by the activities of earthworms and other soil organisms Bartling and others (2011)
Rainfall caught and stored in canopy	Maximum value used (0.3 cm)	Default value for corn given by Carsel and others (1998, table 5-4)	Not simulated	–
Rates of nitrogen and water uptake and biomass formation	–	–	Default values from Generic Crop Growth Model	Bartling and others (2011)
Harvest parameters	–	–	–	Default values provided by RZWQM for corn cultivation (Agricultural Research Service, 2010)
Target crop yield (Y_{goal})	–	–	<ul style="list-style-type: none"> Required for computing nitrogen fertilizer inputs $Y_{goal} = 494$ bushels / ha 	<ul style="list-style-type: none"> Source: Hoskins (2008) Upper limit of range
Concentrations, conversion, composition, and reactivity of organic materials				
Characteristics of crop residue	–	–	<ul style="list-style-type: none"> All residue assumed flat (none standing) Dry mass of residue on surface: 3 metric tons/ha Age of residue at start of simulation: 100 days Average height of residue: 3 cm 	Agricultural Research Service (2010)
Carbon-to-nitrogen ratios of crop residue and soil organic matter.	–	–	<ul style="list-style-type: none"> Dominant residue material: 50 Slow residue pool: 19 Fast residue pool: 80 Fast soil humus pool: 8 Intermediate soil humus pool: 10 Slow soil humus pool: 11 Carbon sink pool: 0 Aerobic heterotroph pool: 8 Autotroph pool: 8 Anaerobic heterotroph pool: 8 	Bartling and others (2011)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
	Concentrations, conversion, composition and reactivity of organic materials—Continued			
Initial amounts of organic carbon in pools of organic residue (slow, fast) and humus (slow, medium, fast)	–	–	<ul style="list-style-type: none"> Residue pools – Default values <ul style="list-style-type: none"> – Slow residue pool: 1 µg C/g soil – Fast residue pool: 1 µg C/g soil Initial distribution of soil organic matter between fast, medium and slow pools (2, 18 and 70 percent, respectively) adjusted to 10, 20 and 70 percent, respectively, to improve fit between simulated and measured nitrate concentrations 	–
Fractions of conversion among the five pools of soil organic matter	–	–	RZWQM default values used for all parameters	Bartling and others (2011)
Efficiencies of conversion among different forms of soil organic matter, including biomass creation	–	–	RZWQM default values used for all parameters	Bartling and others (2011)
Initial sizes of aerobic, autotrophic and anaerobic microbial populations	–	–	Computed by RZWQM from soil organic matter content (f_{om}) for each soil horizon	Bartling and others (2011)
Arrhenius parameters for soil organic matter decay	–	–	RZWQM default values used for all parameters	Bartling and others (2011)
Arrhenius parameters for rates of microbial death	–	–	RZWQM default values used for all parameters	Bartling and others (2011)
Atrazine application				
Land-use settings	Agricultural settings only	Data on spatial distributions of non-agricultural use are not available on a national scale	Agricultural settings only	Same reasoning as for Phase 1
Application frequency	Once per year	Common practice	Once per year	Common practice
Application date	May 2	One day after planting	May 31	One day after planting
Application method	Surface applied (not incorporated)	Common practice	Surface applied (not incorporated)	Common practice

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Application intensity (mass applied per unit area)	<ul style="list-style-type: none"> Option 1: Uniform intensity (2 kg a.i./ha) Option 2: Areally averaged intensities (eq. 10; fig. 1) 	<p>Atrazine application—Continued</p> <ul style="list-style-type: none"> Option 1: Within range for small-scale studies Option 2: U.S. Geological Survey (2014) 	Uniform intensity (2 kg ai/ha)	Preliminary simulations using areally averaged atrazine application intensities resulted in predicted atrazine and DEA concentrations that were less than the reporting limits at all sites.
Application efficiency	95 percent (surface applied)	Estimated	Not quantified	—
Partitioning and transport of atrazine (Phases 1 and 2) and DEA (Phase 2 only)				
Initial concentrations of atrazine and DEA on plant and residue surfaces, and in soil.	Set to zero	All atrazine presumed to have come only from atrazine applied during simulations	Set to zero	All atrazine and DEA was presumed to have come only from atrazine applied during simulations.
Atmospheric input	Assumed negligible	—	Assumed negligible	—
Washoff from crop foliage and crop residues	Assumed negligible	—	<ul style="list-style-type: none"> Proportion of each compound in washoff from plant residue assumed to be identical to that from plant surfaces (Ahuja and others, 2000) Quantified using two parameters from equation of Willis and others (1980): washoff fraction (F_{wo}) and washoff power (P_{wo}) (eqs. 17 and 18) Values of F_{wo} and P_{wo} used for atrazine (obtained by Malone and others [2001] through calibration of RZWQM): $F_{wo} = 0.8$ (80 percent) $P_{wo} = 0.015 \text{ mm}^{-1}$ Values of F_{wo} and P_{wo} used for DEA (obtained by scaling values for atrazine with a QPPR [eq. 19] according to the water solubilities of the two compounds): $F_{wo} = 0.9$ (90 percent) $P_{wo} = 0.099 \text{ mm}^{-1}$ 	Washoff from crop foliage, although accounted for by the P-GWAVA-RZ simulations, was expected to be negligible because atrazine was applied prior to crop emergence.

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Mixing in soil prior to runoff	Not simulated	–	<p>Average degree of mixing between rainfall and soil solution (M_{avg}) expressed by RZWQM as an exponential function of depth in soil (z, in cm) as follows:</p> $M_{avg} = Ae^{-Bz}$ <p>where A is typically equal to unity (Agricultural Research Service, 2010) and B is an empirical parameter</p> <ul style="list-style-type: none"> For all sites: B = 4.4 cm⁻¹ 	<ul style="list-style-type: none"> Values of A and B selected to be consistent with those derived from a laboratory column study (Ahuja and others, 1995), and a field study employing a tilled soil (Malone and others, 2003) Values of A and B also consistent with RZWQM default values (Agricultural Research Service, 2010)
Partitioning between water and air (K_H)	Not simulated	–	<ul style="list-style-type: none"> Atrazine: Henry's law constant (K_H) value at 25 °C (2.88×10^{-4} Pa–m³/mol) obtained from Mackay and others (1997) DEA: K_H value for 25 °C (7.29×10^{-4} Pa–m³/mol) computed by dividing vapor pressure at 25 °C (Neely and Blau, 1985) by water solubility at 22 °C (Mills and Thurman, 1994) 	<p>K_H value for DEA presumed to represent value at 25 °C rather than 22 °C—because vapor pressure is substantially more sensitive to temperature than water solubility</p>
Correcting air-water partitioning (K_H) for variations in temperature	–	–	<p>K_H values for atrazine and DEA adjusted to T_{Meq} at each site using equation 11 and a value for enthalpy change from vapor to dissolved state (ΔH_v) of 47 kJ/mol (from Staudinger and Roberts, 2001)</p>	–
Volatilization from soil	Assumed negligible	–	<ul style="list-style-type: none"> Rate estimated by RZWQM as a nonlinear function of K_H, K_{oc}, and the molecular weight of the solute (Ahuja and others, 2000) Rate not explicitly corrected for variations in temperature or moisture content (Ahuja and others, 2000), except through temperature-correction of K_H 	–

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
First acid-base dissociation constant (pK_a)	–	–	Partitioning and transport of atrazine (Phases 1 and 2) and DEA (Phase 2 only)—Continued <ul style="list-style-type: none"> • <u>Atrazine</u>: Value (1.68) obtained as median among those compiled from literature by Mackay and others (1997); consistent with range of 1.65–1.8 reported from literature by Schmitt and others (1996) • <u>DEA</u>: Value (1.65) obtained from Schmitt and others (1996) 	–
Second acid-base dissociation constant (pK_b)	–	–	<ul style="list-style-type: none"> • <u>Atrazine</u>: Value (12.32) obtained from Mackay and others (1997) • <u>DEA</u>: No value available; presumed equal to that for atrazine (12.32) 	–
Octanol-water partition coefficient (K_{ow})	–	–	<ul style="list-style-type: none"> • <u>Atrazine</u>: Value (562) obtained from Mackay and others (1997) • <u>DEA</u> Value (45.7) computed as average of values obtained by employing a QSPR (eq. 12) to scale atrazine value using K_{ow} estimates computed by Finizio and others (1991) from HPLC retention times (44.6) and from the Hansch and Leo (1979) fragment method (46.8) 	–
Organic carbon-water partition coefficient (K_{oc})	$K_{oc} = 130$ mL/g (atrazine)	Median value among 73 values reported by 25 published studies	<ul style="list-style-type: none"> • Initial values used: <u>Atrazine</u>: 100 mL/g (Mackay and others, 1997) <u>DEA</u>: 57 mL/g, estimated by scaling from atrazine value selected by Mackay and others (1997) using a QSPR (eq. 16) • K_{oc} values for atrazine and DEA reduced by 75 percent to 25 and 14 mL/g, respectively, to bring simulated concentrations closer to those measured in groundwater 	Adjustment of K_{oc} constrained by two criteria: – Ratio between the values for the two compounds (atrazine and DEA) maintained – Selected values remained consistent with the ranges of values reported by previous studies for the two compounds

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Soil-water partition coefficient (K_d)	Partitioning and transport of atrazine (Phases 1 and 2) and DEA (Phase 2 only)—Continued <ul style="list-style-type: none"> Linear, reversible $K_d = f_{oc} K_{oc}$ (eq. 14) Different K_d value for each site 	See entries for f_{oc} and K_{oc}	<ul style="list-style-type: none"> Linear, reversible $K_d = f_{oc} K_{oc}$ (eq. 14) Different K_d value computed by RZWQM for each soil horizon 	<ul style="list-style-type: none"> Freundlich (non-linear) sorption simulation not yet operative in RZWQM (Bartling and others, 2011) See entries for f_{oc} and K_{oc}
Ratio of kinetic constants for adsorption to and desorption from soil surfaces (k_{ads}/k_{des}) [Ek2]	Not simulated	—	<ul style="list-style-type: none"> Value for atrazine, estimated using equations 20–22 and data reported from column experiments by Guo and others (1997): 0.65 cm³/g Value for DEA presumed to be equal to that for atrazine 	—
Kinetic constant for desorption from soil surfaces (k_{des}) [Rk2]	Not simulated	—	<ul style="list-style-type: none"> Value for atrazine, estimated from data reported from column experiments by Guo and others (1997) (see section, “Kinetic Controls on Sorption”): 0.12 h⁻¹ Value for DEA presumed to be equal to that for atrazine 	—
Hydrodynamic dispersion	Mimicked through numerical dispersion by setting dispersion coefficient (D) to zero	Approach recommended by Carsel and others (1998) in absence of field-derived values of D	Simulated through the combined effects of partial piston displacement, molecular diffusion of solutes between zones of mobile and immobile water, and sorption	Ahuja and others (2000)
Effective diffusion coefficient for solute movement between soil mesopores and micropores (D_d^{eff})	Not simulated	—	Computed by RZWQM for each soil horizon from soil bulk density (ρ_b), soil partition coefficient (K_d) volumetric water content (θ) and apparent diffusion coefficient (D_d) using equation 24	Ahuja and others (2000)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Partitioning and transport of atrazine (Phases 1 and 2) and DEA (Phase 2 only)—Continued				
Apparent diffusion coefficient (D_d)	—	—	Computed using a QMIPR (eq. 25) to scale the molecular diffusion coefficient in water (D_w) using the van Genuchten mass-transfer coefficient (α), estimated from clay content and cation exchange capacity (CEC) using a corrected version of a PTF provided by Shaw and others (2000) for bromide (eq. 26)	—
Molecular diffusion coefficient in water (D_w)	—	—	Estimated using the method of Hayduk and Laudie, recommended by Tucker and Nelkin (1990)	—
Plant uptake	Not simulated	—	Calculated by RZWQM as the product of plant water uptake rate, solute concentration in the soil water, and transpiration stream concentration factor (a non-linear function of K_{ow})	Ahuja and others (2000)
Chemical reactions involving atrazine and DEA				
Reference conditions from which transformation rates were adjusted	T_{ref} = average air temperature in May (T_{May})	—	<ul style="list-style-type: none"> $\theta_{ref} \equiv \theta_{FC} \equiv \theta_{33}$ (Ahuja and others, 2000), used to adjust rates of atrazine and DEA disappearance for variations in soil moisture (eq. 36) T_{ref} = average air temperature in May (T_{May}) $pH_{ref} = 7$ (used for computing fraction of atrazine that reacts to form DEA [$F_{air > DEA}$]) 	—
Rates of atrazine and DEA disappearance on plant foliage and crop residue	Neglected (see section entitled “Photochemical Transformations”)	—	Neglected (see section entitled “Photochemical Transformations”)	—
Rates of atrazine and DEA disappearance from photochemical transformation on soil surface ($k_{s,soil}$)	Neglected (see section entitled “Photochemical Transformations”)	—	Neglected (see section entitled “Photochemical Transformations”)	—

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Initial half-life for atrazine disappearance in oxic soil at T_{May}	<ul style="list-style-type: none"> Reaction rates presumed to be identical in the dissolved and sorbed states Initial rate at each site estimated for T_{May} using data reported for three loam soils by Walker and Zimdahl (1981) and equation 29 	–	<ul style="list-style-type: none"> Reaction rates presumed to be identical in dissolved and sorbed states Median half-life at 25 °C: 109 days (from Issa and Wood [1999]), selected from among 125 values reported by 7 laboratory studies Value adjusted to T_{May} using equation 30 	<p>E_a value used for these adjustments (50.9 kJ/mol) represented the median among 31 values that were retrieved or computed from 6 previous studies of the effects of temperature and other factors on atrazine disappearance rates in soil</p>
Half-life for atrazine disappearance in anoxic soil at T_{May}	Not simulated	–	<ul style="list-style-type: none"> Reaction rates presumed to be identical in dissolved and sorbed states Median half-life at 25 °C (372 days) estimated by adjusting value for oxic conditions (109 days) to anoxic conditions using data from Accinelli and others (2001) and a QMRR using equation 31 Value adjusted to T_{May} using equation 32 	<p>In the apparent absence of a more appropriate published value, the E_a value used to adjust reaction rates to T_{May} (50.9 kJ/mol) was identical to the value used to adjust rates of atrazine disappearance in oxic soil to T_{May}</p>
Percentage of reacted atrazine that forms DEA (DEA “formation percentage”), or $F_{atr \rightarrow DEA}$ at T_{May}	Not simulated	–	<ul style="list-style-type: none"> Computed for each SSURGO component as a function of %om and percent sand in the uppermost soil horizon and T_{May} using QMRRs (eqs. 38, B3, and B4) In absence of published data to the contrary, same value presumed to apply for both oxic and anoxic conditions 	–

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Initial half-life for DEA disappearance in oxic soil at T_{May}	Not simulated	–	<ul style="list-style-type: none"> Reaction rates presumed to be identical in dissolved and sorbed states Value estimated by employing a QSRR to scale the reaction rate for atrazine disappearance at T_{May} (obtained from eq. 30) using data reported by Kruger and others (1997) for DEA and atrazine reactions in oxic soil (eqs. 39 and 40) 	In the apparent absence of a more appropriate published value, the E_a value used to adjust reaction rates to T_{May} (50.9 kJ/mol) was identical to the value used to adjust rates of atrazine disappearance in oxic soil to T_{May}
Half-life for DEA disappearance in anoxic soil at T_{May}	Not simulated	–	<ul style="list-style-type: none"> Reaction rates presumed to be identical in dissolved and sorbed states Value estimated by employing a QSRR to scale the reaction rate for atrazine disappearance under anoxic conditions at T_{May} (obtained from eq. 32) using data reported by Kruger and others (1997) for DEA and atrazine reactions in anoxic soil (eqs. 41 and 42) 	In the apparent absence of a more appropriate published value, the E_a value used to adjust reaction rates to T_{May} (50.9 kJ/mol) was identical to the value used to adjust rates of atrazine disappearance in oxic soil to T_{May}
Adjustment of rates of disappearance of atrazine and DEA in soil for variations in temperature	<ul style="list-style-type: none"> Rates of atrazine disappearance in soil corrected for T_{May} at each site using equation 29 Arrhenius pre-exponential factor, A_0 (2,920,024 d⁻¹) and activation energy, E_a (46.2 kJ/mol) computed from data reported by Walker and Zimdahl (1981) 	–	<ul style="list-style-type: none"> Initial half-lives for the disappearance of atrazine and DEA at T_{May}—under either oxic or anoxic conditions—adjusted by RZWQM for subsequent temperature variations using the Arrhenius equation (eq. 33 for atrazine, eq. 43 for DEA) Activation energy (E_a) value used (50.9 kJ/mol) represented median among 31 values that were retrieved or computed from data reported by 6 laboratory studies 	In the apparent absence of a more appropriate published value, the E_a value used to adjust reaction rates to T_{May} for DEA (50.9 kJ/mol) was identical to the value used to adjust rates of atrazine disappearance in oxic soil to T_{May}

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
	Chemical reactions involving atrazine and DEA—Continued			
Adjusting transformation rates for variations in soil moisture	Not corrected. (PRZM provides moisture corrections of transformation rates for nutrients, but not for pesticides)	–	Accounted for by RZWQM using a variation of the Walker equation (eq. 36)	Data from previous studies of the effect of soil moisture content on disappearance rates appear to be available for atrazine, but not DEA, and only in oxic soils
Adjusting disappearance half-lives for variations in depth below land surface	Not corrected	–	<ul style="list-style-type: none"> Disappearance half-lives presumed by RZWQM to exhibit a uniform value ($[t_{1/2}]_{z=0}$) from the land surface to a depth of 25 cm, increase linearly from 25–100 cm depth, and exhibit a uniform value ($[t_{1/2}]_{z=100}$) below 100-cm depth (Ahuja and others, 2000) RZWQM uses V_{mif}, the ratio of the two values, ($[t_{1/2}]_{z=100} / [t_{1/2}]_{z=0}$), to adjust disappearance rates with depth (eqs. 45 and 46) V_{mif} values used: <ul style="list-style-type: none"> Atrazine: 6.58 DEA: 7.95 	Variations in transformation rates with depth are presumed to be a reflection of concomitant decreases in microbial populations, soil organic matter, nutrients and temperature with depth
Nitrogen application, transport, and fate				
Initial concentrations of nitrate, ammonia and urea in soil	–	–	Set to zero	All nitrogen species in the soil presumed to have come only from fertilizer applied during simulations
Form of nitrogen applied	–	–	N fertilizer only (as nitrate)	Nationwide data on manure-derived N applied to corn apparently not available at the time of study
Application date	–	–	First application on June 1 (2 days after planting)	–

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
	Nitrogen application, transport, and fate—Continued			
Application rate	–	–	Overall recommended N application rate calculated for corn as a function of desired yield (Y_{goal}), planting population (P_{pop}), and f_{oc} using the Missouri N algorithm (Ahuja and others, 2000)	See entries for Y_{goal} , P_{pop} , and f_{oc}
Application method	–	–	<ul style="list-style-type: none"> Applied in irrigation water (“fertigation”) No nitrification inhibitors used 	–
Nitrogen-related crop parameters (N content; efficiency of N uptake and use)	–	–	RZWQM default values (for the Generic Crop Growth Model for corn) used for all parameters	Bartling and others (2011)
Arrhenius parameters for conversions among different forms of nitrogen	–	–	RZWQM default values used for all parameters	Bartling and others (2011)
Fate	–	–	<ul style="list-style-type: none"> Lag time for nitrification to resume following application of anhydrous ammonia: 14 days Additional time required for nitrification to fully recover after it resumes following application of anhydrous ammonia: 14 days RZWQM default values used for other parameters Rates of formation and transformation of nitrate dependent upon microbial population sizes which, in turn, are dependent on relative sizes of organic-matter pools showing fast, medium and slow oxidation rates 	<ul style="list-style-type: none"> Bartling and others (2011) Ahuja and others (2000)

Table 14. Approaches used to obtain or estimate input parameter values for the simulations conducted with the P-GWAVA-PR (Phase 1) and P-GWAVA-RZ (Phase 2) modeling systems.—Continued

Process, factor, or parameter	Phase 1 (P-GWAVA-PR)		Phase 2 (P-GWAVA-RZ)	
	Approach	Rationales / remarks / data source(s)	Approach	Rationales / remarks / data source(s)
Output and calibration				
Water flow	Total flow past the 1-m assessment depth	–	Total flow past the 3-m assessment depth	Maximum depth in soil for which SSURGO data are available
Atrazine and DEA concentrations	FWM concentration of atrazine computed at the 1-m assessment depth using equation 47	–	FWM concentrations of atrazine and DEA computed at the 3-m assessment depth using equation 48	–
Nitrogen species concentration	Not simulated	–	<ul style="list-style-type: none"> • RZWQM predicts concentrations of nitrate plus ammonium, as well as the total amounts of N in different environmental compartments • Ammonium concentrations presumed negligible 	–
Input parameters or model features modified to improve fit between simulated and measured solute concentrations (table 4)	Grid cell size for 10–100 cm depth interval (final value: 30 cm)	–	<ul style="list-style-type: none"> • Spatially uniform atrazine application rate used, rather than the areally averaged rates, because atrazine concentrations simulated with the latter approach were below reporting limits at all sites • Approach for estimating atrazine disappearance rates changed from use of updated Fenner-Borsuk relation (eq. B3) to use of median among literature values reported for 25 °C • K_{oc} values for atrazine and DEA reduced to 25 percent of their median values from previous studies, while maintaining their relative magnitudes and remaining consistent with the range of values obtained from the published literature • Initial distribution of soil organic matter between fast, medium, and slow pools (2, 18, and 80 percent, respectively) adjusted to 10, 20, and 70 percent, respectively, to improve fit between simulated and measured nitrate concentrations 	–

Glossary

(*italicized* terms in text)

Active ingredient Chemical compound in a commercial pesticide formulation (for example, atrazine) that is included to kill or otherwise control the target pest.

Adjuvants Chemical compounds in a commercial pesticide formulation that are included to enhance the effectiveness of the active ingredient (often referred to as “inert ingredients”).

Aerobic Characterized by, or occurring in the presence of detectable concentrations of dissolved oxygen (that is, equal or greater than 0.5 mg/L).

Anaerobic Characterized by, or occurring under conditions where the concentrations of dissolved oxygen are low enough (typically less than 0.5 mg/L) to allow denitrification, iron reduction, manganese reduction, and (or) methanogenesis, to occur.

Anoxic Environmental condition (for example, within the subsurface or in a surface water body) where the concentrations of dissolved oxygen are low enough (typically less than 0.5 mg/L) to allow denitrification, iron reduction, manganese reduction, and (or) methanogenesis to occur.

Application intensity Areally averaged rate of delivery of a given substance (for example, a pesticide) to the land surface.

Assessment depth Depth within the soil column where flow-weighted estimates of solute concentration or recharge were computed from computer simulations.

Atrazine residue yield The mole percentage of applied atrazine represented by the cumulative amount of atrazine and its transformation products that is either simulated or observed to have passed a particular depth in the subsurface over a specified period following atrazine application.

Available water capacity Amount of water in soil that is presumed to be available for uptake by plants, calculated as the water content at field capacity minus the water content at the wilting point.

Brooks-Corey parameters Variables used to describe simplified versions of the quantitative relations between soil matric suction and either hydraulic conductivity or water content.

Characteristic curve Functional relation describing the manner in which either water content or hydraulic conductivity vary with matric suction in the vadose zone.

Chemical ranking method A groundwater vulnerability assessment approach that differentiates among different potential contaminants on the basis of their propensity to reach groundwater in detectable concentrations following their application (either intentional or unintentional) to the land surface.

Chemograph Plot showing variations in concentration of a given solute in a given environmental medium (for example, water or soil) over time.

Cligen A program embedded in RZWQM to simulate weather.

Cold simulation Computer simulation conducted without calibration.

Compartment Environmental medium (for example, soil organic matter, plant tissues, crop residues, groundwater or surface water).

Complex model Computer model that simulates water movement using well-established equations derived from the fundamental principles of fluid flow.

Component Sequence of soil horizons described within a SSURGO or STATSGO map unit.

Continuous corn The practice of planting corn in the same field every year.

Corn-and-soybean area An agricultural location where corn and soybeans are grown in rotation.

Corn Belt Corn-growing areas of the northern midcontinental United States.

Correct prediction A model-simulated concentration that represents either a true positive or a true negative.

Cropping Period in the annual cycle of agricultural activity during which crops are grown.

Crust factor Ratio between the hydraulic conductivity of soil after it has been subjected to rainfall and the hydraulic conductivity of the same soil when it has been protected from rainfall.

Daughter product formation percentage Proportion of the mass of a compound that is transformed to another compound through either abiotic or biochemical processes.

DEA fraction Percentage of atrazine that is transformed to DEA through either abiotic or biochemical processes.

Dead-end pores Channels within a porous medium that are connected at one end to macropores, cracks or other continuous pores, and through which water flow is relatively restricted.

Degradate Transformation product.

Disappearance The aggregate influence of all processes, either biological or abiotic, that convert a compound to one or more transformation products.

Drainage rules Algorithms used to simulate the movement of water within a soil profile

Dry volume heat capacity The amount of energy required to raise the temperature of a dry material (for this study, dry soil) by one degree (Fahrenheit or Kelvin), per unit volume.

Fallow Period in the annual cycle of agricultural activity, between harvest and planting, during which no crops are grown.

False negative A predicted non-detection of a chemical substance at a site where the substance was, in fact, detected.

False positive A predicted detection of a chemical substance at a site where the substance was not, in fact, detected.

Fast organic matter Soil organic matter that is metabolized relatively rapidly by soil microorganisms.

Fertigation The practice of applying fertilizer in water used for irrigation.

Field capacity The water content remaining in the soil after most gravity drainage has ceased.

Groundwater vulnerability Likelihood of detecting a particular surface-derived contaminant at a concentration equal to or greater than a given value (such as its reporting limit or a water-quality criterion) in shallow groundwater.

Immobile water Water contained in dead-end pores and other locations within the soil where water flow is restricted or stagnant, and solute movement occurs predominantly through diffusion, rather than advection.

Incorrect prediction A model-simulated concentration that represents either a false positive or a false negative.

Index method A groundwater vulnerability assessment approach that uses linear combinations of semi-arbitrary numerical values that have been assigned to specific ranges or categories of explanatory variables in order to identify spatial variations in the likelihood with which a specific chemical will reach groundwater in detectable concentrations following its application (either intentional or unintentional) to the land surface. Also referred to as a *scoring method*.

Lumped process An overall process that is the result of several individual processes occurring simultaneously (for example, the disappearance of a compound that results from several different transformation processes taking place at the same time).

Macropores Root channels, worm burrows, cracks or other conduits in the soil in which the aqueous phase is predominantly mobile water, and through which water and solutes move relatively rapidly by advection.

Map unit Irregularly shaped area containing a particular soil type (or set of soil types), as specified by the SSURGO and STATSGO soil databases of U.S. Department of Agriculture Natural Resources Conservation Service. Map units are irregularly shaped because their boundaries are determined by the spatial distributions of the soil type(s) they contain.

Medium organic matter Soil organic matter that is metabolized at an intermediate rate by soil microorganisms.

Mesopores Voids within the soil that are intermediate in size between micropores and macropores, and through which water and solutes move by both advection and diffusion.

Microbial adaptation The observed increase in the rate of microbial transformation of a pesticide or other applied compound that occurs in the soil with repeated applications of the compound.

Micropores Voids within the soil matrix that are sufficiently small that any water they contain is considered to be immobile water, and solute movement occurs primarily through diffusion.

Mobile water Water within macropores, cracks, mesopores and other regions within the soil where the rates of water flow are comparatively high, and solute movement occurs primarily by advection, as well as by diffusive exchange with regions of immobile water.

Model residual A measure of the agreement between the value of a given parameter (such as a solute concentration or detection frequency, or recharge rate) predicted by a computer simulation and its corresponding measured value, quantified for this report as the simulated value minus the measured value.

Nonleacher A chemical that purportedly will not reach groundwater in detectable concentrations following its release (either intentional or unintentional) to the land surface.

Overlay method A groundwater vulnerability assessment approach that uses a superposition of multiple data layers related to climate, soil properties, and other site-specific parameters to identify spatial variations in the likelihood with which a specific chemical will reach groundwater in detectable concentrations following its release (either intentional or unintentional) to the land surface.

Oxic An environmental condition (for example, within the subsurface or in a surface water body) where detectable concentrations of dissolved oxygen are present (that is, equal to or greater than 0.5 mg/L).

Pedotransfer function (PTF) A statistical relation that is used to estimate a particular soil parameter (for example, water content at field capacity) from other properties of the soil (for example, sand content).

Pesticide A chemical that is used to kill or otherwise control unwanted plants, insects or other organisms.

Pool A specific form of soil organic matter, the formation and decay of which are simulated by RZWQM.

Post-harvest Period in the annual cycle of agricultural activity between harvest and planting.

Raised reporting limit A reporting limit that is temporarily elevated relative to the one that is usually used for the analyte of interest (the routine reporting limit) because of matrix interferences, instrument issues, or other transient circumstances.

Redistribution Gradual movement of water between micropores, mesopores and macropores within soil that occurs between significant recharge events.

Residual water content Fitting parameter in the Brooks-Corey water-content curve that is often inferred to be the water content of a soil at infinite suction, when water can no longer be extracted under suction.

Retention time Amount of time required for a chemical to migrate through a chromatographic column under specified conditions.

Routine reporting limit Reporting limit for a given analyte that is most commonly used for a particular analytical method.

Scoring method A groundwater vulnerability assessment approach that uses linear combinations of semi-arbitrary numerical values that have been assigned to specific ranges or categories of explanatory variables in order to identify spatial variations in the likelihood with which a specific chemical will reach groundwater in detectable concentrations following its application (either intentional or unintentional) to the land surface. Also referred to as an *index method*.

Shallow groundwater Groundwater located a relatively short distance below the water table (for this report, within a depth of 6.3 ± 0.5 m below the water table).

Simple model Computer model that simulates water movement using a simplified, tipping-bucket approach.

Simulation period Time interval during which a computer model simulates a given process or set of processes (for example, the transport and fate of solutes within soil).

Slow organic matter Soil organic matter that is metabolized relatively slowly by soil microorganisms.

Soil hydrologic group A class of soil that is characterized by a particular range of permeability, runoff potential, swelling potential and other hydrologic properties.

Stabilization period Time interval at the beginning of a computer simulation that is used to dissipate the transient response to the initial conditions specified.

Stream-tube model A numerical model that simulates the movement of water and solutes in one dimension (as if through a narrow tube).

Study unit Major hydrologic basin in which water quality has been examined by the NAWQA program.

Subsurface All regions below the land surface, including the vadose and saturated zones.

Thermal reactions

Transformations of a chemical that are driven by the kinetic energy of the reactants, rather than by the input of photochemical energy.

Thiessen polygon Geographical region surrounding a particular location, or sample point, at which the value of a particular parameter (for example, a meteorological variable such as air temperature) is presumed to be known. Each Thiessen polygon defines an area of influence around its sample point such that any location inside the polygon is closer to that point than to any of the other sample points.

Tipping bucket A simplified approach for simulating downward water movement through a soil profile, in which water collects in each individual depth increment until a particular water-content threshold is exceeded (the bucket “tips”) and the water is allowed to flow to the next layer below.

Tortuosity Degree to which a path between two points deviates from a straight line.

True negative A predicted non-detection of a chemical substance at a site where the substance was, in fact, not detected.

True positive A predicted detection of a chemical substance at a site where the substance was, in fact, detected.

Use intensity *See application intensity.*

Wilting point Soil water content below which most plants are not able to extract water from the soil.

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Appendix A. Previous Assessments of Groundwater Vulnerability

Previous groundwater vulnerability assessments (GWAVAs) have spanned more than three decades. Several earlier reviews provided summaries and classifications of the various approaches that have been used by GWAVAs in the past (for example, National Research Council, 1993; U.S. Environmental Protection Agency, 1993; Barbash and Resek, 1996; Corwin and others, 1997; Nolan, 1998; Focazio and others, 2002; Pavlis and others, 2010). [Table A1](#) lists key features of several GWAVAs that were either not included in these reviews or mentioned only briefly by them. For the sake of brevity, the table excludes publications that provided updates of GWAVAs already described in one or more of the earlier reviews (for example, Druliner and others, 1996; Kellogg and others, 2000; Kookana and others, 2005). The GWAVAs listed in the table involved characterizing groundwater vulnerability either with respect to different compounds (*chemical ranking methods*) or among geographic locations; none of the investigations examined changes in groundwater vulnerability over time. The studies are presented in general groups that represent an expansion of the framework originally provided by the National Research Council (1993). Several of the investigations, however, could have been placed in more than one category, such as those using regression methods to assess vulnerability using chemical indicators (Lopes, 2006), multiple data layers (for example, Nolan and Hitt, 2006; Stackelberg and others, 2006, 2012), or the results from process-based simulation modeling (for example, Gurdak and Qi, 2006).

Chemical Ranking Methods

Many of the chemical ranking methods that have been proposed to date incorporate site-specific characteristics such as soil properties, estimated recharge rates, or agronomic practices (for example, Jury and others, 1987; Rao and others, 1985; Goss, 1992; Vickery, 2000; Reus and others, 2002). The chemical ranking approaches that do not incorporate such information (for example, Laskowski and others, 1982; Britt and others, 1992)—including the widely cited Groundwater Ubiquity Score (Gustafson, 1989; Suzuki and others, 1998; Fava and others, 2000; Barra Caracciolo and others, 2005; Kördel and others, 2008; Milfont and others, 2008; Silva and others, 2012)—have the drawback of neglecting the potential influence of local environmental and land-use factors on contaminant mobility and persistence in the subsurface. Perhaps the greatest concern associated with the chemical

ranking methods, however, is that several pesticides that these techniques have predicted would not reach groundwater—compounds often referred to as *nonleachers* (Creeger, 1986; Gustafson, 1989; Cohen, 1990; Johnson, 1991; Barra Caracciolo and others, 2005; Silva and others, 2012)—have, in fact, been detected in groundwater (Barbash and Resek, 1996; U.S. Geological Survey, 2012).

Overlay Methods

Most of the fundamental mathematical relations among the various physical, hydrologic, chemical, and biological parameters that control the transport and fate of contaminants in the subsurface have been known for more than three decades (for example, van Genuchten and others, 1977; Freeze and Cherry, 1979). However, before high-speed computers became widely available, it was largely infeasible to use these equations to conduct GWAVAs over large spatial scales. As a result, many methods have been devised to infer spatial variations in the likelihood of detecting surface-derived contaminants in groundwater on the basis of one or more environmental and (or) anthropogenic factors known to affect contaminant transport and fate. The simplest of these approaches have been *overlay methods*, in which differences in vulnerability among locations are identified on the basis of geographic variations in the values of one or more explanatory parameters, all of which are weighted equally.

Index and Scoring Methods

By contrast with overlay methods, *scoring or index methods* use linear combinations of semi-arbitrary numerical values that are assigned to specific ranges or categories of selected explanatory variables to infer spatial variations in groundwater vulnerability to contamination by surface-derived chemicals. Among these methods, the most well-known and widely used has been the DRASTIC system (Aller and others, 1987; Banton and Villeneuve, 1989). Such systems provide some indication of the relative vulnerability of groundwater to contamination among land-use settings, but neither the magnitudes of the scores (or indexes) that have been assigned to different parameter ranges or system characteristics (for example, well depths, types of geologic materials, or land-use settings), nor the relative weights assigned to these factors,

have been shown to be correlated with the magnitudes of specific, measurable parameters. These and other difficulties with scoring and indexing systems have been discussed in detail (see, for example, U.S. Environmental Protection Agency, 1993; Barbash and Resek, 1996). Despite these shortcomings, [table A1](#) indicates that GWAVA systems using scoring and weighting schemes continue to be proposed (for example, Zhang and others, 1996; Hamerlinck and Arneson, 1998a, 1998b; Vickery, 2000; Rupert, 2001; Reus and others, 2002; Cook and Baker, 2006), although their use has been discouraged (Alley, 2000).

Hydrogeologic or Chemical Indicator Methods

Several investigations have used indirect methods to infer the likelihood that surface-derived contaminants may be detected in groundwater. At least two such studies have focused solely on hydrogeologic phenomena, on the basis of responses of water-table depth to variations in atmospheric pressure (Landmeyer, 1996) or measured rates of recharge (Nolan and others, 2003). All the other studies listed for this category in [table A1](#) (as well as all the studies listed in other categories where one or more indicator solutes are listed in the table) used either the concentrations or simply the detection of other solutes as indirect indicators of the potential for surface-derived contamination. Many of these solutes are clearly anthropogenic (for example, synthetic pesticides, chlorofluorocarbon compounds [CFCs] and other volatile organic compounds [VOCs]). Others represent naturally occurring indicators of hydrologic connection with the land surface, the magnitudes of which may also have been influenced by human activities (for example, $^2\text{H}/^1\text{H}$, $^{16}\text{O}/^{18}\text{O}$, or the concentrations of ^3H [tritium], ^{14}C , SF_6 , nitrate, iron, or other redox-active solutes). One limitation that all these indicator methods share, however, is that they require the availability of locally derived data, and therefore cannot be used to infer groundwater vulnerability in areas where the concentrations (or ratios) of these indicators have not been measured.

Statistical Models

Early awareness of the problem of groundwater contamination by surface-derived anthropogenic compounds in the 1970s led to the initiation of efforts to collect data on the occurrence of pesticides (Cohen and others, 1984), VOCs (Barbash and Roberts, 1986), and other contaminants (Pye and Patrick, 1983) in groundwater over large spatial scales. The availability of results from such large-scale sampling

investigations, coupled with technological improvements in computational speed and software, made it possible to examine statistical relations between quantitative measures of the occurrence of contaminants in groundwater across large geographic areas and the various explanatory variables that govern their likelihood of detection in the subsurface. As indicated by [table A1](#), such statistical models—which use logistic regression, linear regression, neural networks and other multivariate techniques—are among the most commonly used approaches for predicting spatial patterns in the occurrence of surface-derived contaminants in groundwater. These efforts have involved the construction and application of statistical GWAVAs across a broad spectrum of spatial scales, ranging from individual counties (Burow and others, 1998), to major hydrologic basins (Rupert, 1997; Tesoriero and Voss, 1997; Frans, 2000), individual states (Ryker and Williamson, 1996), large multi-state regions (Nolan, 1999; Gurdak and Qi, 2006), and the entire Nation (Squillace and others, 1999a, 1999b; Kolpin and others, 2002; Nolan and Hitt, 2006; Stackelberg and others, 2006, 2012).

A related use of statistical methods to identify the controls on groundwater chemistry involves the application of principal components analysis (PCA) to water-quality data. Nolan (1999) applied PCA to the concentrations of a broad range of chemical constituents to examine the possible geochemical reasons that nitrate has been detected in groundwater in the southeastern United States much less frequently than might have been expected from the high rates of fertilizer and manure application in that region. Troiano and others (1998, 1999, 2000) devised an approach that uses cluster analysis, PCA, and other related methods to distinguish locations in agricultural areas of California where pesticides are likely to be detected in groundwater from those where pesticides are not likely to be detected. Burow and others (1998) used PCA over a more limited geographic area in California to investigate correlations among pesticide detections, soil characteristics, and concentrations of several major ions and redox-sensitive solutes in shallow groundwaters beneath agricultural areas of the eastern San Joaquin Valley. PCA was also used by Ator (2008), in conjunction with logistic regression, to examine the extent to which similar predictive variables explained the occurrence of pesticides, nitrate, VOCs, and major ions in shallow groundwater beneath the Northern Atlantic Coastal Plain. Stackelberg and others (2012) used PCA to develop a site-based parameter referred to as a “residence time indicator” that explained 25 percent of the variability in the summed concentrations of atrazine and deethylatrazine (DEA) predicted in groundwater across the United States by a Tobit regression model—half of the total variability explained by the overall model (pseudo- $R^2 = 0.50$). Silva and others (2012) used joint correspondence analysis—a technique similar to PCA—to examine some of the factors related to pesticide occurrence in shallow groundwater in central Portugal.

Process-Based Simulation Methods

The equations introduced for most of the statistical GWAVA methods that have been described to date are empirical relations among a specific set of explanatory and response parameters for a particular compound, time period, and spatial domain. As a result, such equations typically exhibit substantial differences from one study to the next with respect to the sets of parameters that they include (table A1), the magnitudes of the coefficients assigned to a given parameter and, in some cases, the mathematical transformations to which individual parameters are subjected (for example, compare Rupert, 2003 with Stackelberg and others, 2006). By contrast, the equations that have been elucidated by mechanistic studies of solute transport and fate in the hydrologic system are conceptually designed to be independent of the specific location, time, or compound in question, although calibration for specific applications may result in variations in the values of individual coefficients among different studies.

Thus, one of the primary advantages of a simulation-based approach for assessing the vulnerability of groundwater to surface-derived contamination, relative to the other methods listed in table A1, is that it can, in principle, predict contaminant occurrence among different compounds, locations or times with little or no additional modification. Another advantage of using process-based simulations for GWAVAs is that the equations used for such simulations can, with the selection of suitable values for their input parameters, be used to predict the effects of a variety of different land-management techniques, chemical use patterns or climate change on the transport and fate of the solutes of interest without further modification. To be useful, such an approach requires that these equations provide relatively accurate descriptions of the physical, hydrologic, chemical and biological processes that control the transport and fate of surface-derived solutes in the subsurface (Focazio and others, 2002). Model calibration may be used, however, to improve the accuracy of the resulting predictions by adjusting the values of individual parameters that cannot be measured easily (for example, parameters associated with hydrodynamic dispersion or pore dimensions) or, for parameters with multiple independent measurements reported by earlier studies, by adjusting the parameter values within the ranges established by previous research.

Most early applications of numerical models in the field of contaminant hydrogeology involved using computer simulations to predict the transport and fate of individual solutes in soils contained in laboratory columns or beneath individual fields (Anderson, 1979). Indeed, systematic discrepancies between the simulated and observed behavior of solutes in these experimental systems led to the discovery of some of the complex phenomena that are now known to affect solute transport and fate in porous media, such as preferential transport (for example, van Genuchten and others, 1977; Bilkert and Rao, 1985) and kinetically controlled sorption (for example, van Genuchten and others, 1974; James and Rubin, 1979). Numerous studies to date have used solute transport-and-fate simulations to predict the concentrations of contaminants in the subsurface at selected sites across the Nation (for example, Jones and others, 1986; Shaffer and Penner, 1991; Flury, 1996; Cowdery, 1997; Mullaney and Grady, 1997; Saad and Thorstenson, 1998; Burow and others, 1999; Tesoriero and others, 2000, 2001; Bayless, 2001; Malone and others, 2004b; Bayless and others, 2008; McMahon and others, 2008; Webb and others, 2008; Nolan and others, 2010; Webb and others, 2011; Liao and others, 2012).

Dramatic improvements in the availability of large-scale electronic repositories for data on soil properties, weather, land use, and other environmental information (for example, Carsel and Jones, 1990; U.S. Environmental Protection Agency, 2007; Kipka and others, 2013; Natural Resources Conservation Service, 2014; U.S. Geological Survey, 2014)—as well as advances in computational speed and in the sophistication of numerical techniques—have facilitated the practice of linking solute transport-and-fate models with geographic information systems to predict the concentrations of surface-derived solutes in the subsurface over large spatial scales (Corwin and others, 1997; Eason and others, 2004; Sood and Bhagat, 2005). Many of the process-based assessments to date, however, did not compare their predictions with actual monitoring data on the occurrence of the target solutes in groundwater (table A1). Furthermore, most of the comparisons that have been carried out between simulated and measured concentrations in groundwater have been applied across spatial scales ranging from individual fields to counties (for example, Khakural and Robert, 1993; Wu and others, 1996). Relatively few such studies to date have focused on regional to national scales (for example, Holman and others, 2004; Mouvet and others, 2004; Tiktak and others, 2005; Nolan and others, 2012).

Table A1. Groundwater vulnerability assessment systems (GWAVAs) that were not included, or mentioned only briefly, in earlier reviews.

[Previous reviews were published by National Research Council (1993), U.S. Environmental Protection Agency (1993), Barbash and Resek (1996), Corwin and others (1997), Nolan (1998), Focazio and others (2002), and Pavlis and others (2010). **Contaminant use or release:** Includes direct measures of use, such as pesticide, fertilizer or manure application rates, as well as indirect measures of use, that is, land use (LU), population density (PD) and proximity to areas of likely use (PALU) such as residential, agricultural, or livestock-confinement areas. **Hydrogeology:** Includes parameters related to water-table depth, hydraulic conductivity, recharge rates, subsurface geology, subsurface residence times, proximity to surface waters and, for the Environmental Performance Indicator for Pesticides (Reus and others, 2002), the (undefined) “vulnerability of aquifer.” Hydrogeology also includes parameters related to well characteristics, that is, depth of well screen below water table (DWS), well age (WA), well depth (WD) and well type (WT). **Predictions compared with independent monitoring data:** Indicates whether or not predictions from the method of interest were compared with actual observations of contaminant occurrence in groundwater or soil, either in the cited reference or in other publications cited in the reference. Because the statistical models are derived from monitoring data, a “yes” in this column for these models implies that the cited study included a comparison between model simulations and a set of data different from those used to develop the model. **Abbreviations:** ³H, tritium; ³He, helium-3; ¹³C, carbon-13; ¹⁴C, carbon-14; CaCO₃(s), calcium carbonate (solid); CFCs, chlorofluorocarbon compounds; E_H, oxidation-reduction potential, referenced to hydrogen; Fe, iron; H, hydrogen; K_{oc}, organic carbon-water partition coefficient; Mn, manganese; O, oxygen; O₂, dissolved oxygen; NH₃, ammonia; NO₃, nitrate; NO₂, nitrite; SF₆, sulfur hexafluoride; SO₄, sulfate; VOCs, volatile organic compounds]

Reference or system name (reference)	Types of parameters used to assess vulnerability							Predictions compared with independent monitoring data
	Contaminant properties	Contaminant use or release	Soil properties	Hydro-geology	Weather data	Agronomic practices	Indicator chemical concentrations	
Chemical ranking methods								
Johnson, 1991	✓							Yes
Kookana and Aylmore, 1994	✓		✓		✓			Yes
McLaughlin and others, 1993, 1994	✓	✓	✓			✓		No
Newman, 1995	✓	✓					Pesticides	No
Hippe and Hall, 1996	✓		✓					Yes
Shukla and others, 1996	✓	✓	✓					Yes
Kolpin and others, 1998	✓	✓						Yes
IATP, 2000 ¹	✓	✓	✓			✓		No
Worrall and others, 2000	✓							Yes
Environmental Performance Indicator for Pesticides ¹ (Reus and others, 2002)	✓	✓		✓		✓		No
Environmental Potential Risk Indicator for Pesticides ^{1,2} (Reus and others, 2002)	✓	✓	✓	✓				No
Environmental Yardstick for Pesticides ² (Reus and others, 2002)	✓	✓	✓	✓	✓	✓		No
Hasse Diagram (Reus and others, 2002)	✓	✓						Yes
Pesticide Environmental Impact Indicator ¹ (Reus and others, 2002)	✓	✓	✓			✓		No
Pesticide Environmental Risk Indicator ¹ (Reus and others, 2002)	✓	✓	✓		✓			No
SYNOPS_2 (Reus and others, 2002)		✓						No
System for Predicting the Environmental Impact of Pesticides ^{1,2} (Reus and others, 2002)	✓	✓	✓	✓	✓	✓		No
Overlay methods								
Carter, 1989			✓					No
Lemme and others, 1990			✓	✓				No
Loague and others, 1990	✓		✓	✓	✓			No
Hollis, 1991	✓	LU	✓	✓	✓			No
Hoyer and Hallberg, 1991				✓				No
McKenna and Keefer, 1991				✓				No
Rupert and others, 1991			✓	✓		✓		No
Leidy and Taylor, 1992 ²		✓		✓				No
Lampman, 1995			✓					Yes
Richards and others, 1996		LU	✓	WA, WD, WT				Yes
Ryker and Williamson, 1996		LU		WD			NO ₃	No
Nolan and others, 1997		✓; LU	✓					Yes

Table A1. Groundwater vulnerability assessment systems (GWAVAs) that were not included, or mentioned only briefly, in earlier reviews.—Continued

Reference or system name (reference)	Types of parameters used to assess vulnerability							Predictions compared with independent monitoring data
	Contaminant properties	Contaminant use or release	Soil properties	Hydro-geology	Weather data	Agronomic practices	Indicator chemical concentrations	
Overlay methods—Continued								
Desimone and Ostiguy, 1999		LU	✓	✓			NO ₃	Yes
Lin and others, 1999			✓	✓				Yes
Bernknopf and others, 2001	✓		✓	✓				No
Lowe and Sanderson, 2003	✓		✓	✓		✓		No
Pfaff and Glennon, 2004		LU						No
Miller and others, 2006		✓	✓	✓; WD		✓		Yes
Index and scoring methods								
Corte-Real, 1986	✓	✓; LU	✓	✓		✓		No
Schmidt, 1987			✓	✓				No
Porcher, 1989			✓	✓				No
Trojan and Perry, 1989			✓	✓	✓			No
Chilton and others, 1990	✓	LU		✓				Yes
DeLuca and others, 1990; National Park Service, 2009	✓	✓	✓	✓		✓		No
Ray and O'dell, 1993				✓				No
Seelig, 1994	✓		✓	✓			CaCO ₃ (s)	No
Engel and others, 1996	✓	✓	✓	✓				Yes
Vowinkel, 1996		LU	✓	✓; WD				Yes
Zhang and others, 1996			✓	✓				No
Rupert, 1997		✓; LU		✓				Yes
Hamerlinck and Arneson, 1998a,b		✓	✓	✓	✓			No
Hanson, 1998			✓	✓				Yes
Arizona Department of Environmental Quality, 2000	✓	✓	✓	✓				No
Cook and Baker, 2006			✓	✓	✓	✓		Yes
Hydrogeologic or chemical indicator methods								
Landmeyer, 1996				✓				No
Thomas, 2000							Pesticides, NO ₃	No
Nelms and others, 2003				✓; WT			CFCs, SF ₆ , ³ H, ³ He, ¹⁴ C, ¹³ C	No
Moran and others, 2002							H and O isotopes, VOCs	Yes
Trojan and others, 2002							O ₂ , E _H , Fe	Yes
Nolan and others, 2003			✓	✓				Yes
Worrall and Kolpin, 2003							Pesticides	No
Tesoriero and others, 2004							Major ions, redox-active solutes	Yes
Manning and others, 2005							³ H, ³ He	Yes
Lopes, 2006			✓	✓			CFCs, NO ₃ , H and O isotopes, VOCs, pesticides	Yes
Rupert and Plummer, 2009			✓	✓	✓		CFCs, NO ₃ , H and O isotopes, VOCs, pesticides	No
Statistical models								
Anderson and others, 1985	✓	✓	WD		✓	✓		No
Steichen and others, 1988 ¹		LU; PALU		WA				No
Tesoriero and Voss, 1997		LU		✓; WD	✓			Yes
Troiano and others, 1998, 1999		✓	✓	✓	✓		Pesticides	Yes
Rupert, 1998		LU	✓	WD	✓	✓		Yes
Tesoriero and others, 1998		LU		✓; WD	✓			Yes

Table A1. Groundwater vulnerability assessment systems (GWAVAs) that were not included, or mentioned only briefly, in earlier reviews.—Continued

Reference or system name (reference)	Types of parameters used to assess vulnerability							Predictions compared with independent monitoring data
	Contaminant properties	Contaminant use or release	Soil properties	Hydro-geology	Weather data	Agronomic practices	Indicator chemical concentrations	
Statistical models—Continued								
Lin and others, 1999	✓	✓	✓	✓			Nutrients, major ions	No
Squillace and others, 1999b		✓; LU; PD			DWS			No
Squillace and others, 1999a		PD						Yes
Frans, 2000		✓	✓		WD			No
Kolpin and others, 2000	✓	✓						No
Nolan, 2001		✓; LU; PD	✓	✓				No
Rupert, 2001 ¹		LU	✓	✓				Yes
SCIGROW (U.S. Environmental Protection Agency, 2001)	✓	✓						No
Kolpin and others, 2002		✓	✓	✓			Total dissolved N (NO ₂ + NO ₃ + NH ₃) ³	No
Nolan and others, 2002		✓	✓	✓				Yes
Ramasamy and others, 2003		PALU			Season		Fe	Yes
Rupert, 2003		✓	✓	✓; WT	✓			Yes
Worrall and Kolpin, 2004	✓		✓	✓				No
Greene and others, 2005		LU	✓	✓		✓		Yes
Gurdak and Qi, 2006 ²			✓	✓		✓		No
Nolan and Hitt, 2006		✓		✓		✓		Yes
Sahoo and others, 2006				✓; WD, DWS				Yes
Stackelberg and others, 2006		✓	✓			✓		No
Fram and Belitz, 2011 ¹		LU; PALU		✓; WD, DWS	✓		NO ₃ , pesticides, solvents, fuel compounds, trihalomethanes, other redox-active solutes	No
Hynds and others, 2012		LU; PALU	✓	✓; WT, DWS	✓			Yes
Stackelberg and others, 2012		✓	✓	✓	✓	✓	NO ₃ , other redox-active solutes, major ions, pH	Yes
Process-based simulation methods								
Petach and others, 1991; Hutson, 1993	✓	✓	✓		✓			No
Goss, 1992; Goss and others, 1998	✓	✓	✓		✓	✓		No
Hoag and Hornsby, 1992	✓							No
Foussereau and others, 1993	✓	✓	✓		✓			No
Khakural and Robert, 1993		✓	✓		✓			Yes
Franklin and others, 1994	✓	✓						No
Bleecker and others, 1995		✓	✓		✓	✓		No
Görres and Gold, 1996		✓	✓			✓		No
Soutter and Pannatier, 1996	✓	✓	✓		✓			No
Tiktak and others, 1996	✓	✓	✓		✓	✓		No
Wilson and others, 1996	✓	✓	✓		✓			No
Wu and others, 1996		✓	✓		✓	✓		Yes
Zhang and others, 1996			✓	✓				No
Williamson, 1997	✓	✓	✓	✓	✓	✓		No
Holtschlag and Luukkonen, 1998	✓ ⁴		✓	✓	✓		CFCs	Yes
Hoogeweg and Hornsby, 1998	✓	✓	✓		✓	✓		No
Snyder and others, 1998				✓				Yes
Morgan, 1999, 2002	✓		✓	✓	✓	✓		No

Table A1. Groundwater vulnerability assessment systems (GWAVAs) that were not included, or mentioned only briefly, in earlier reviews.—Continued

Reference or system name (reference)	Types of parameters used to assess vulnerability							Predictions compared with independent monitoring data
	Contaminant properties	Contaminant use or release	Soil properties	Hydro-geology	Weather data	Agronomic practices	Indicator chemical concentrations	
Process-based simulation methods—Continued								
van Wesenbeeck and Havens, 1999	✓	✓	✓		✓			No
Macur and others, 2000	✓	✓	✓		✓	✓		Yes
Ulery, 2000; Ulery and Rogers, 2005		✓	✓	✓				Yes
Schlosser and McCray, 2002	✓		✓	✓				No
Schlosser and others, 2002	✓		✓	✓				Yes
Stewart and Loague, 2003	✓	✓	✓	✓				No
Eason and others, 2004			✓		✓			No
Holman and others, 2004	✓	✓	✓		✓			Yes
Jørgensen and others, 2004	✓		✓	✓	✓			No
Mouvet and others, 2004	✓	✓	✓	✓	✓			Yes
Tiktak and others, 2005	✓	✓	✓	✓	✓	✓		Yes
Clark and others, 2006		✓		✓				Yes
FOOTPRINT project (Dubus, 2006)	✓	✓	✓	✓	✓	✓		No
Jackson and others, 2006	✓	✓	✓	✓	✓			No
Almasri and Kaluarachchi, 2007	✓	✓	✓	✓		✓		Yes
Kauffman and Chapelle, 2010	✓		✓	✓	✓		pH, O ₂ , NO ₃ , Fe, Mn, SO ₄	Yes
Miller, 2010	✓	✓	✓		✓	✓		No
Kourakos and others, 2012		✓		✓				No
Nolan and others, 2012		✓	✓		✓	✓		Yes

¹Method also involves the use of numerical scores or indices to quantify one or more of its explanatory factors.

²Method also incorporates results from simulations of solute transport.

³Explanatory parameters considered in constructing the statistical model (though not included in its final form) also included pH and the concentrations of dissolved oxygen, iron, phosphorus, and chloride measured in groundwater at the time the concentrations of the target contaminants (atrazine and metolachlor) were measured.

⁴Study involved adjusting K_{oc} and transformation half-life for atrazine within the ranges established by variations in literature values.

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Appendix B. Equations Used to Estimate Deethylatrazine Formation Percentage

Equation 38 was used to estimate the DEA formation percentage in each SSURGO component for which P-GWAVA-RZ simulations were carried out during Phase 2 of this study. Values of $k_{atr>DEA}$ and k_{atr} for equation 38 were estimated using modified versions of the Fenner-Borsuk equation, a quantitative medium-reactivity relation (QMRR) introduced by Fenner and others (2007) to predict the rates of atrazine disappearance in oxic, non-sterile soil in the dark. The original version of the Fenner-Borsuk equation, rearranged to present its two temperature-related terms in the same form as the others, may be expressed as follows:

$$\ln(k_{atr}) = -780.5 + (5.31 * \text{pH}) - (0.43 * [\text{pH}]^2) - (1.21 * \ln[\% \text{ sand}]) - (0.53 * \ln[d_{diff}]) \quad (\text{B1})$$

$$- (0.60 * \ln[\% \text{ oc}]) - (0.36 * \{\ln[\% \text{ oc}]\}^2) - (0.39 * \ln[d_{min}]) + \left(\frac{4.52 \times 10^5}{T} \right) - \left(\frac{6.66 \times 10^7}{T^2} \right)$$

where

- pH is the soil pH;
- % sand is the percentage of sand content of the soil, by weight;
- d_{diff} is the depth interval from which the soil was obtained (cm);
- % oc is the percentage of organic carbon content of the soil, by weight;
- d_{min} is the minimum depth from which the soil was obtained (cm); and
- T is the temperature at which the transformation rate was measured (K).

According to Mark Borsuk, Dartmouth College (written commun., October 2007), the coefficient in the term expressed as “147 T¹” in the original version of the equation presented by Fenner and others (2007) was incomplete, and should have read “147.41”. Equation B1 incorporates this correction. Equation B1 explained 71 percent of the overall variance ($R^2 = 0.71$; $P \leq 0.0001$) among the 111 laboratory-derived values of $\ln(k_{atr})$ from which it was developed by Fenner and others (original data provided on July 1, 2007, by Kathrin Fenner, Swiss Federal Institute of Aquatic Science and Technology).

A separate search of the literature for this study yielded 300 measured values of k_{atr} from 18 laboratory investigations that provided data for all of the explanatory parameters in equation B1 (Roeth and others, 1969; Walker, 1978; Winkelmann and Klaine, 1991a and 1991b; Kruger and others, 1993; Assaf and Turco, 1994; Topp and others, 1994; Rocha and Walker, 1995; Stolpe and Shea, 1995; Kruger and others, 1997; Rodriguez and Harkin, 1997; Baer and Calvet, 1999; Issa and Wood, 1999; Dinelli and others, 2000; Accinelli and others, 2001; Jacobsen and others, 2001; Zablotowicz and others, 2006 and 2007). Because of differences between this study and Fenner and others (2007) in the criteria used to select data for inclusion in the calculations (and limitations in the availability of the original publications used by Fenner and others [2007]), only 4 of the 18 laboratory studies were among the 10 from which Fenner and others (2007) derived equation B1. In instances where the studies of interest reported the humic material content of the soil in terms of percent soil OM (%om), rather than %oc, %om values were converted to %oc using the assumption that soil OM contains an average of 58 percent organic carbon (Chiou, 2002), that is:

$$\% \text{ oc} = 0.58 * \% \text{ om} \quad (\text{B2})$$

The data from the 18 laboratory studies of interest were used to recalculate the coefficients in equation B1, yielding the following, modified version of the Fenner-Borsuk relation for predicting the rate of atrazine disappearance in oxic, non-sterile soil in the absence of light:

$$\begin{aligned} \ln(k_{atr}) = & -84.0141 - (1.92561 * \text{pH}) + (0.145612 * [\text{pH}]^2) - (0.194685 * \ln[\% \text{ sand}]) \\ & - (0.478998 * \ln[d_{diff}]) + (0.263303 * \ln[\% \text{ oc}]) + (0.00586421 * \{\ln[\% \text{ oc}]\}^2) \\ & - (0.211478 * \ln[d_{min}]) + \left(\frac{57586.5}{T} \right) - \left(\frac{9297840}{T^2} \right) \end{aligned} \quad (\text{B3})$$

Equation B3 explained 68 percent of the overall variation among the 300 laboratory-derived values of $\ln(k_{atr})$ from which it was derived ($R^2 = 0.68$; $P \leq 0.0001$), similar to the percentage of the variation in measured atrazine disappearance rates explained by the original Fenner-Borsuk relation (equation B1). However, because it was derived from nearly three times as many laboratory observations as were used for equation B1, equation B3 was the QMRR used to estimate the values of k_{atr} required to compute $F_{atr>DEA}$ with equation 38.

Because of the incomplete coverage of data for soil pH across the Nation, the use of equation B3 to compute k_{atr} for the P-GWAVA-RZ simulations assumed that the soil pH was neutral ($\text{pH} = 7$) at all of the sites of interest. Additionally, because the transformation rates computed with equation B3 pertained to reactions that initially occurred close to the soil surface, the $\% \text{ oc}$ and $\% \text{ sand}$ values used in the equation for each SSURGO soil component were from the uppermost soil horizon, and d_{diff} and d_{min} were assumed to be 1 cm for all sites. Given that the agrichemicals of interest were presumed to have been applied at the end of May, the temperature used to compute k_{atr} for each SSURGO component was the average air temperature in May (T_{May}) at that location.

Using data retrieved or calculated from eight laboratory studies of the rates of DEA production from atrazine dealkylation in non-sterile, oxic soils in the dark (Winkelmann and Klaine, 1991a and 1991b; Kruger and others, 1993; Assaf and Turco, 1994; Topp and others, 1994; Kruger and others, 1997; Rodriguez and Harkin, 1997; Zablutowicz and others, 2006), as well as the same explanatory variables and transformations used in the Fenner-Borsuk relation, an approach similar to that used to develop equation B3 was used to obtain the following QMRR for predicting $k_{atr>DEA}$ for each SSURGO component of interest:

$$\begin{aligned} \ln(k_{atr>DEA}) = & -118.437 + (6.54703 * \text{pH}) - (0.44668 * [\text{pH}]^2) + (0.921228 * \ln[\% \text{ sand}]) \\ & - (1.52988 * \ln[d_{diff}]) - (0.133383 * \ln[\% \text{ oc}]) - (0.292146 * \{\ln[\% \text{ oc}]\}^2) \\ & - (0.203394 * \ln[d_{min}]) + \left(\frac{41294.1}{T} \right) - \left(\frac{4334410}{T^2} \right) \end{aligned} \quad (\text{B4})$$

Each $k_{atr>DEA}$ value used to develop equation B4 was computed from published data by multiplying the k_{atr} value for the experiment in question by the fraction of reacted atrazine that appeared as DEA. Equation B4 accounted for 62 percent of the variability among the 58 values of $\ln(k_{atr>DEA})$ computed from the results reported by the eight laboratory investigations ($R^2 = 0.62$; $P \leq 0.0001$). Data from the eight studies were then used in conjunction with equations B3, B4, and 38 to compute a predicted value of $F_{atr>DEA}$ corresponding to each of the 58 measurements derived from the laboratory studies. The computed values explained 64 percent of the variability in the measured values ($R^2 = 0.64$; $P \leq 0.0001$; $N = 58$). The extent of agreement between the computed and measured $F_{atr>DEA}$ values is shown in figure B1.

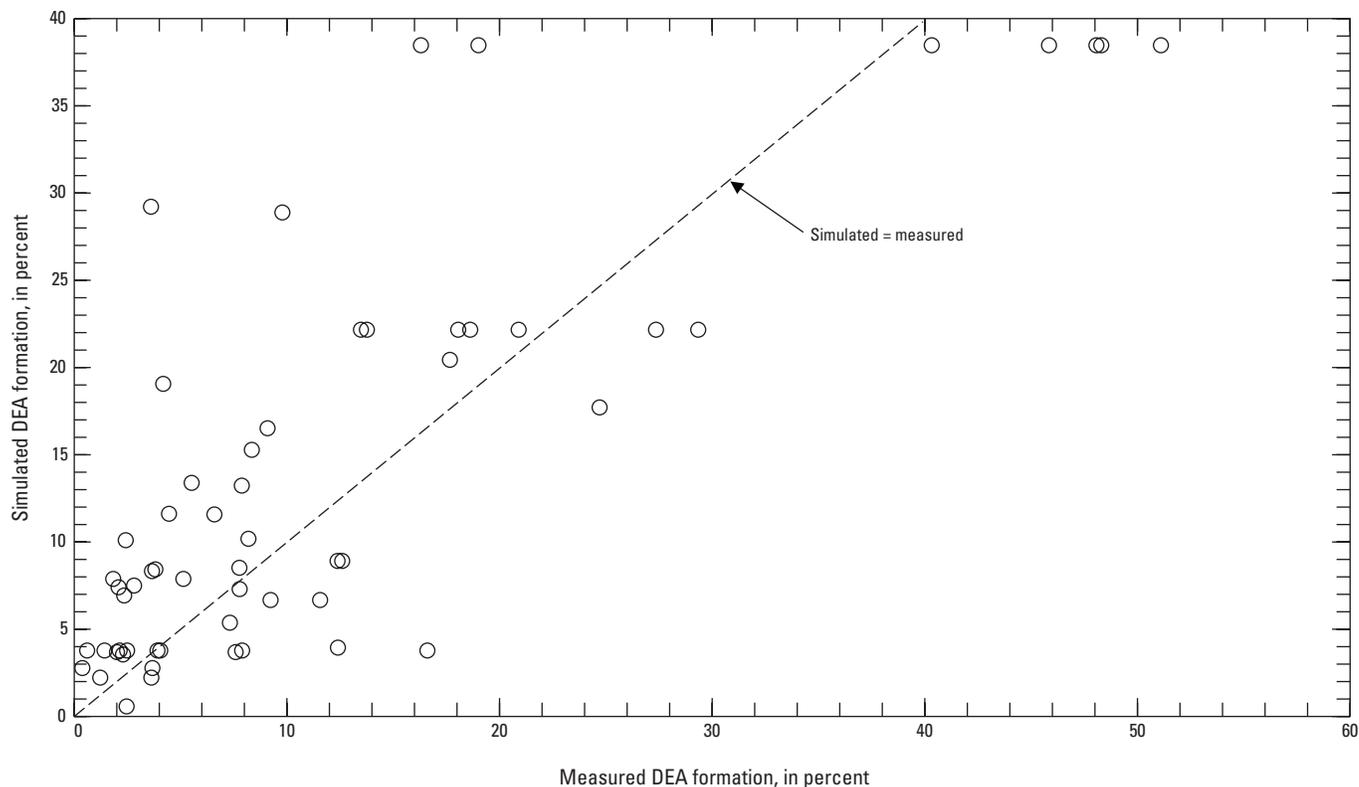


Figure B1. Deethylatrazine (DEA) formation percentages ($F_{atr>DEA}$) in non-sterile, oxic soils in the absence of light computed with equations 38, B3, and B4 using explanatory data associated with 58 measurements from eight laboratory studies, compared with the values computed from the measurements reported by the same studies.

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Appendix C. Groundwater Sampling Networks Examined

Table C1. Groundwater sampling networks examined for this study.

[The names, locations, land-use settings and numbers of sites in the National Water-Quality Assessment (NAWQA) groundwater sampling networks examined during the two phases of this study are listed. For locations of, and summaries of major findings from the NAWQA studies conducted in each area, see U.S. Geological Survey (2013). **NAWQA network type:** See table 2 for general descriptions of the NAWQA networks. ACT, Agricultural Chemicals Team; LUS, NAWQA land-use study; FPS, flow path study. **Abbreviations:** DTW, average depth to water; NE, Northeast; SE, Southeast; USGS, U.S. Geological Survey; m, meter; >, greater than; -, not applicable]

Groundwater network code	Hydrologic basin	Region	NAWQA network type	Land-use setting	Phase 1 networks		Phase 2 networks	
					Total number of sites	Number of sites with DTW greater than Phase 1 assessment depth (> 1 m)	Total number of sites	Number of sites with DTW greater than Phase 2 assessment depth (> 3 m)
acfbusag1	Apalachicola-Chattahoochee-Flint River Basin	SE	LUS	cropland and pasture	17	17	-	-
acfbuscr1	Apalachicola-Chattahoochee-Flint River Basin	SE	LUS	cropland and pasture	10	10	-	-
albelusag1	Albemarle-Pamlico Drainage Basin	SE	LUS	cropland and pasture	17	11	-	-
albelusag2	Albemarle-Pamlico Drainage Basin	SE	LUS	cropland and pasture	6	3	-	-
cazbluscr1	Central Arizona Basins	West	LUS	cropland and pasture	4	4	-	-
ceptlusag1	Central Columbia Plateau	West	LUS	cropland and pasture	28	28	-	-
ceptlusag2	Central Columbia Plateau	West	LUS	cropland and pasture	49	49	-	-
ceptluscr1	Central Columbia Plateau	West	LUS	orchards and vineyards	40	40	-	-
cnbract	Central Nebraska Basins	Corn Belt	ACT study	cropland and pasture	-	-	2	0
cnbrluscr1	Central Nebraska Basins	Corn Belt	LUS	cropland and pasture	-	-	27	21
connlusag1	Connecticut, Housatonic and Thames River Basins	NE	LUS	cropland and pasture	40	40	-	-
eivaluscr1	Eastern Iowa Basins	Corn Belt	LUS	cropland and pasture	31	28	24	2
hdnslusag1	Hudson River Basin	NE	LUS	cropland and pasture	14	11	-	-
hgwusag3	High Plains Regional Groundwater Study	West	LUS	cropland and pasture	-	-	1	1
leriluscr1	Lake Erie-Lake Saint Clair Drainages	Corn Belt	LUS	cropland and pasture	30	27	28	12
linjluscr1	Long Island-New Jersey Coastal Drainages	NE	LUS	cropland and pasture	15	15	-	-
lirbluscr1	Lower Illinois River Basin	Corn Belt	LUS	cropland and pasture	27	26	25	14
lirbluscr2	Lower Illinois River Basin	Corn Belt	LUS	cropland and pasture	29	29	28	16
lsuslusag1	Lower Susquehanna River Basin	NE	LUS	cropland and pasture	30	30	-	-
lsuslusag2	Lower Susquehanna River Basin	NE	LUS	cropland and pasture	30	29	-	-
lsuslusag3	Lower Susquehanna River Basin	NE	LUS	cropland and pasture	30	30	-	-
miamluscr1	Great and Little Miami River Basins	Corn Belt	LUS	cropland and pasture	-	-	24	16
miamluscr1a	Great and Little Miami River Basins	Corn Belt	LUS	cropland and pasture	-	-	8	6
nvbrlusag1	Las Vegas Valley Area and the Carson and Truckee River Basins	West	LUS	cropland and pasture	20	12	-	-
ozrklusag1	Ozark Plateaus	Corn Belt	LUS	cropland and pasture	17	8	-	-
ozrklusag1a	Ozark Plateaus	Corn Belt	LUS	cropland and pasture	2	1	-	-
ozrklusag2	Ozark Plateaus	Corn Belt	LUS	cropland and pasture	13	12	-	-
ozrklusag2a	Ozark Plateaus	Corn Belt	LUS	cropland and pasture	7	7	-	-
potolusag1	Potomac River Basin	NE	LUS	cropland and pasture	29	29	-	-
potolusag2	Potomac River Basin	NE	LUS	cropland and pasture	25	21	-	-
pugffpscr1	Puget Sound Basin	West	FPS	cropland and pasture	6	5	-	-
pugtluscr1	Puget Sound Basin	West	LUS	cropland and pasture	8	8	-	-

Table C1. Groundwater sampling networks examined for this study.—Continued

[The names, locations, land-use settings and numbers of sites in the National Water-Quality Assessment (NAWQA) groundwater sampling networks examined during the two phases of this study are listed. For locations of, and summaries of major findings from the NAWQA studies conducted in each area, see U.S. Geological Survey (2013). **NAWQA network type:** See table 2 for general descriptions of the NAWQA networks. ACT, Agricultural Chemicals Team; LUS, NAWQA land-use study; FPS, flow path study. **Abbreviations:** DTW, average depth to water; NE, Northeast; SE, Southeast; USGS, U.S. Geological Survey; m, meter; >, greater than; –, not applicable]

Groundwater network code	Hydrologic basin	Region	NAWQA network type	Land-use setting	Phase 1 networks		Phase 2 networks	
					Total number of sites	Number of sites with DTW greater than the Phase 1 assessment depth (> 1 m)	Total number of sites	Number of sites with DTW greater than the Phase 2 assessment depth (> 3 m)
rednfpag1	Red River of the North Basin	Corn Belt	FPS	cropland and pasture	–	–	2	1
rednfpag2	Red River of the North Basin	Corn Belt	FPS	cropland and pasture	–	–	6	2
rednlsag1	Red River of the North Basin	Corn Belt	LUS	cropland and pasture	29	28	25	18
rednlsag2	Red River of the North Basin	Corn Belt	LUS	cropland and pasture	29	24	22	4
rioglusag1	Rio Grande Valley	West	LUS	cropland and pasture	23	23	–	–
riogluscr1	Rio Grande Valley	West	LUS	cropland and pasture	35	35	–	–
sacrluser1	Sacramento River Basin	West	LUS	cropland and pasture	28	15	–	–
sanjluser1	San Joaquin-Tulare Basins	West	LUS	cropland and pasture	9	9	–	–
sanjluser1a	San Joaquin-Tulare Basins	West	LUS	cropland and pasture	11	11	–	–
sanjluser1	San Joaquin-Tulare Basins	West	LUS	orchards and vineyards	8	8	–	–
sanjlsor1a	San Joaquin-Tulare Basins	West	LUS	orchards and vineyards	12	12	–	–
sanjlsor2	San Joaquin-Tulare Basins	West	LUS	orchards and vineyards	8	8	–	–
sanjlsor2a	San Joaquin-Tulare Basins	West	LUS	orchards and vineyards	12	12	–	–
santluser1	Santee River Basin and Coastal Drainages	SE	LUS	cropland and pasture	31	31	–	–
sofluser1	Southern Florida	SE	LUS	cropland and pasture	7	4	–	–
sofluser1	Southern Florida	SE	LUS	orchards and vineyards	31	19	–	–
spltluser1	South Platte River Basin	West	LUS	cropland and pasture	28	28	–	–
uirbluser1	Upper Illinois River Basin	Corn Belt	LUS	cropland and pasture	–	–	29	7
umistuser1	Upper Mississippi River Basin	Corn Belt	LUS	cropland and pasture	29	29	21	18
usnkluser1	Upper Snake River Basin	West	LUS	cropland and pasture	29	28	–	–
usnkluser2	Upper Snake River Basin	West	LUS	cropland and pasture	31	30	–	–
usnkluser3	Upper Snake River Basin	West	LUS	cropland and pasture	30	30	–	–
usnkluser4	Upper Snake River Basin	West	LUS	cropland and pasture	14	14	–	–
utenluser1	Upper Tennessee River Basin	NE	LUS	cropland and pasture	30	18	–	–
whitfipag1	White River Basin	Corn Belt	FPS	cropland and pasture	–	–	13	6
whitfipag2	White River Basin	Corn Belt	FPS	cropland and pasture	–	–	2	0
whitluser1	White River Basin	Corn Belt	LUS	cropland and pasture	22	22	26	14
whitluser2	White River Basin	Corn Belt	LUS	cropland and pasture	21	20	22	9
whitluser3	White River Basin	Corn Belt	LUS	cropland and pasture	7	7	–	–
whitluser3a	White River Basin	Corn Belt	LUS	cropland and pasture	17	17	23	11
whitluser3b	White River Basin	Corn Belt	LUS	cropland and pasture	–	–	6	3

Table C1. Groundwater sampling networks examined for this study.—Continued

[The names, locations, land-use settings and numbers of sites in the National Water-Quality Assessment (NAWQA) groundwater sampling networks examined during the two phases of this study are listed. For locations of, and summaries of major findings from the NAWQA studies conducted in each area, see U.S. Geological Survey (2013). **NAWQA network type:** See table 2 for general descriptions of the NAWQA networks. ACT, Agricultural Chemicals Team; LUS, NAWQA land-use study; FPS, flow path study. **Abbreviations:** DTW, average depth to water; NE, Northeast; SE, Southeast; USGS, U.S. Geological Survey; m, meter; >, greater than; -, not applicable]

Groundwater network code	Hydrologic basin	Region	NAWQA network type	Land-use setting	Phase 1 networks		Phase 2 networks	
					Total number of sites	Number of sites with DTW greater than the Phase 1 assessment depth (> 1 m)	Total number of sites	Number of sites with DTW greater than the Phase 2 assessment depth (> 3 m)
whmiact	White-Miami River Basins	Corn Belt	ACT study	cropland and pasture	-	-	7	1
willusag1	Willamette Basin	West	LUS	cropland and pasture	15	15	-	-
willusag2	Willamette Basin	West	LUS	cropland and pasture	28	27	-	-
wmicfpsag1a	Western Lake Michigan Drainages	Corn Belt	FPS	cropland and pasture	-	-	6	5
wmicfpsag1b	Western Lake Michigan Drainages	Corn Belt	FPS	cropland and pasture	-	-	3	0
wmicfpsag2a	Western Lake Michigan Drainages	Corn Belt	FPS	cropland and pasture	-	-	17	11
wmicfpsag2b	Western Lake Michigan Drainages	Corn Belt	FPS	cropland and pasture	-	-	2	0
wmiclusag1	Western Lake Michigan Drainages	Corn Belt	LUS	cropland and pasture	3	2	-	-
wmiclusag1a	Western Lake Michigan Drainages	Corn Belt	LUS	cropland and pasture	23	19	24	14
wmiclusag1b	Western Lake Michigan Drainages	Corn Belt	LUS	cropland and pasture	-	-	2	0
wmiclusag2	Western Lake Michigan Drainages	Corn Belt	LUS	cropland and pasture	30	30	28	24

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