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Mercury Loads in the South River and Simulation of Mercury Total Maximum Daily Loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River: Shenandoah Valley, Virginia

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U.S. Department of the Interior
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Cover. South River. View looking downstream from the old Route 611 bridge near Dooms, Virginia. Water-quality monitoring equipment in foreground. (Photograph by Jack Eggleston, U.S. Geological Survey, June 2005.)

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By Jack Eggleston

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U.S. Department of the Interior
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KEN SALAZAR, Secretary

U.S. Geological Survey
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Contents

Abstract.....1
Introduction.....1
    Background and History.....3
    Regulatory Approach and Total Maximum Daily Load Scope.....3
    Description of the Study Area.....4
    Previous Studies.....6
    Modeling Approach.....6
Data Collected by the U.S. Geological Survey for This Study.....7
    Streamflow.....7
    Water Quality.....7
    Methods.....8
    Suspended Sediment.....9
    Turbidity.....10
    Mercury.....10
        Units and Terms.....10
        Surface Water.....10
        Groundwater.....12
        Sediment.....12
        Mercury Sorption to Suspended Solids.....16
Data Compiled From Other Sources.....16
    Suspended Sediment.....16
    Mercury in Surface Water.....16
    Atmospheric Mercury Deposition.....16
    Mercury in Fish Tissue.....18
    Mercury in Soil.....18
    Mercury in Groundwater.....19
Development of Time-Series Data.....19
    Streamflow Time Series.....19
    Suspended Sediment Concentration Time Series.....20
    Meteorological and Climatic Data.....21
    Point Sources.....23
    Additional Model Flows to the River.....23
Conceptual Model of Mercury Fate and Transport in the Watershed.....23
Watershed Model Development.....24
    Functional Description of Hydrological Simulation Program–FORTRAN (HSPF).....24
    Representation of the Watershed.....26
        Development of Hydrologic Response Units (HRUs).....27
        Stream Reaches.....29
    Hydrologic Model.....29
    Point-Source Discharges.....30
    Sediment Transport Model.....30
        Impervious Land Area Sediment Transport.....31

Pervious Land Area Sediment Transport 31
Sediment Point Sources 32
Sediment Transport in the River 32
Mercury Transport Model 32
Mercury Sources to the River 34
Atmospheric Deposition 34
Land-Surface Runoff 34
Groundwater and Interflow 35
Point-Source Discharges 35
Riverbank and Channel Margin Inputs 35
Mercury Transport Within the River 35
Watershed Model Results 36
Streamflow Model Calibration Results 36
Sediment Transport Model Calibration Results 45
Mercury Transport Model Calibration Results 52
Limitations of the South River Watershed Model and Suggestions for Future Investigations 58
Simulation of Mercury Total Maximum Daily Load (TMDL) 58
Designation of Endpoints 58
Existing Conditions 59
Scenarios for Mercury Load Reductions 61
Future Conditions 61
Single Source Reductions 62
Multiple Source Reductions and Total Maximum Daily Load (TMDL) Scenario 65
Sensitivity of Total Maximum Daily Load (TMDL) Results to Model Parameter Values 67
Implications for the Downstream South Fork Shenandoah River and Shenandoah River 69
Summary 72
Acknowledgments 72
References Cited 73
Appendix 1. Data sources used to define point-source loading in the model 78
Appendix 2. User’s Control Input File for the Calibrated South River Watershed Model Under Existing Conditions (Available only online at http://pubs.usgs.gov/sir/2009/5076/)

Figures

1–2. Maps showing locations of—

1. Rivers in the Shenandoah Valley, Virginia, on the 303d list of contaminated water for elevated concentrations of methylmercury in fish tissue 2
2. The South River watershed study area in the Shenandoah Valley, Virginia 5

3. Timeline for data collection and model simulation, South River, Virginia 6

4–10. Graphs showing—

4. Annual streamflow for the South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500), water years 1926–2007 7
5. Observed suspended sediment concentrations and streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007....10
6. Streamflow and turbidity from June 2005 through April 2007 for the South River at Harriston, Virginia (USGS station number 01627500) 11
7. Observed total unfiltered mercury concentration and concurrent instantaneous streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007....13
8. Observed aqueous concentration of filterable mercury and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007....13
9. Observed aqueous concentration of mercury associated with particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007....14
10. Observed concentration of mercury on suspended particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007 14

11. Map showing location of mercury deposition and precipitation monitoring sites....17

12–14. Graphs showing—

12. Fish tissue mercury concentrations in smallmouth bass, 1999–2007, South River, South Fork Shenandoah River, and Shenandoah River, Virginia....18
13. Time series of regressed and sampled suspended sediment concentrations, South River at Harriston, Virginia (USGS station number 01627500), April 1, 2005, through March 31, 2007 21
14. Cumulative precipitation at sites in and near the South River watershed, Virginia, for the period April 1, 2005, through March 31, 2007....22

15. Conceptual model of total mercury sources, sinks, and transport in the South River, Virginia 23

16. Schematic showing hydrologic routing in the South River numerical watershed model....25

17–18. Maps showing—

17. Location of South River watershed model subbasins....26
18. Land use in the South River watershed....28

19–22. Diagrams showing—
19. Major hydrologic components for pervious land areas and river reaches simulated in the South River numerical watershed model 29
20. Sediment transport processes for pervious land areas 31
21. Sediment routing processes in the South River numerical watershed model..........32
22. Mercury routing in the South River numerical watershed model..........33
23–59. Graphs showing—
23. Observed mean annual flow, South River at Harriston, Virginia (USGS station number 01627500), water years 1926–2007 37
24. Simulated and observed daily streamflow for the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000)..........39
25. Simulated and observed daily streamflow during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000)..........40
26. Simulated and observed daily streamflow during the calibration period water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 40
27. Simulated and observed daily streamflow for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 41
28. Simulated and observed annual runoff during the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000)..........41
29. Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000) 42
30. Simulated and observed annual runoff during the calibration period water years 1991–2000, calibrated, South River at Harriston, Virginia (USGS station number 01627500) 42
31. Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 43
32. Flow duration curves for observed and simulated streamflow, calibration period water years 1991–2000, calibrated model, for the South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500)..........43
33. Flow duration curves for observed and simulated daily streamflow, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500), verification period April 1, 2005, through March 31, 2007 44
34. 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000), water years 1991–2000 and April 2005 through March 2007..........44
35. 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River at Harriston, Virginia (USGS station number 01627500), water years 1991–2000 and April 2005 through March 2007 45
36. Simulated depth of sediment in model river reaches 1 and 4, calibrated South River model, water years 1991–2000 46

37. Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the calibration period, water years 1991–2000, South River near Waynesboro, Virginia (USGS station number 01626000) 48
38. Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000) 48
39. Simulated and observed (regressed) suspended sediment concentrations for the calibration period water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 49
40. Simulated and observed (regressed) suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 49
41. Annual simulated and observed (regressed) suspended sediment loads for the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000)................50
42. Annual simulated and observed (regressed) suspended sediment loads for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000) 50
43. Annual simulated and observed (regressed) suspended sediment loads for the calibration period, water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 51
44. Annual simulated and observed (regressed) suspended sediment loads for the verification period, April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500) 51
45. Duration plots for simulated and observed (regressed) daily suspended sediment concentrations, calibration period water years 1991–2000, calibrated model, South River, Virginia..52
46. Duration plots for simulated and observed (regressed) daily suspended sediment concentration for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia................................53
47. Simulated and observed total unfiltered mercury concentration distributions showing poor calibration obtained with no channel margin inputs, simulation period April 1, 2005, through March 31, 2007, South River at Dooms, Virginia (USGS station number 01626920)...............................54
48. Simulated total unfiltered mercury concentration time series and observed concentrations, calibrated model, existing conditions, April 2005 through March 2007, South River near Waynesboro, Virginia (USGS station number 01626000), South River at Dooms, Virginia (USGS station number 01626920), and South River at Harriston, Virginia (USGS station number 01627500) 55
49. Duration curves for simulated and observed (USGS samples only) total unfiltered mercury concentrations, calibrated model, existing conditions, April 1, 2005, to March 31, 2007, South River near Waynesboro, Virginia (USGS station number 01626000), at Dooms, Virginia (USGS station number 0162920), and at Harriston, Virginia (USGS station number 01627500) 57

50. Percent mercury loading to the South River from sources upstream (model reach 1) and downstream (model reaches 2–5) of the plant site, calibrated model, existing conditions....60
51. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions, Scenario 2 62
52. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with point sources cleaned up, Scenario 3A 63
53. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with channel margin mercury sources cleaned up, Scenario 3B 64
54. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with runoff cleaned up, Scenario 3C 64
55. Simulated total unfiltered mercury concentrations for Scenario 4A, reduced channel margin and runoff mercury loads, South River at Harriston, Virginia (USGS station number 01627500)....65
56. Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South River at Harriston, Virginia (USGS station number 01627500)....66
57. Comparison of total unfiltered mercury concentrations (Virginia Department of Environmental Quality samples only) from the South River at Harriston, Virginia (USGS station number 01627500) to same-day total unfiltered mercury concentrations from the South Fork Shenandoah River near Luray, Virginia (USGS station number 01629500) 69
58. Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South Fork Shenandoah River near Luray, Virginia (USGS station number 01629500) 70
59. Estimated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, Shenandoah River at the confluence with Craig Run, Clarke County, Virginia....71

Tables

1. Selected characteristics of the North, South, South Fork Shenandoah, and Shenandoah Rivers, Virginia 3
2. Streamflow-gaging stations and water-quality monitoring sites used in the study, South River, Virginia, 2005–2007 4
3. Water-quality sample treatments and laboratories used in the study 8
4. Detection limits for mercury analyses 8
5. Suspended sediment concentrations and turbidity values, South River, Virginia, April 2005 through March 2007....9
6. Description of units for mercury concentrations used in this report 11
7. Aqueous total mercury concentrations for the South River, April 1, 2005, through March 31, 2007....12
8. Concentrations of total mercury on suspended sediment in the South River, April 1, 2005, through March 31, 2007 12
9. Observed flow-weighted average sediment and mercury concentrations in the South River, Virginia, April 1, 2005, through March 31, 2007....15
10. Observed flow-weighted average mercury concentrations in rivers neighboring the South River, Virginia, January 2002 through March 2006 15
11. Concentrations of filterable total mercury THG_F in riverbank pore water, South River, Virginia, June 2006 15
12. Concentrations of total mercury in riverbank sediment, South River, Virginia, June 2006....15
13. Average concentrations of mercury in soil, South River watershed, Virginia, April 2003 through October 2006....19
14. Sources of time-series data used in the South River watershed model....19
15. Linear multi-regression models for suspended sediment concentration 20
16. Organization of dataset numbers in the watershed data management file for the South River watershed model, Virginia 25
17. Land-use representation in the watershed model, South River, Virginia....27
18. River reach characteristics in the calibrated South River watershed model 29
19. Point sources in the South River watershed model, average flow, sediment loads, and mercury loads for the period April 1, 2005, through March 31, 2007 30
20. Modules in Hydrological Simulation Program–FORTRAN used to simulate mercury transport....33
21. Mercury sources to the South River in the watershed model 34
22. Primary model transport parameters changed from Chesapeake Bay Model Phase 5 values during calibration of the South River watershed model 38
23. Simulation results for the calibration period water years 1991 through 2000, calibrated model, South River, Virginia 38
24. Simulation results for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia 39
25. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, calibration period water years 1991 through 2000, calibrated model, South River, Virginia 47

26. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia 47
27. Input mercury concentrations to the calibrated watershed model 54
28. Statistics for hourly simulated and observed total mercury concentrations, calibrated watershed model, South River, Virginia, calibration and verification periods combined, April 1, 2005, through March 31, 2007 56
29. Simulated annual total mercury loads to the South River, calibrated model, existing conditions, April 1, 2005, through March 31, 2007 56
30. Target total mercury water column concentrations for rivers in the study 59
31. Simulated total mercury concentrations for the South River, Virginia, existing conditions, median hourly concentrations for the period April 1, 2005, through March 31, 2007 59
32. Simulated annual mercury loads by reach in the South River, existing conditions, April 1, 2005, through March 31, 2007 59
33. Mercury loading rates to watersheds and subwatersheds by model reach, calibrated model, existing conditions, South River, Virginia, April 1, 2005, through March 31, 2007 60
34. Mercury load-reduction simulation scenarios 61
35. Changes in median simulated total mercury concentrations, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia 61
36. Percentage change to in-stream total mercury loads, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia 62
37. Percentage of time that simulated 90-day median total mercury concentrations exceed the 3.8 nanogram per liter target concentration, April 1, 2005, through March 31, 2007, South River, Virginia 63
38. Annual mercury loads under Total Maximum Daily Load conditions (Scenario 4B), South River, Virginia 66
39. Model input parameters changed during sensitivity analysis 67
40. Results of sensitivity analysis for existing conditions, changes to median concentrations for the period April 1, 2005, through March 31, 2007, resulting from + or –50 percent in model parameter values, South River at Harriston, Virginia (U.S. Geological Survey station number 01627500) 68
41. Results of sensitivity analysis under the Total Maximum Daily Load Scenario, changes to percent of time that 90-day median concentrations exceed the 3.8 ng/L target concentration, resulting from + or –50 percent in model parameter values, South River at Harriston, Virginia (U.S. Geological Survey station number 01627500), April 1, 2005, through March 31, 2005 68
42. Estimated total maximum daily loads (TMDLs) for mercury for listed waters in the Shenandoah Valley, Virginia 71

Conversion Factors and Datum

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
Million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
Million gallons per day (Mgal/d)	1.5472	cubic foot per second (ft^3/s)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
pound (lb)	453.592	gram (g)
ton	0.9072	megagram (Mg)

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

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

The term "water year" is defined as the 12-month period from October 1 for any given year through September 30 of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1999, is called the "1999" water year.

Abbreviations and Acronyms

CBM5	Chesapeake Bay Watershed Model, Phase 5
HRU	Hydrologic Response Unit
HSPEXP	Expert System for the Calibration of the Hydrological Simulation Program–FORTRAN
HSPF	Hydrological Simulation Program–FORTRAN
TMDL	Total Maximum Daily Load
USGS	U.S. Geological Survey

Mercury Loads in the South River and Simulation of Mercury Total Maximum Daily Loads (TMDLs) for the South River, South Fork Shenandoah River, and Shenandoah River: Shenandoah Valley, Virginia

By Jack Eggleston

Abstract

Due to elevated levels of methylmercury in fish, three streams in the Shenandoah Valley of Virginia have been placed on the State's 303d list of contaminated waters. These streams, the South River, the South Fork Shenandoah River, and parts of the Shenandoah River, are downstream from the city of Waynesboro, where mercury waste was discharged from 1929–1950 at an industrial site. To evaluate mercury contamination in fish, this total maximum daily load (TMDL) study was performed in a cooperative effort between the U.S. Geological Survey, the Virginia Department of Environmental Quality, and the U.S. Environmental Protection Agency. The investigation focused on the South River watershed, a headwater of the South Fork Shenandoah River, and extrapolated findings to the other affected downstream rivers. A numerical model of the watershed, based on Hydrological Simulation Program–FORTRAN (HSPF) software, was developed to simulate flows of water, sediment, and total mercury. Results from the investigation and numerical model indicate that contaminated flood-plain soils along the riverbank are the largest source of mercury to the river. Mercury associated with sediment accounts for 96 percent of the annual downstream mercury load (181 of 189 kilograms per year) at the mouth of the South River. Atmospherically deposited mercury contributes a smaller load (less than 1 percent) as do point sources, including current discharge from the historic industrial source area. In order to determine how reductions of mercury loading to the stream could reduce methylmercury concentrations in fish tissue below the U.S. Environmental Protection Agency criterion of 0.3 milligrams per kilogram, multiple scenarios were simulated. Bioaccumulation of mercury was expressed with a site-specific exponential relation between aqueous total mercury and methylmercury in smallmouth bass, the indicator fish species. Simulations indicate that if mercury loading were to decrease by 98.9 percent from 189 to 2 kilograms per year, fish tissue methylmercury concentrations would drop below 0.3 milligrams per kilogram. Based on the simulations, the estimated maximum load of total mercury that can enter the South River without causing fish tissue methylmercury concentrations to rise above 0.3 milligrams per kilogram is 2.03 kilograms per year for the South River, and 4.12 and 6.06 kilograms per year for the South Fork Shenandoah River and Shenandoah River, respectively.

Introduction

Three rivers in the Shenandoah Valley of Virginia are contaminated with mercury and have been designated as "impaired" on Virginia's 303d list of contaminated waters due to fish consumption advisories issued by the Virginia Department of Health. These rivers, the South River, South Fork Shenandoah River, and the Shenandoah River between Front Royal and the confluence with Craig Run (fig. 1), are regulated by the Virginia Department of Environmental Quality (VDEQ) under the Total Maximum Daily Load (TMDL) Program, which develops plans to restore and maintain water quality for impaired waters.

This study by the U.S. Geological Survey (USGS), performed in cooperation with the U.S. Environmental Protection Agency (USEPA), VDEQ, and the South River Science Team, an interdisciplinary scientific group studying mercury in the South River, provides a scientific foundation for the VDEQ to establish mercury TMDLs for the three rivers. Results of this study will be used by VDEQ to develop an implementation plan to restore water quality in the three rivers so that fish tissue methylmercury concentrations are below 0.3 mg/kg (milligrams mercury per kilogram of fish tissue). The watershed modeling approach used to develop a mercury TMDL for the South River could be applied in other watersheds with comparable legacy mercury contamination.

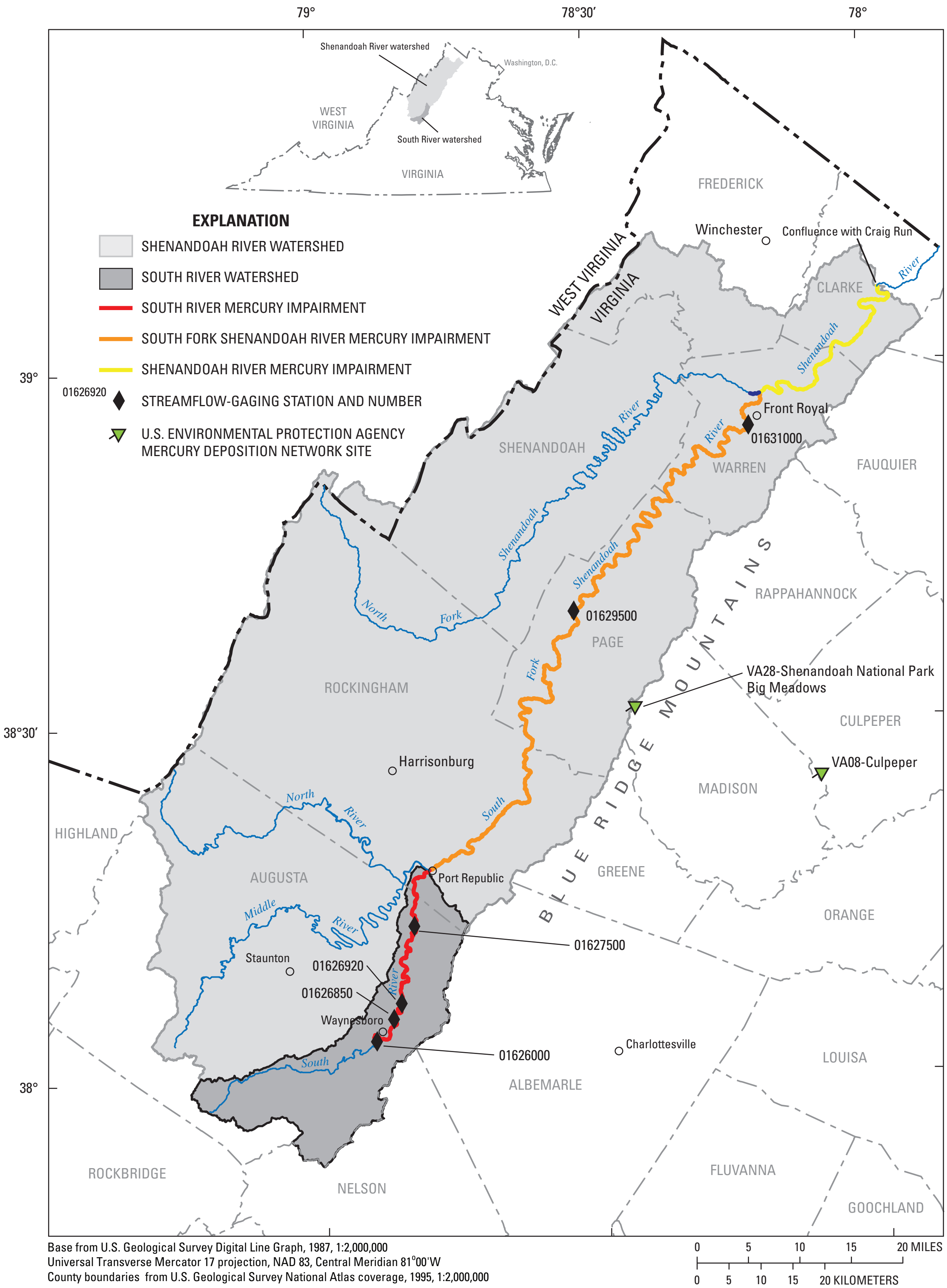


Figure 1. Location of rivers in the Shenandoah Valley, Virginia, on the 303d list of contaminated water for elevated concentrations of methylmercury in fish tissue.

Background and History

Elevated levels of methylmercury in fish tissue have caused parts of the South River, the South Fork of the Shenandoah River, and the Shenandoah River to be placed on Virginia's 303(d) list of impaired waters, and the Virginia Department of Health has restricted fish consumption from these rivers (fig. 1). The affected rivers are: 24.63 mi (miles) of the South River from the DuPont foot bridge in Waynesboro downstream to the headwaters of the South Fork Shenandoah River; the entire 100.96 mi of the South Fork Shenandoah River; 0.67 mi of the North Fork Shenandoah River from its mouth upstream to the Riverton Dam; and 29.83 mi of the Shenandoah River from the confluence of the North Fork and South Fork Shenandoah Rivers downstream to the confluence with Craig Run. Selected characteristics of the three rivers and the uncontaminated North River are listed in table 1.

A textile plant in Waynesboro is known to have discharged mercury to the South River from 1929 to 1950 (Bolgiano, 1980), when it was owned and operated by DuPont. Mercury released during that period has spread downstream, with the highest concentrations found within the 24 mi of the South River from the plant site downstream to its confluence with the South Fork Shenandoah River. DuPont has performed extensive site assessment and investigations at the plant site under the USEPA Resource Conservation and Recovery Program (DuPont Corporate Remediation Group, 2003a, b, 2006a, b). The State of Virginia began regular monitoring of mercury in the late 1970s and is scheduled to continue monitoring through the year 2092. Other studies of mercury in the South River watershed are being conducted by members of the South River Science Team, a group of scientists and representatives from local universities, conservation groups, state and federal government agencies, DuPont, and its consultants. Data collected for these other studies provided an important foundation for this study.

Table 1. Selected characteristics of the North, South, South Fork Shenandoah, and Shenandoah Rivers, Virginia.

[mi², square miles; Avg., average; R., river]

Name of river	Drains to	Drainage area (mi²)	On 303(d) list for mercury	Known industrial mercury sources
North	South Fork Shenandoah	818	No	No
South	South Fork Shenandoah	235	Yes	Yes
South Fork Shenandoah	Shenandoah	1,649	Yes	Yes, from South R.
Shenandoah	Potomac	2,899 (*to Craig Run*)	Yes	Yes, from South R.

Mercury concentrations remain elevated above background levels in soil and groundwater at the plant site, and some mercury still enters the river from the plant site through surface runoff, groundwater, and permitted point-source discharges (DuPont Corporate Remediation Group, 2006a, b). Atmospheric mercury is deposited on the watershed by wet and dry deposition (U.S. Environmental Protection Agency, 2007). The largest current (2009) source of mercury to the river may be erosion of contaminated flood-plain and channel margin sediments, which have elevated mercury concentrations and were estimated to contain at least 57,000 lbs (pounds) of mercury along the South River alone (Bolgiano, 1980).

The present study was performed to quantify sources of mercury to the river and develop a simulation model that could be used to examine relations between mercury loading to the river and mercury concentrations in the water column. The model was then used to estimate mercury TMDLs for the listed rivers.

Regulatory Approach and Total Maximum Daily Load Scope

When a water body is placed on the 303d list of contaminated waters, a regulatory requirement is triggered for a cleanup plan to be developed for the water body. The TMDL approach is based on the idea that if contaminant concentrations in a water body need to be below a specified maximum level, then only a limited amount of the contaminant can be allowed to enter the water body. A study is typically performed to determine a daily total maximum contaminant load (TMDL) so that contaminant concentrations remain below the maximum level. This study estimates the maximum daily loads of mercury to the South River, South Fork Shenandoah River, and Shenandoah River so that methylmercury concentrations in fish tissue can be kept below the USEPA ambient water-quality criterion of 0.3 mg methylmercury/kg fish (U.S. Environmental Protection Agency, 2001).

Fish tissue total mercury and methylmercury concentrations have been monitored in the South River, the South Fork Shenandoah River, and the Shenandoah River by the VDEQ since 1990. Methylmercury typically makes up about 90 percent of the total mercury present in South River fish (Virginia Department of Environmental Quality, 1999, 2008a). Total mercury concentrations in smallmouth bass, the indicator fish, have been consistently elevated in the South River since at least 1990, averaging above 1.0 ppm (parts per million), and individual fish have had concentrations higher than 3.0 ppm. In the South Fork Shenandoah River and Shenandoah River, average methylmercury concentrations have been somewhat lower, but in 2007 were still above 0.3 mg/kg at all monitoring stations. Although mercury concentrations in the water column itself have not exceeded any regulatory standards set by the USEPA or the VDEQ, high concentrations of mercury have been observed in fish because mercury bioaccumulates as it moves up the food chain. How fish tissue methylmercury concentrations correlate with water column concentrations in the South River and how a site-specific bioaccumulation factor (BAF) is used in this study are described in the VDEQ companion report to this study (Virginia Department of Environmental Quality, 2008b).

The purpose of the present report is to describe the current understanding of mercury transport in the South River watershed and to provide estimates of the mercury loading reductions needed to protect human health from risks posed by consumption of fish from the river. The area of investigation focused on the South River because the original mercury source was located there and the South River has had the highest mercury concentrations in the Shenandoah River watershed. This focus permitted a spatially intensive data-collection effort. Results from the South River are extrapolated downstream to estimate loading reductions needed to meet methylmercury fish tissue targets for the South Fork Shenandoah and Shenandoah Rivers.

Description of the Study Area

The 234.6 mi^2 (square mile) South River watershed in the Shenandoah Valley of Virginia comprises the study area (fig. 1). The downstream (northern) end of the study area is at the town of Port Republic, where the South River joins the South Fork Shenandoah River. The southern and southeastern boundaries of the watershed are defined by the Blue Ridge Mountains, whereas the northwestern boundary is a low rise of hills. Elevations range from 1,037 ft (feet) at the mouth of the South River to 3,848 ft at the peak of the Blue Ridge Mountains. Land use is primarily forested (58 percent) or agricultural (31 percent) with developed (8 percent) land accounting for most of the remainder (Chesapeake Bay Program, 2002). The largest population center in the study area is Waynesboro, with a 2000 census population of 19,520. The entire study area had an estimated 2000 population of 34,184 (U.S. Census, 2000). The South Fork Shenandoah River and Shenandoah Rivers are included in the TMDL part of the study.

Precipitation in the study area averaged 43.0 in/yr (inches per year) from October 2000 through March 2005, on the basis of precipitation data from the Waynesboro sewage treatment plant. Average evapotranspiration (ET) for the city of Waynesboro is 29.6 in/yr, on the basis of spatially averaged data from multiple weather-monitoring stations outside the watershed from January 1984 through March 2007 (Chesapeake Bay Program, 2006). Annual streamflow at Harriston (01627500), the most downstream streamflow-gaging station in the study area, averaged 261.3 ft^3/s (cubic feet per second) for the full period of record (fig. 2 and table 2). This flow is equivalent to 16.7 in/yr over the 212-mi^2 watershed above the Harriston gage.

Table 2. Streamflow-gaging stations and water-quality monitoring sites used in the study, South River, Virginia, 2005–2007.

[USGS, U.S. Geological Survey; mi^2, square miles; "–" before a number indicates upstream; ft^3/s, cubic feet per second]

USGS streamflow-gaging stations and water-quality monitoring sites				
USGS station name	**South River near Waynesboro**	**South River near Dooms**	**South River at Dooms**	**South River at Harriston**
Station number	**01626000**	**01626850**	**01626920**	**01627500**
Location	Waynesboro	Hopeman Parkway	Dooms	Harriston
Streamflow monitoring (this study)	yes	yes	none	yes
Water-quality sampling (this study)	yes	none	yes	yes
Drainage area (mi^2)	127	148	164	212
River miles downstream from plant site	–2.8	2.3	5.3	16.5
Streamflow record period	1952–2008	1974–1997, 2005–2008	none	1926–1951, 1969–2008
Mean annual flow (ft^3/s)	150	214	no data	261

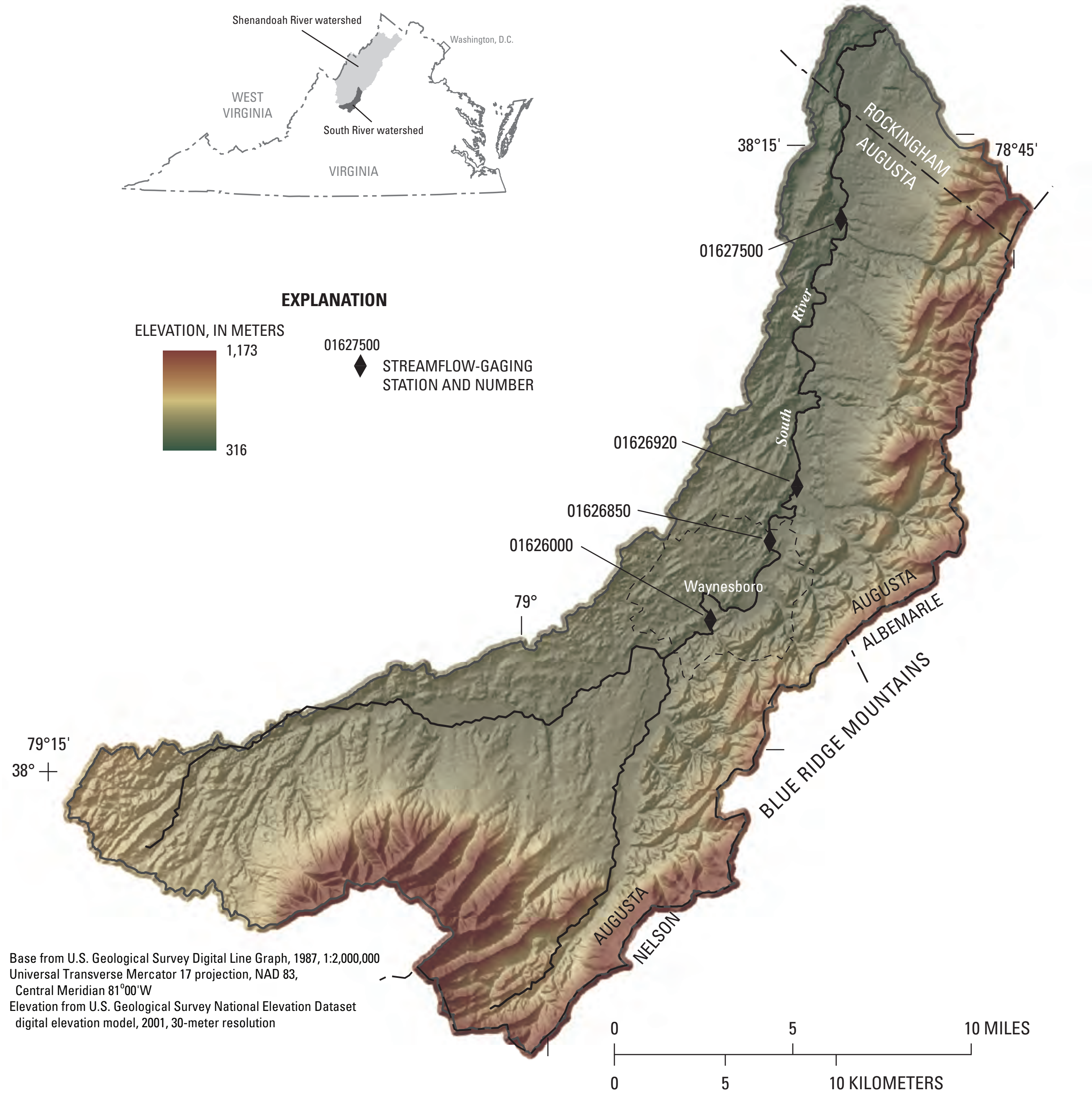


Figure 2. Location of the South River watershed study area in the Shenandoah Valley, Virginia.

Previous Studies

A history of mercury in the South River was obtained from studies and reports located in the VDEQ office in Harrisonburg, Virginia. Since DuPont announced in the fall of 1977 that mercury had been found in the soil at its Waynesboro plant, numerous studies have documented mercury contamination at the plant site and in the downstream watershed (Paylor, 1977; Bolgiano, 1980; Todd, 1980; Old Dominion University, 1996, 1997, 1998; Messing and Winfield, 1998). Mercury sulphate was used by DuPont as a catalyst in fabric manufacturing from 1929 to 1950. Although the majority of the mercury catalyst was captured and reused, losses to the river resulted in widespread mercury contamination downstream (Bolgiano, 1980). Other potential sources of mercury in the watershed, including agricultural fungicides, mercury in precipitation, and hydraulic seals in industrial equipment, have been documented, but appear insignificant relative to the large mass of mercury released from the plant site.

The Bolgiano study (1980) estimated that there were 57,000 lbs of mercury in the South River and the adjacent flood plain and a further 20,000 lbs in the South Fork Shenandoah River and the adjacent flood plain. A later study estimated 1,800 lbs of mercury in river sediments downstream from the plant site and 97,200 lbs of mercury in flood-plain soils (Lawler, Matusky, & Skelly Engineers, 1989).

Environmental concentrations of mercury in the South River have not changed appreciably since they were first measured in the late 1970s (Bolgiano, 1980; Old Dominion University 1996, 1997, 1998; Virginia Department of Environmental Quality, 1999, 2008a). Mercury concentrations in water, sediment, and biota vary with time and location, but do not show an obvious temporal trend, either positive or negative. Previous studies used different sampling and analytical methods, which makes comparison of results more difficult. The development of low-concentration analytical methods for mercury in the 1980s that lowered detection limits by a factor of 1,000, from about 0.1 mg/L (milligrams per liter) to about 0.1 ng/L (nanograms per liter), has made it possible to detect aqueous mercury in the South River.

Modeling Approach

This study used the numerical model Hydrological Simulation Program–FORTRAN (HSPF) to simulate the transport of water, sediment, and mercury in the South River watershed. The model allows mass-balance calculations of all three media and captures the transient fluctuations in flows and concentrations that occur in the watershed. After calibrating model parameters to match observed existing conditions, the model was then used to simulate hypothetical future conditions such as reductions in mercury loads to the river. The model can be modified in the future to incorporate new observations or additional processes that are found to affect mercury transport and fish tissue concentrations in the South River.

The choice of modeling software was guided by needed capabilities and potential regulatory acceptance. HSPF was chosen primarily because of its ability to simulate all media of interest in the South River watershed and stream system at the desired time scales. HSPF is capable of simulating the transport of water, sediment, and mercury as well as phase exchange of mercury, all of which are important to mercury transport in the South River watershed. The time-series based simulations performed by HSPF allow for a 1-hour simulation period; this is fast enough to simulate changing river conditions during floods while still allowing long-term simulations that reflect average conditions. HSPF is also readily accepted by the regulatory community for TMDL purposes, and many TMDL studies approved by the USEPA have used it.

The timeline for this study is presented in figure 3, along with the timeframes used for the modeling. Data collection in the South River watershed by the VDEQ and other groups has been ongoing since the 1970s. USGS streamflow monitoring has been ongoing since 1926, and data were collected specifically for this study from April 2005 through March 2007. The three components of the watershed model were calibrated and verified separately using the time periods shown in figure 3.

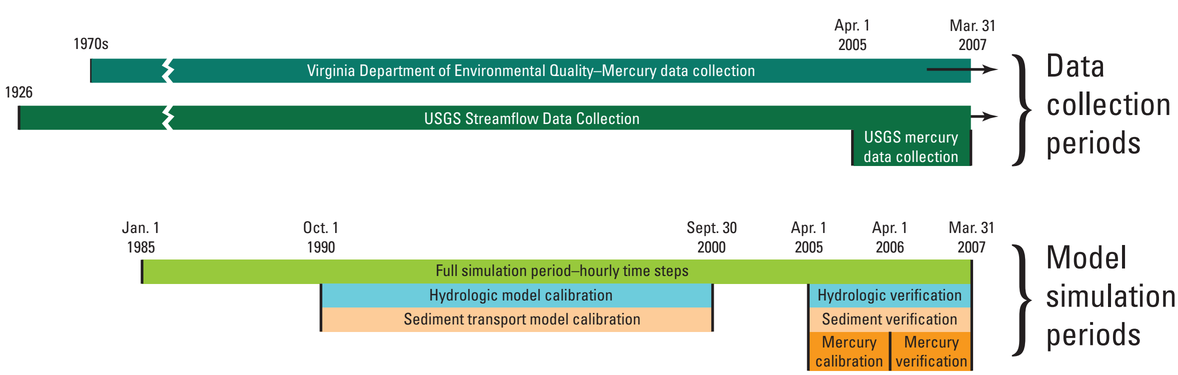


Figure 3. Timeline for data collection and model simulation, South River, Virginia.

Data Collected by the U.S. Geological Survey for This Study

Data were collected by USGS personnel over a 2-year (April 2005 through March 2007) field program. Goals of the field sampling and monitoring program were to collect data that would (1) characterize the locations and concentrations of mercury, (2) improve understanding of mercury loads in the watershed, and (3) allow calibration of a watershed mercury transport model. Most of the data were collected from three USGS monitoring stations along the South River near Waynesboro (01626000), at Dooms (01626920), and at Harriston (01627500) (fig. 2; table 2). Samples also were collected periodically from other sites along the river and at other locations such as pipe outfalls, groundwater wells, and riverbanks to guide model parameterization.

Data were also compiled from other organizations and from previous studies. These additional data help in understanding mercury in other media, such as fish and groundwater, and provide an independent measure for checking model calibration.

Streamflow

At three streamflow-gaging stations (01626000, 01626850, and 01627500) on the South River, 15-minute and daily average streamflow values were collected using standard USGS methods (Rantz and others, 1982; Kennedy, 1983). The daily streamflow data are available online and at the USGS National Water Information System (NWIS) website http://waterdata.usgs.gov/nwis/. Streamflow data were used to calibrate the watershed model and, in combination with concentration values, used to calculate sediment and mercury loads.

The average of annual mean streamflow for the period of record increased from 150 ft^3/s at Waynesboro 2.8 mi upstream from the plant to 261 ft^3/s at Harriston 16.5 mi downstream from the plant site (table 2). Annual average flows varied widely, with a lowest measured annual average flow at Harriston of 70 ft^3/s and highest of 516 ft^3/s (fig. 4).

Water Quality

At the beginning of the project, it was not clear which water-quality parameters would control or correlate with fish tissue methylmercury concentrations and therefore be important to study. Therefore data collection was designed to measure water-quality parameters that had been shown at other mercury contaminated sites to correlate with mercury transport and mercury concentrations in fish (Gilmour and others, 1998; Yin and Balogh, 2002). The following water-quality parameters were selected for monitoring in the South River: mercury (particulate and filtered concentrations of total mercury and methylmercury in various media), suspended sediment concentration, turbidity, dissolved organic carbon, chloride, sulfate, pH, and temperature. The last five parameters were

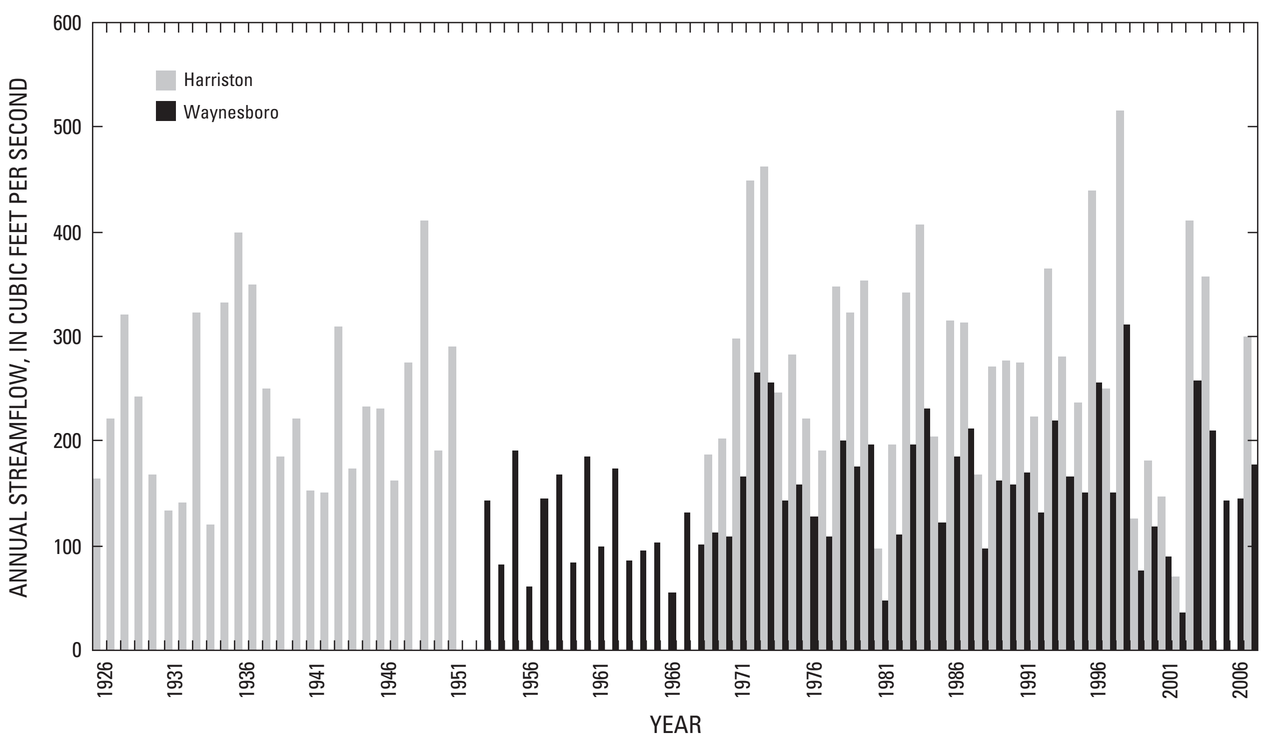


Figure 4. Annual streamflow for the South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500), water years 1926–2007.

selected with the specific intent of discovering correlations to methylmercury concentrations in water. Near the end of the data-collection program, it was decided that the study should focus only on total mercury because total mercury had the strongest correlation with fish tissue methylmercury concentrations in the South River. For this reason, only water-quality results for suspended sediment concentration, turbidity, and mercury concentrations are presented. The other parameters (dissolved organic carbon, chloride, sulfate, pH, and temperature) are not presented because they did not show a strong correlation with methylmercury concentrations.

Methods

At each stream monitoring site, vertically integrated grab samples were collected from a single lateral location at the centroid of flow under base-flow conditions. All water-quality samples were taken as single vertically integrated grab samples. Continuous water-quality and grab sample data from this study can be accessed at the USGS NWIS website http://waterdata.usgs.gov/nwis/. Surface-water samples were collected from bridges at the monitoring locations: Waynesboro (01626000), Dooms (01626920), and Harriston (01627500) (fig. 2). After each sampling event, bottles were sent for analysis to the USGS Eastern Region Sediment Laboratory, the USGS National Water Quality Laboratory, and the USGS Mercury Laboratory (tables 3, 4).

A large percentage of mercury in the water column is typically bound to suspended particulate matter (Hem, 1989), so suspended sediment concentrations were measured in this study. Suspended sediment data were used to calibrate the numerical model for sediment transport as discussed in a later section, Sediment Model Calibration Results. Raw water samples were collected in 1-pint glass bottles and filtered with a 1.5-µm (micrometer) glass fiber filter during analysis of suspended sediment concentration (Guy, 1969). (Sampling and processing details are available online at http://ky.water.usgs.gov/technical_info/dist_sedlab_files/sed_lab.htm.)

Horizontal variability in water-quality constituent concentrations is not reflected in a single vertically integrated sample, unlike a full representative cross-sectional sample. The decision to collect single vertically integrated samples was made to decrease the possibility of contaminating trace-level mercury concentrations due to the extra handling and equipment involved. A full concurrent cross-sectional

Table 3. Water-quality sample treatments and laboratories used in the study.

[mg/L, milligrams per liter; mL, milliliter; °C, degrees Celsius; USGS, U.S. Geological Survey]

Analyte	Laboratory	Sample container	Field treatment	Detection limit (mg/L)
Dissolved organic carbon	National Water Quality Laboratory	125-mL amber glass	Filter immediately, acidify with H_2SO_4, and preserve at 4 °C	0.33
Sulfate		250-mL plastic	Filter immediately and preserve at 4 °C	0.18
Chloride				0.20
Suspended sediment concentration	USGS Eastern Region Kentucky Sediment Lab	1-pint glass	Preserve at 4 °C	1

Table 4. Detection limits for mercury analyses.

[USGSML, U.S. Geological Survey Mercury Laboratory; mL, milliliters; ng/L, nanograms per liter; µg/g, micrograms per gram; °C, degrees Celsius; see table 6 for description of analyte abbreviations]

Analyte	Laboratory	Sample container	Field treatment	Detection limit	Units
Total filterable mercury (THG_F), aqueous methylmercury (MHG)	USGSML	Precleaned Teflon from USGSML (250, 500, 1,000, and 2,000 mL)	Preserve at 4 °C	0.04	ng/L
Aqueous total mercury associated with non-filterable particulates (THG_P)				0.06	ng/L
Total mercury on soils or surface sediment (THG_{SED})				0.30	µg/g

sampling event was performed at the Harriston station in August 2005 under base-flow conditions to test the representativeness of a single vertically integrated sample. The results indicated no consistent patterns of horizontal variation in the water-quality parameters tested (THG, THG_F, THG_P, THG_{SS}, MHG, chloride, sulfate, pH, suspended sediment, and specific conductivity). Data from other studies have shown higher filtered mercury (THG_F) concentrations in the South River closer to riverbanks and to sediment-water interfaces (Turner and Jensen, 2007) under base-flow conditions, however.

Continuous monitoring of in-stream water quality was performed by hanging probes from bridges into the river near Waynesboro, at Dooms, and at Harriston (table 2). Probes were located close to the centroid of flow at deep points in the river so that they would remain submerged under low water conditions. Continuous water-quality data for the three South River monitoring stations are available on the USGS NWIS website at http://waterdata.usgs.gov/nwis/. Probes were calibrated and serviced on a monthly basis. The continuous parameters were collected using a YSI multi-parameter field meter (model 6920 or similar) following standard USGS protocol (Wagner and others, 2000).

Water-quality samples analyzed for mercury were collected according to established sampling protocol for ultra-trace metals; aqueous and sediment samples were collected using the “clean hands – dirty hands” technique (Ward and Harr, 1990; Horowitz, 1991; Horowitz and others, 1994; U.S. Environmental Protection Agency, 1996). Surface-water samples were collected in 2-L (liter) Teflon bottles precleaned by the USGS Mercury Laboratory. The precleaned 2-L Teflon bottles were placed into a stainless steel bottle holder, and then lowered into the river from a bridge. A single vertically integrated sample was collected at each monitoring site and capped, placed on ice, and shipped to arrive at the USGS Mercury Laboratory within 24 hours. Laboratory personnel then processed the sample using techniques based on USEPA Method 1631 (Olson and DeWild, 1999; DeWild and others, 2002; U.S. Environmental Protection Agency, 2002; Olund and others, 2004). Filtering of mercury samples through a 0.7-μm filter was performed in the laboratory; no filtering of mercury samples was performed in the field. Detection limits for laboratory analyses of mercury are shown in table 4.

During a base-flow period in June 2006, pore-water samples were collected from the riverbank along the river’s edge at one location upstream from the plant site at Waynesboro (01626000), and at three locations downstream from the plant site: Basic Park, 0.2 mi upstream from monitoring station 01626850; Steeles Run confluence, 0.4 mi upstream from monitoring station 01626850; and at Dooms (01626920). Pore-water samples were collected using a Teflon drivepoint connected to Teflon tubing driven by a peristaltic pump. Samples were drawn from depths of 5 and 15 cm (centimeters) below land surface into precleaned Teflon bottles and shipped to the USGS Mercury Laboratory for analysis as previously described. Sediment samples were collected from the same 5- and 15-cm depths using precleaned stainless steel implements, placed into precleaned Teflon bottles, and shipped on ice to the USGS Mercury Laboratory.

Suspended Sediment

Results from the USGS suspended sediment concentration data collected for this study are summarized in table 5. Suspended sediment concentration was strongly affected by streamflow, generally increasing with increasing flows (fig. 5). Although the raw data show that Waynesboro had higher suspended sediment concentration values than Dooms and Harriston, this result is biased due to a greater proportion of stormflow samples collected at Waynesboro. When flow-corrected mean suspended sediment concentrations are calculated, Waynesboro exhibited a lower mean suspended sediment concentration than Dooms (table 5). Flow correction is performed by taking a weighted average that accounts for the magnitude of flow, assessed by streamflow duration at the time of sampling, and removes bias towards either low-flow or stormflow sampling. Results from the Harriston site show slightly lower mean and flow-weighted mean suspended sediment concentration values than the values from either the Waynesboro or Dooms sites.

Table 5. Suspended sediment concentrations and turbidity values, South River, Virginia, April 2005 through March 2007.

[U.S. Geological Survey samples only; FNU, Formazin nephelometric units; SSC, suspended sediment concentration; mg/L, milligrams per liter; %, percent]

Statistic		Monitoring Site		
		Waynesboro (01626000)	Dooms (01626920)	Harriston (01627500)
Suspended sediment concentration (mg/L)	Count	29	28	36
	Mean	56.4	39.4	38.2
	Median	8.0	6.5	7.5
	Standard deviation	112.0	99.7	83.9
	Range	1–434	1–433	1–377
Flow weighted SSC* (mg/L)	Mean	37.2	38.7	26
Turbidity (FNU)	Period	5/1/2005 to 4/1/07	4/21/2005 to 4/1/2007	6/3/2005 to 4/1/2007
	Count	62,588	63,052	58,595
	Data coverage	93%	93%	92%
	Mean	9.1	8.2	7.1
	Standard deviation	39.9	32.1	38.1

* Corrected for flow bias as described in the Mercury/Surface Water section.

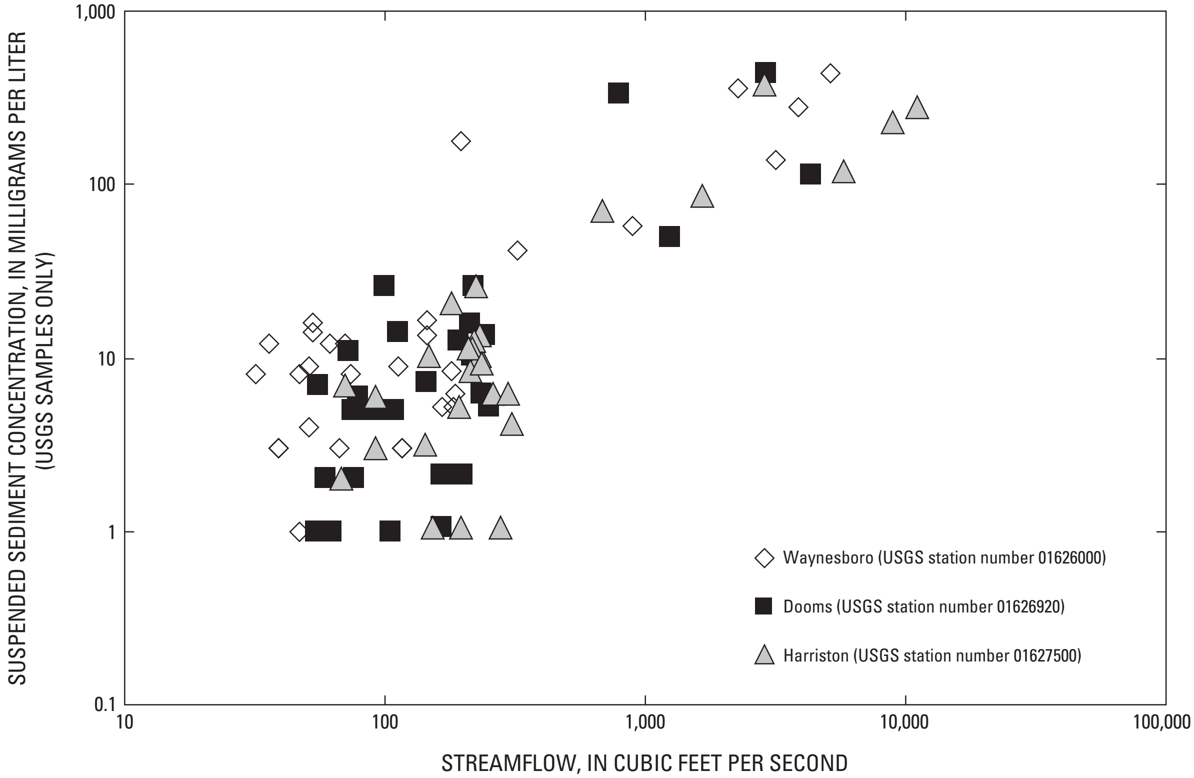


Figure 5. Observed suspended sediment concentrations and streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007.

Turbidity

Turbidity indicates the ability of a fluid to transmit light without scattering or absorption (Gray and Glysson, 2003). Turbidity was measured using the multiparameter probes and is reported in formazin nephelometric units (FNU) (fig. 6). Turbidity is used to develop a suspended sediment concentration time series. Turbidity results for the three monitoring stations in the study are summarized in table 5. Mean turbidity decreased from Waynesboro downstream to Harriston. Turbidity data collection from each probe was periodically interrupted due to conditions such as high water velocity and algae growth. During high-flow events, interruptions in turbidity data were common and, because turbidity typically rose during storms by one to two orders of magnitude, the statistics in table 5 are almost certainly affected by the missing data.

Mercury

Data were collected during this study to describe mercury concentrations in the South River, in piped discharges to the river, in groundwater, and in soils. Collection of mercury data was made using standard USGS sample-collection techniques and followed a quality assurance plan to ensure that data were comparable, complete, and representative. Mercury analyses were performed by the USGS Mercury Laboratory in Middleton, Wisconsin.

Units and Terms

Mercury concentrations are expressed in per mass or per volume units that depend on the medium being considered. The various mercury concentration units used in this report are defined in table 6.

Surface Water

Mercury concentrations for the monitoring stations on the South River are shown in tables 7 and 8. Downstream from the plant site, mean THG concentrations were more than 70 times higher than at the Waynesboro monitoring station. Concentrations of mercury on suspended sediment (THG_{SS}) increased by a factor of more than 100 downstream from the plant site.

During most sampling events, the majority of mercury in the water column was associated with suspended particulate matter (Meybeck and Helmer, 1989). At the background reference station (Waynesboro), about 78 percent of aqueous mercury was particulate-bound, whereas downstream from the plant site, 98 percent and 96 percent of the mercury was particulate-bound, at Dooms and Harriston, respectively.

Total mercury (THG) concentrations increased with increasing streamflow (fig. 7). Filterable mercury THG_F concentrations in nanograms per liter showed a slight positive correlation with streamflow (fig. 8), particularly at the Waynesboro reference station. The increase of filterable

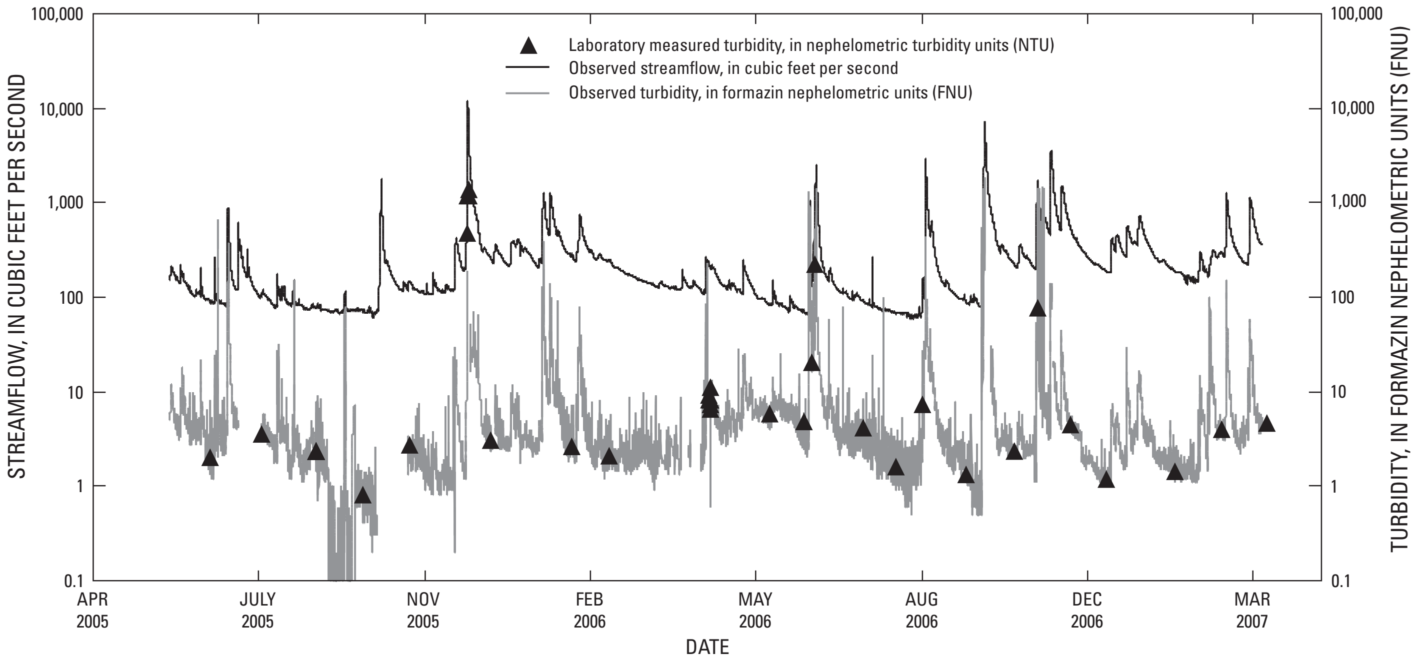


Figure 6. Streamflow and turbidity from June 2005 through April 2007 for the South River at Harriston, Virginia (USGS station number 01627500). (Data recorded at 15-minute intervals.)

Table 6. Description of units for mercury concentrations used in this report.

[ng/L, nanograms per liter; µm, micrometer; µg/g, micrograms per gram]

Acronym	Description of concentration	Units
THG	Aqueous total mercury, typically calculated as the sum of THG_F and THG_P.	Nanograms total Hg per liter of water (ng/L).
THG_F	Aqueous filterable total mercury.	Nanograms total Hg passing a 0.7-µm filter per liter of water (ng/L).
THG_P	Aqueous total mercury associated with non-filterable particulates.	Nanograms total Hg not passing a 0.7-µm filter per liter of water (ng/L).
THG_{SS}	Total mercury on solids suspended in water, calculated as THG_P/suspended sediment concentration.	Micrograms total Hg per gram of dry suspended solids (µg/g).
THG_{Sed}	Total mercury on soils or surface sediment.	Micrograms total Hg per gram of dry soil (µg/g).
MHG	Aqueous methylmercury.	Nanograms MeHg per liter of water (ng/L).

Table 7. Aqueous total mercury concentrations for the South River, April 1, 2005, through March 31, 2007.

[U.S. Geological Survey samples only; THG_F, filterable total mercury; THG_P, particulate total mercury; THG, unfiltered mercury; ng/L, nanograms per liter; n, sample size]

Station ID	n	Aqueous total mercury								
		THG_F (ng/L)			THG_P (ng/L)			$THG = THG_F + THG_P$		
		Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
Waynesboro (01626000)	30	1.0	0.4	0.1–3.7	3.3	0.8	0.3–19.8	4.3	1.3	0.5–23.5
Dooms (01626920)	28	7.4	7.2	2.7–14.5	291.9	100.3	14–2,730	299.3	103.6	17–2,740
Harriston (01627500)	36	13.6	12.9	4.0–33.2	319.2	99.6	13–4,020	332.8	115.0	18–4,042

Table 8. Concentrations of total mercury on suspended sediment in the South River, April 1, 2005, through March 31, 2007.

[U.S. Geological Survey samples only; THG_{SS}, mercury on suspended sediment; µg/g, micrograms per gram; n, sample size]

Station ID	n	Mercury on suspended sediment		
		THG_{SS} (µg/g)		
		Mean	Median	Range
Waynesboro (01626000)	30	0.1	0.1	0.0–0.7
Dooms (01626920)	28	17.4	13.1	2–66
Harriston (01627500)	36	13.5	10.8	2–48

mercury concentrations with streamflow may be due to desorption of mercury from contaminated sediment entering the stream and(or) from higher inflows of precipitation and interflow, both of which have average THG_F concentrations above 1.0 ng/L, or possibly from an increase in the concentration of colloidal particles passing the laboratory filter. THG_P concentrations, the aqueous concentration of mercury associated with suspended particulates, showed a strong positive correlation with streamflow at all monitoring stations (fig. 9). THG_{SS} concentration, the concentration of mercury on suspended particulates, showed a slight negative correlation with streamflow (fig. 10). Therefore, it can be concluded that the large increase in THG seen during high flows was driven by the large increase in suspended sediment concentration (fig. 5).

The concentrations of mercury and suspended sediment based on sample data from the South River are listed in table 9. Mercury concentrations for two other rivers—the North River near Burketown (01622000), which is an uncontaminated tributary to the South Fork Shenandoah River, and the South Fork Shenandoah River near Luray (01629500), which is located 69 mi downstream from the mouth of the South River—are listed in table 10. Concentrations listed in tables 9 and 10 are flow-weighted to remove sampling bias towards either stormflow or base-flow periods. Concentration values were grouped into 10 bins according to streamflow magnitude at time of sampling, defined by flow duration deciles of 0–10 percent, 10–20 percent, 20–30 percent, and so forth. To calculate the mean concentrations shown in tables 9–10, mean concentrations were calculated for each decile and then these 10 decile mean concentrations were averaged.

Of the surface-water samples collected from the South River, 17 percent were either field blanks or replicate samples used for quality control and assurance. Of the 22 THG_F and THG_P analytical values from the field blank samples, one was above 0.2 ng/L and was determined to be a laboratory clerical error and was dropped from the dataset. Of the 26 THG_F and THG_P analytical values from replicate samples, the average paired concentration difference was 0.8 ng/L with no sampling biases found, and the data were determined to be comparable and reproducible.

Groundwater

In June 2006, pore-water samples were collected at multiple locations at the edge of the South River and analyzed for THG_F concentrations. Results are shown in table 11. Pore-water THG_F concentrations were higher than those found in either groundwater from a contaminated flood plain (described later) or from the South River. Sediment collected during the same sampling events at these locations had high levels of mercury, and presumably, mercury in the soil is the source of the high dissolved mercury concentrations. No beads of elemental mercury were observed at the sampling locations.

Sediment

Sediment samples were collected from the river's edge during the June 2006 pore-water sampling event. These concentrations, shown in table 12, are similar to concentrations seen on suspended sediment in the South river (fig. 10) and to mean THG_{Sed} concentration values for flood-plain and riverbank soils compiled from the South River Science Team database, described in a later section, Mercury in Soil.

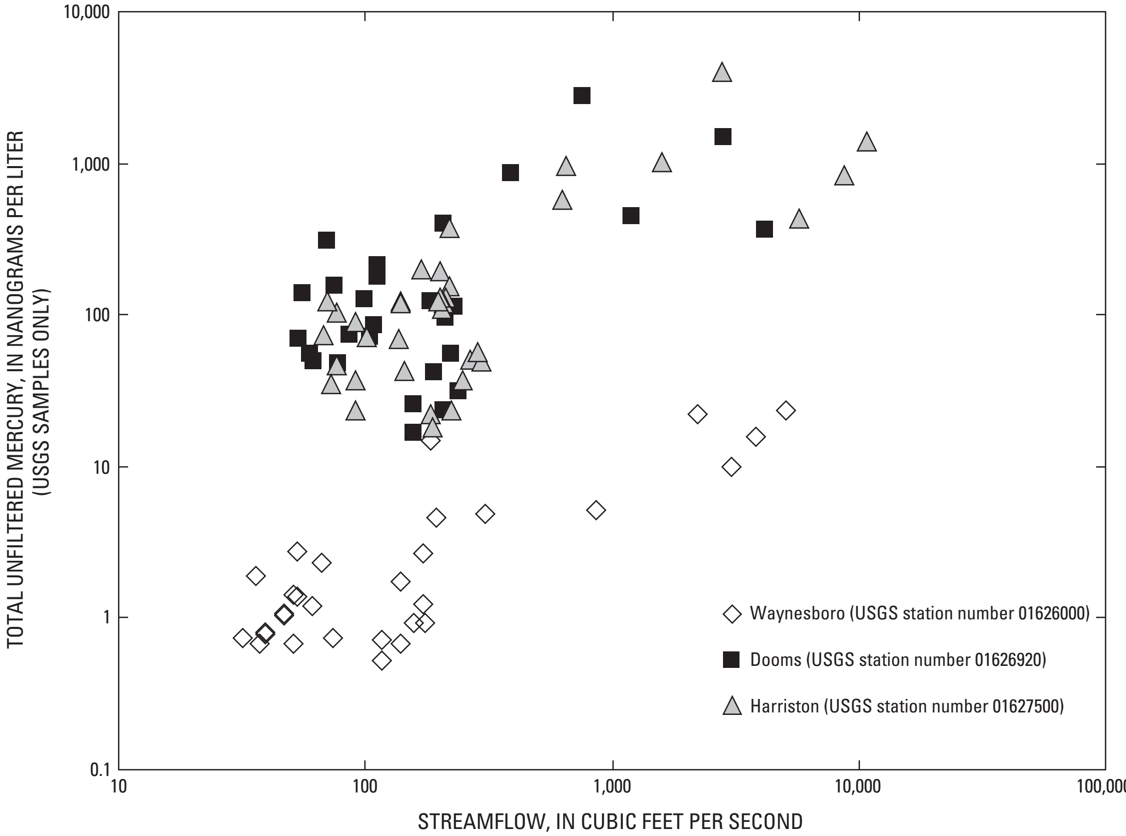


Figure 7. Observed total unfiltered mercury concentration and concurrent instantaneous streamflow in the South River, Virginia, April 1, 2005, through March 31, 2007.

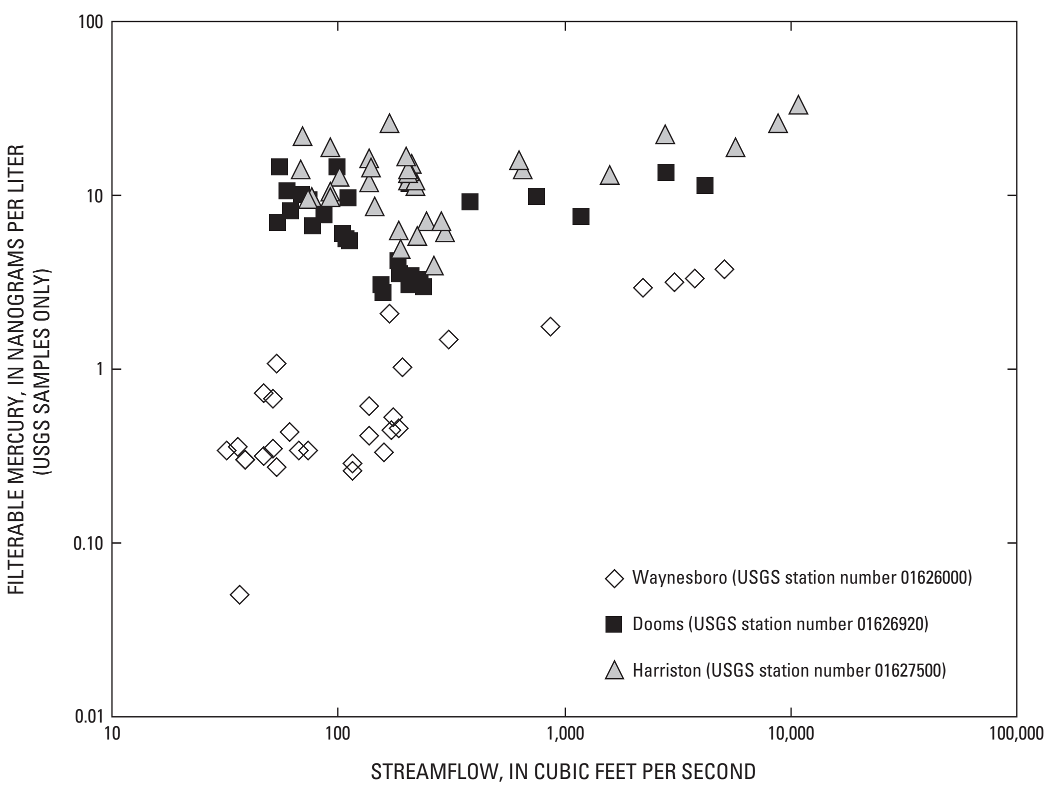


Figure 8. Observed aqueous concentration of filterable mercury and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

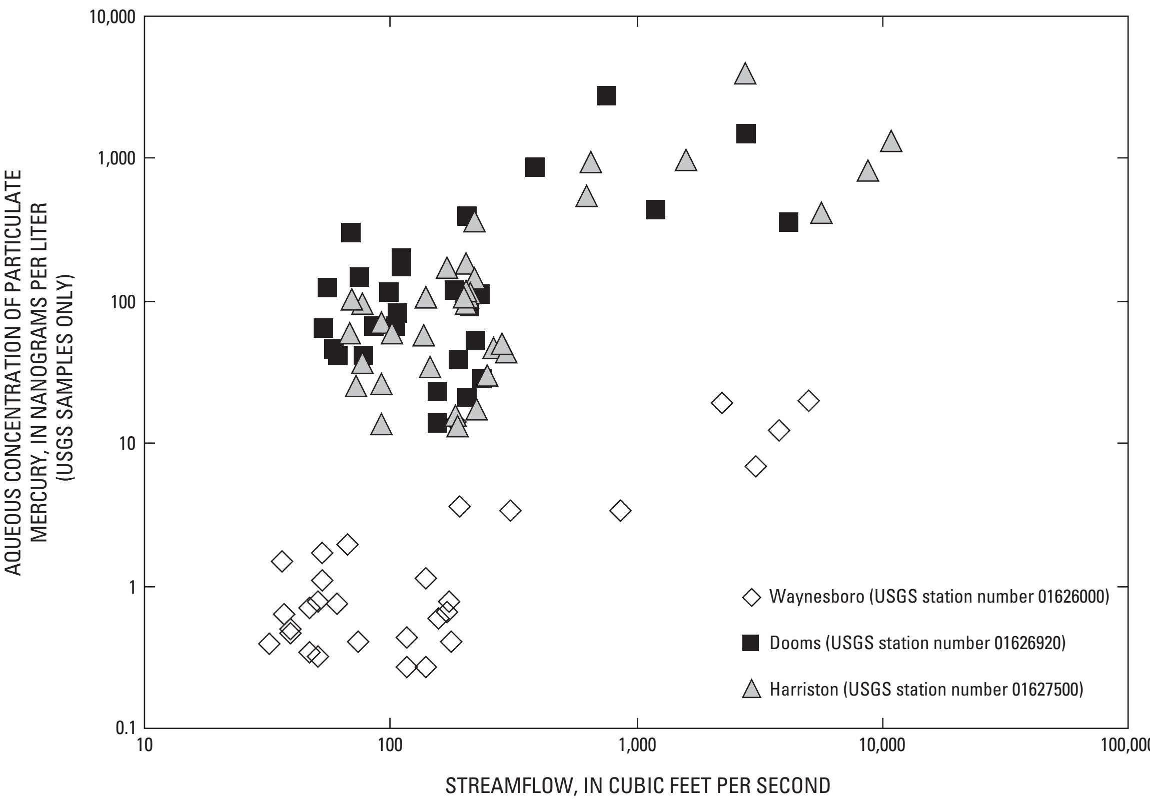


Figure 9. Observed aqueous concentration of mercury associated with particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

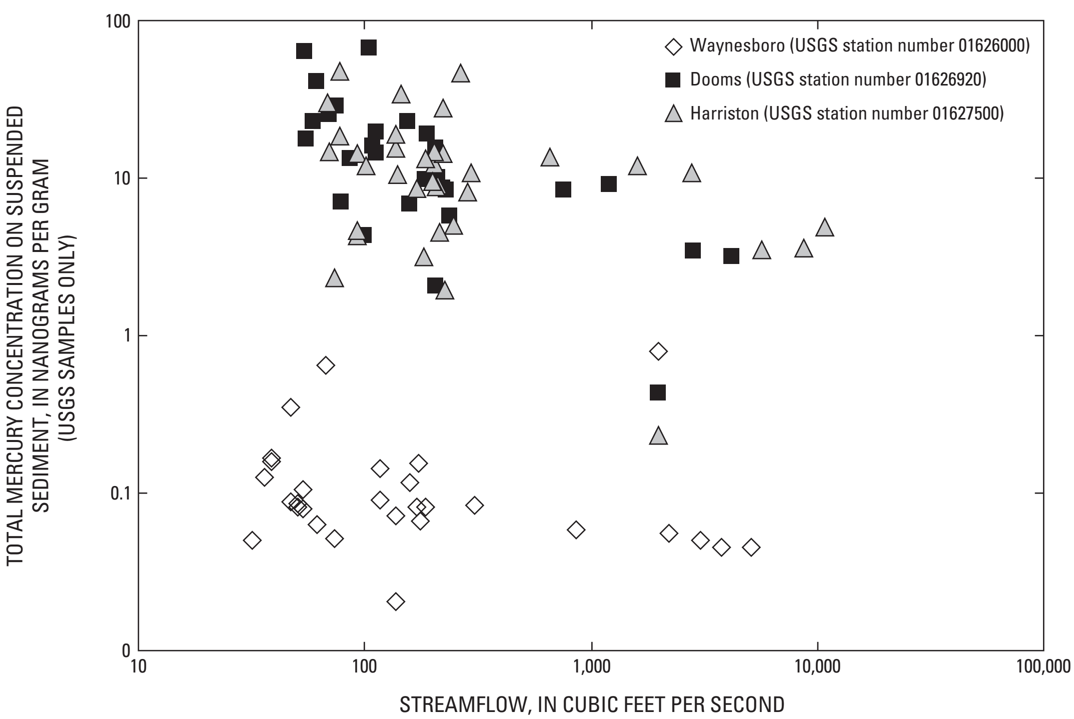


Figure 10. Observed concentration of mercury on suspended particulate matter and concurrent instantaneous streamflow, South River, Virginia, April 1, 2005, through March 31, 2007.

Table 9. Observed flow-weighted average sediment and mercury concentrations in the South River, Virginia, April 1, 2005, through March 31, 2007.

[U.S. Geological Survey samples only; ft^3/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter]

USGS monitoring station	Observed average daily streamflow (ft^3/s)	Flow-weighted average concentration	
		Suspended sediment (mg/L)	Total mercury concentration (ng/L)
Waynesboro (01626000)	167	37.2	3.2
Dooms (01626920)	225	38.7	336
Harriston (01627500)	276	26.0	237

Table 10. Observed flow-weighted average mercury concentrations in rivers neighboring the South River, Virginia, January 2002 through March 2006.

[Virginia Department of Environmental Quality samples only; ft^3/s, cubic feet per second; ng/L, nanograms per liter; n, sample size]

U.S. Geological Survey monitoring station ID	Drains to	Type	Average daily streamflow (ft^3/s)	Total mercury concentration	
				n	(ng/L)
North River near Burketown, VA (01622000)	South Fork Shenandoah River	Reference site	387	25	1.9
South Fork Shenandoah near Luray, VA (01629500)	Shenandoah River	Mercury contaminated site	1,422	25	10.8

Table 11. Concentrations of filterable total mercury THG_F in riverbank pore water, South River, Virginia, June 2006.

[U.S. Geological Survey samples only; cm, centimeters; BLS, below land surface; mi, miles; n, sample size; nd, no data]

Depth of sample	Filterable total mercury concentration (nanograms mercury per liter of water)			
	Waynesboro (01626000)	Steeles Run (0.4 mi upstream from station 01626850)	Basic Park (0.2 mi upstream from station 01626850)	Dooms (01626920)
5 cm BLS	nd	158.0 (n=2)	35.6 (n=2)	164.0 (n=1)
15 cm BLS	1.4 (n=1)	326.5 (n=2)	217.7 (n=2)	nd

Table 12. Concentrations of total mercury in riverbank sediment, South River, Virginia, June 2006.

[U.S. Geological Survey samples only; cm, centimeters; BLS, below land surface; mi, miles; n, sample size; nd, no data]

Depth of sample	Total mercury concentration on sediment (micrograms mercury per gram dry sediment)			
	Waynesboro (01626000)	Steeles Run (0.4 mi upstream from station 01626850)	Basic Park (0.2 mi upstream from station 01626850)	Dooms (01626920)
5 cm BLS	nd	11.2 (n=2)	4.2 (n=2)	nd
15 cm BLS	nd	11.3 (n=2)	3.4 (n=2)	nd

Mercury Sorption to Suspended Solids

Mercury (THG) in the South River partitions between sorbed and dissolved phases. The data in tables 7 and 8 indicate a distribution coefficient (Kd) for total mercury in the South River of about 1,000,000 L/kg (liters/kilogram), or a log Kd of about 6, assuming that sorption was at equilibrium in the samples at the time of analysis. This Kd value of about 6 is seen both in the ratio of sampled mean THG_F and THG_{SS} concentrations (tables 7 and 8) and in laboratory batch tests by Mason (2006). A lot of spatial and temporal variation is present in this distribution coefficient, however, some of which corresponds to the location relative to the plant site. Average log Kd was lowest (5.1) upstream from the former DuPont plant site at the Waynesboro monitoring station (01626000), highest (log Kd = 6.4) downstream at the Dooms monitoring station (01626920), and lower again (log Kd = 6.0) further downstream at the Harriston monitoring station (01627500). Partitioning ratios also correlated negatively with streamflow. Log Kd values, determined from the ratio of sampled THG_F and THG_{SS} concentrations, were higher during low flow than high flow at all three monitoring stations. At monitoring station 01626920, for example, mean log Kd was 6.25 for base-flow samples and 5.80 for stormflow samples. This variation may be due to various causes; non-equilibrium sorption (time delay to reach equilibrium) in combination with loads having varying proportions of dissolved and sorbed mercury, runoff sediment characteristics varying with river location, different mixing in the water column according to river location, chemical variations such as pH along the river, or other possible variables whose effects on mercury partitioning are currently not well understood for the South River. A constant and uniform Kd value of 1,000,000 was used in the mercury transport model.

Data Compiled From Other Sources

The South River is the subject of many past and ongoing studies, which provided valuable supplemental data to this study. Selection of data from other sources to include in this study was prioritized according to need, reliability, and public availability. Many other datasets not used or mentioned in this study are available from the VDEQ in Harrisonburg, Virginia, or by request from the South River Science Team website (http://www.southriverscienceteam.org).

Suspended Sediment

Suspended sediment data previously collected by the VDEQ were compiled. The VDEQ data were reported in units of milligrams per liter and, like USGS suspended sediment samples, are filtered with a 1.5-μm filter. However, they were reported as "total suspended sediment" rather than "suspended sediment concentration" because of differences in laboratory methods, such as a sample split rather than a whole sample being analyzed. An additional difference between USGS and VDEQ suspended sediment data is that concentrations below detection limits were generally reported as 3 mg/L. This 3 mg/L value for VDEQ data was maintained for analysis in this study. The USGS suspended sediment concentration data had a reporting limit of 1.0 mg/L, and reporting limit values were maintained at 1.0 for data analysis. In later sections of this report, the VDEQ total suspended sediment data and the USGS suspended sediment concentration data are treated as equivalent for purposes of discussion and illustration.

Mercury in Surface Water

Mercury concentrations in surface water measured by the VDEQ were compiled to provide representation of time periods before April 2005, and coverage of rivers other than the South River. The VDEQ has had an extensive sampling program for mercury in the Shenandoah River watershed in place since the 1980s. Mercury concentration values used in this report were drawn from the VDEQ's database in August 2008. These data were not used in calibrating the watershed model, but provided an independent basis for checking model results. These data were also used to estimate mercury loads in the South Fork Shenandoah and Shenandoah Rivers.

Mercury concentrations in runoff and wastewater discharge from the plant site are measured by DuPont. These mercury data were made available to this study by DuPont, DuPont's contractors, and the USEPA.

Atmospheric Mercury Deposition

Mercury is deposited from the atmosphere in both wet and dry forms. Data describing atmospheric mercury deposition were obtained from the USEPA Mercury Deposition Network (MDN) website (http://nadp.sws.uiuc.edu/mdn/). Two MDN sites are about 50 mi northeast of Waynesboro: Big Meadows (VA28), located on top of the Blue Ridge Mountains at an elevation of 3,524 ft, and Culpeper (VA08), located east of the Blue Ridge Mountains at an elevation of 535 ft (fig. 11). Annual mercury wet deposition at both stations was 13.2 $\mu g/m^2$ during 2003. Actual mercury deposition rates in the study area may differ from this value. There is at least one coal-fired electric generation plant in the watershed (at the Invista/DuPont plant site), which has the potential to locally elevate mercury deposition rates. Dry deposition of mercury (the transfer of mercury from the atmosphere to the ground in the absence of precipitation) likely occurs, but no reliable data are available describing rates near the study area. A 1997 modeling study by the USEPA (U.S. Environmental Protection Agency, 1997, table 3–3) found that wet deposition accounts for 51 percent of total atmospheric mercury deposition in the continental United States, whereas dry deposition accounts for 49 percent. Data shown in figures from the 1997 U.S. Environmental Protection Agency report indicate that most of the State of Virginia, including the South River study area, has a total Hg dry deposition rate ranging from 3 to 10 $\mu g/m^2/yr$.

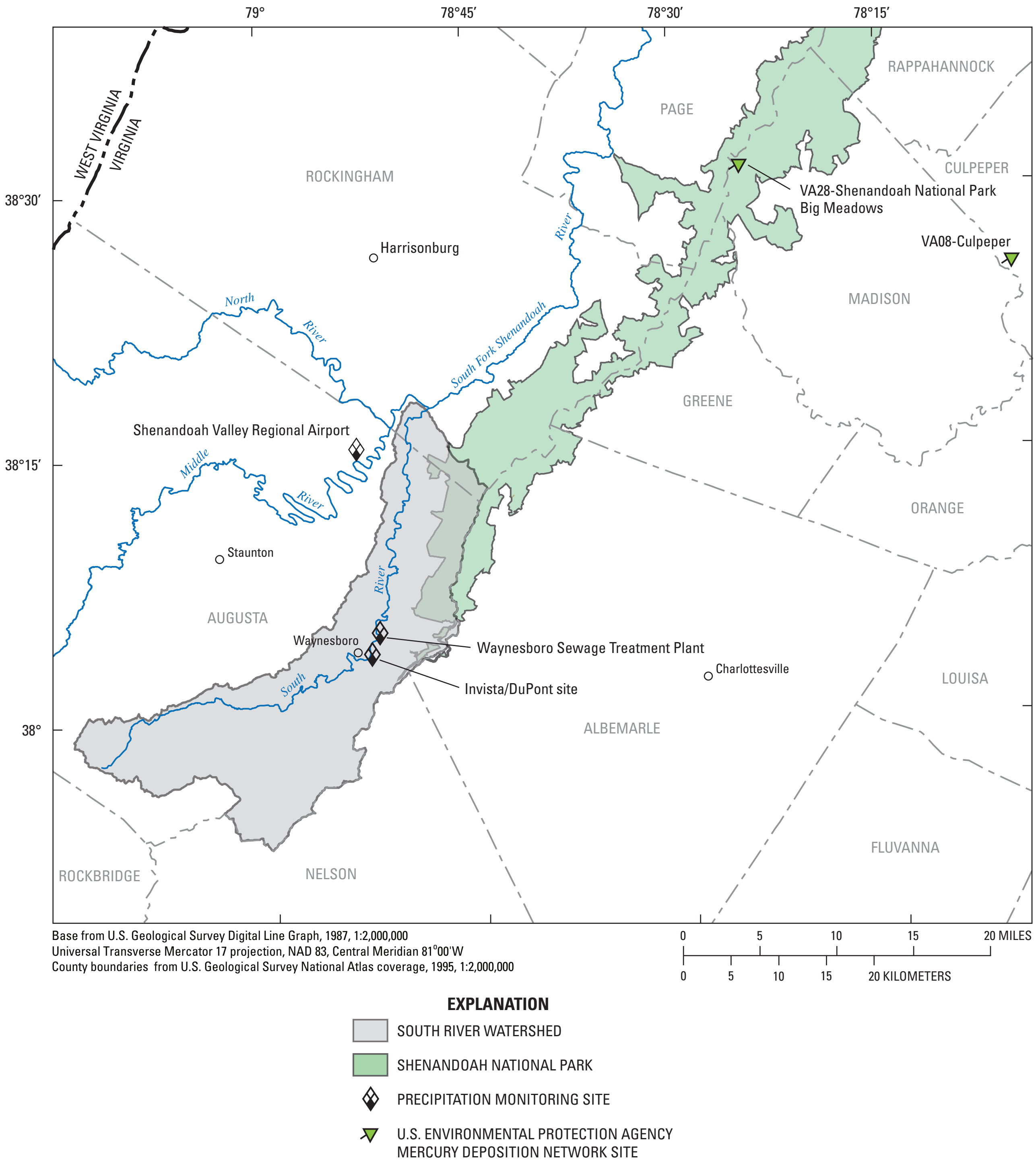


Figure 11. Location of mercury deposition and precipitation monitoring sites.

On the basis of the MDN numbers and the 1997 USEPA study, it is assumed that total atmospheric mercury deposition in the study area was 20.0 μg/m^2/yr for the simulation period. Multiplying this value by 234 mi^2 (6.1×10^{8}m^2) results in estimated atmospheric mercury input to the study area of 12.1 kg/yr. The modeling efforts described later use average atmospheric mercury concentrations that assume all mercury deposition takes place in the wet form. To calculate an average THG_F concentration in precipitation, the total deposition of 20.0 μg/m^2/yr was multiplied by average annual precipitation of 1.02 m/yr and by a unit correction factor to yield an average THG_F concentration in precipitation of 21.79 ng/L.

Most of the atmospheric mercury deposited on the South River watershed binds to surface soils and does not reach the South River, as has been found in other watersheds (U.S. Environmental Protection Agency, 1997, vol. 3). This is evident from a mercury mass balance at the upstream Waynesboro river monitoring site. Using the same decile-weighting procedures that were used for the values in table 9 yields an estimated mercury load for the South River at the Waynesboro monitoring station of 0.7 kg/yr. The estimated annual mass of mercury deposited from the atmosphere to the watershed above the Waynesboro monitoring station is 6.6 kg/yr, estimated by multiplying the deposition rate (20.0 μg/m^2) by the Waynesboro watershed area (127 mi^2). Comparing the two loads, only 11 percent of the estimated atmospheric mercury deposition upstream from the Waynesboro monitoring station reaches the South River.

Mercury in Fish Tissue

Virginia State agencies have collected fish from the South River for mercury analysis since the late 1970s. The Virginia Department of Health has placed fish consumption bans or advisories on the South River and the South Fork Shenandoah River since 1977 (Bolgiano, 1980). The VDEQ currently collects fish for mercury analysis, and the findings are summarized in their reports (Virginia Department of Environmental Quality, 1999, 2000, 2008a). Fish tissue mercury concentrations have not changed appreciably since monitoring started (Virginia Department of Environmental Quality, 2001). Fish tissue mercury concentrations along the South River from smallmouth bass collected and analyzed by the VDEQ from 1999 through 2007 are shown in figure 12. Upstream from the plant site, concentrations were generally below the USEPA 0.3 mg/kg criterion. Downstream from the plant site, fish tissue methylmercury concentrations rose rapidly for about 5 mi, and showed the highest concentrations between 5 and 12 mi downstream from the plant site.

Compared to fish tissue methylmercury concentrations from 20 other regions in the U.S. (Brumbaugh and others, 2001), the South River had higher fish tissue methylmercury concentrations than all water bodies except one, the Nahontan Reservoir in Nevada, which has been contaminated as a result of mercury mining. Unlike the sites studied by Brumbaugh and others (2001), the South River exhibits a strong correlation between fish Hg concentrations and aqueous THG concentrations. This strong correlation is discussed in the VDEQ TMDL report accompanying this study (Virginia Department of Environmental Quality, 2008b). In the nearby North River watershed, where there is no known industrial mercury contamination, fish tissue methylmercury concentrations averaged 0.2 mg/kg in 2007 (Virginia Department of Environmental Quality, 2008a).

Mercury in Soil

Additional data describing mercury concentrations in soils were compiled for use as input to the model. The THG_{Sed} values in table 13 were derived from a database of field sample results collected by South River Science Team members and maintained by DuPont (http://www.southriverscienceteam.org) (DuPont, 2008). The mercury concentrations were measured in soils collected from depths of 0 to 1.0 m below land surface, and from a variety of settings including the river channel, riverbanks, and agricultural and forested flood plains. Values were grouped according to location along the river, and mean values were calculated. In the model, these values are multiplied by loading coefficients that control the

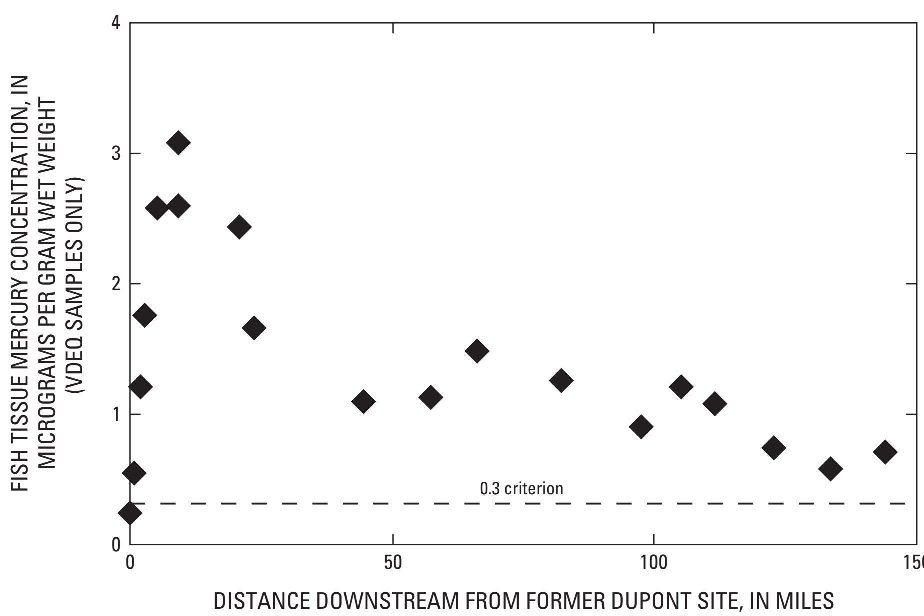


Figure 12. Fish tissue mercury concentrations in smallmouth bass, 1999–2007, South River, South Fork Shenandoah River, and Shenandoah River, Virginia.

Table 13. Average concentrations of mercury in soil, South River watershed, Virginia, April 2003 through October 2006.

[Samples from multiple sources compiled in the South River Science Team database. Hg, mercury; THG_{Sed}, mercury concentration on sediment or soil; µg/g, micrograms per gram; negative values indicate upstream from plant site]

Reach	Miles from plant site		Soil HG samples		Model THG_{Sed} value µg/g
	From	To	Count	Average THG_{Sed} µg/g	Final calibrated value
1	–30.0	–2.5	2	0.01	0.07
2 (upstream)	–2.5	0	24	0.27	0.07
2 (downstream)	0	2.3	145	13.9	13.9
3	2.3	5.3	137	16.2	16.7
4	5.3	16.5	245	17.2	16.7
5	16.5	24.0	41	7.6	7.6

amount of mercury entering each model river reach from each hydrologic response unit representing contaminated flood-plain areas. During calibration, the loading coefficients were adjusted to match simulated THG values in the river reaches to observed values.

Mercury in Groundwater

Groundwater samples were collected in October 2006, from a pastured flood plain 1 mile upstream from the Dooms station (01626920) in a joint effort by the U.S. Environmental Protection Agency, the Virginia Department of Environmental Quality, and the U.S. Geological Survey. The flood plain is downstream from the plant site and known to have mercury contamination in surface soils. Groundwater samples were pumped from 18 wells that had been installed to depths within 30 ft of land surface. The samples analyzed for total mercury were collected and analyzed by the VDEQ following USEPA methods 1669 and 1631, Rev. E (U.S. Environmental Protection Agency, 1996, 2002), which have THG_F detection limits of 1.5 ng/L.

Thirteen of the 18 samples had THG_F concentrations below the detection limit of 1.5 ng/L. The maximum THG_F concentration was 25.8 ng/L. When the non-detect values are set to zero, the mean THG_F value of the 18 samples was 2.9 ng/L, which was later used as an input to the numerical watershed model.

Development of Time-Series Data

The complex hydrologic conditions within the South River watershed are constantly changing, sometimes rapidly, when the river rises in response to a storm, for example. Time-series data describing these changing hydrologic conditions are needed to run the numerical watershed model and to calibrate the model. Time series were developed containing values for each required model input variable in regular intervals, typically 1 hour, to match the time step of the HSPF watershed model. These time-series data and their sources are summarized in table 14.

Streamflow Time Series

Observed streamflow data were used to calibrate the hydrologic part of the numerical watershed model and to calculate regressed suspended sediment concentration values. Daily mean streamflow time series for the period October 1, 1990, through September 30, 2007, were developed for streamflow-gaging stations 01626000, 01626850, and 01627500 for calibration and verification of the hydrologic model. Hourly streamflow values for the same period were used to estimate suspended sediment concentration values as described in the next section(s). Both hourly and daily streamflow data were drawn from USGS-NWIS databases.

Table 14. Sources of time-series data used in the South River watershed model.

[CBM5, Chesapeake Bay Community Watershed Model, Phase 5, (Chesapeake Bay Program, 2006); NOAA, National Oceanic and Atmospheric Administration; VDEQ, Virginia Department of Environmental Quality; VPDES, Virginia Pollutant Discharge Elimination System; USGS, U.S. Geological Survey]

Time series	Source of data
Streamflow	Stage monitoring, USGS
Meteorology: rainfall, snowfall	CBM5 datasets, NOAA weather station data, and data supplied by Invista and the City of Waynesboro
Climatic conditions: air temperature, wind speed, cloud cover, dew point, evapotranspiration, solar radiation	CBM5 datasets, NOAA weather station data
Suspended sediment concentration	Sample analyses and multiple linear regression, USGS and VDEQ datasets
Mercury concentrations	Sample analyses, VDEQ and USGS datasets
Point-source discharges	VPDES data, permittee records

Suspended Sediment Concentration Time Series

A time series of suspended sediment concentration was needed to calibrate the sediment part of the numerical watershed model. Time series allow more detailed and accurate model calibration than periodic grab sample values alone. Hourly time series of suspended sediment concentration at the primary monitoring stations (01626000, 01626920, and 01627500) were developed to match the hourly time step of the watershed model for the periods October 1, 1990, through September 30, 2000, and April 1, 2005, through March 31, 2007.

Suspended sediment concentration values were regressed using linear multiple regression models with independent variables of turbidity and various transformations of streamflow. Use of turbidity and transformed streamflow as independent parameters generally improves predictions of suspended sediment concentration by linear regression models, as has been demonstrated in other investigations (Rasmussen and others, 2005; Jastram, 2007). Suspended sediment concentration data available for the regression are from analyses of 78 grab samples (USGS only) collected at the three South River water-quality monitoring stations. The samples were collected during both base-flow and stormflow conditions at all three stations, as described earlier.

A suitable regression model had to be formulated from the many possible explanatory (independent) variables. At the start of the regression analysis, a suite of variables was tested for correlation with suspended sediment concentration. The following variables were then retained as possible explanatory variables in the linear regression model:

Q = Streamflow (ft^3/s) measured concurrently with water sampling;
$log_{10}Q$ = Log of Q;
$Q^{1/2}$ = Square root of Q;
Q_{slope} = Percent change in Q from 1 hour previous;
$Q_{increase}$ = Absolute value change in Q (ft^3/s) from 1 hour previous, (no negatives);
Q_A = Q normalized by watershed area; and
$Turb$ = Turbidity (FNU).

Of the several streamflow parameters, Q_A exhibited the highest correlation with suspended sediment concentration (R^2 = 0.744). Q_A was therefore retained in the regression model whereas Q, $log_{10}Q$, and $Q^{1/2}$ were excluded from the model because though they each have predictive value on their own, they correlate too strongly with Q_A to be included in the multiple regression model. $Q_{increase}$ and Q_{slope} were then redefined as follows:

Q_{slope} = Percent change in Q_A from 1 hour previous; and
$Q_{increase}$ = Change in Q_A (ft^3/s) from 1 hour previous, negative values = 0.

The remaining four independent variables (Q_{slope}, Q_A, $Q_{increase}$, and $Turb$) were then analyzed to determine the best multiple linear regression model for suspended sediment concentration. The best model(s) were selected primarily on the basis of three statistics—adjusted r-squared (R_a^2), Mallow's Cp, and the maximum variance inflation factor (*Max VIF*). All three statistics indicate a regression model's goodness of fit, while also handicapping models that use a greater number of explanatory variables (Helsel and Hirsch, 2002). Results of the multiple linear regression analysis are shown in table 15.

Table 15. Linear multi-regression models for suspended sediment concentration.

[U.S. Geological Survey samples only; R^2, goodness of fit; R_a^2, adjusted r-squared; Cp, Mallow's statistic; *Max VIF*, maximum variance inflation factor; Q_A, discharge normalized by watershed area; *Turb*, turbidity; $Q_{increase}$, change in Q_A from 1 hour previous; Q_{slope}, percent change in Q_A from 1 hour previous]

Model number	Number of variables	Mean squared error	R^2	R_a^2	Cp	Max VIF	Dark gray cells indicate the variable is included in the regression model			
							Q_A	Turb	$Q_{increase}$	Q_{slope}
1	1	1,622.9	0.744	0.744	101.9	—	■			
2	1	888.2	0.896	0.895	22.3	—		■		
3	1	5,002.6	0.434	0.426	468.2	—			■	
4	1	8,239.8	0.035	0.023	819.0	—				■
5	2	897.2	0.896	0.894	24.0	3.91	■	■		
6	2	706.3	0.918	0.916	3.5	1.00		■		■
7	2	1,115.3	0.871	0.868	47.3	1.00	■		■	
8	2	857.4	0.901	0.898	19.7	1.69		■	■	
9	3	804.2	0.908	0.905	14.9	3.91	■	■	■	
10	3	1,123.6	0.872	0.867	48.6	1.38	■		■	■
11	3	701.2	0.920	0.917	4.0	3.91	■	■		■
12	4	705.2	0.920	0.916	5.4	3.91	■	■	■	■

Multiple regression model no. 6, which uses turbidity and the slope of streamflow, is the best predictive model for suspended sediment concentration because it has the lowest *Cp* and *Max VIF* values and the second highest R_a^2 value. During periods when turbidity data are not available, such as prior to 2005 and periodically after 2005, the best regression model is no. 7, which has the lowest *Cp* and *Max VIF* values, and second highest R_a^2 values of the models that do not use turbidity.

A basis of comparison for the regressed suspended sediment concentration values is given by Gellis and others (2004), who used alternate linear estimation methods to calculate suspended sediment concentration for the South Fork Shenandoah River at Front Royal, Virginia (USGS station no. 01631000), about 100 mi downstream and to the northeast of the South River watershed. Their results show 50th and 90th percentile suspended sediment concentration values of 10.5 and 157 mg/L at monitoring station 01631000, which has a drainage area of 1,634 mi^2. Compared to the regressed values in this study, for the combined periods October 1, 1990, through September 30, 2000, and April 1, 2005, through March 31, 2007, Waynesboro (01626000) exhibits 50th and 90th percentile values of 1.7 and 19.3 mg/L, whereas Harriston (01627500) exhibits values of 3.4 and 42.3 mg/L, respectively. Because rivers with larger drainage areas have higher suspended sediment concentrations, the statistics for the regressed suspended sediment concentration values compare reasonably well (Gellis and others, 2004).

The regressed suspended sediment concentration time series from model no. 7 is shown in figure 13. There is reasonable agreement between the observed and regressed values, except at very low values where analytical detection limits are approached. The value of the regression method can be seen in the storm peak values of regressed suspended sediment concentration, which generally exceed the observed values. This is beneficial to the calibration because infrequent large storms carry most of the suspended sediment load, but grab samples are unlikely to have been collected at the moment of peak suspended sediment concentration values during a storm. The regression equation provides a means of extrapolating beyond the highest observed suspended sediment concentration values, although the extrapolated values have considerably less certainty than regressed values within the range of observed data.

Meteorological and Climatic Data

The numerical watershed model requires a variety of climatic and meteorological input time-series data. Following Chesapeake Bay Community Watershed Model, Phase 5 (CBM5) structure, the following data were input to the model: precipitation, cloud cover, dew point, wind speed, solar radiation, air temperature, and potential evapotranspiration (Chesapeake Bay Program, 2006). These data all were in the form of time series with hourly time steps. HSPF uses these input data to calculate actual evapotranspiration, soil moisture storage, snow melt, and runoff, among other hydrologic variables.

For the period January 1985 through August 2005, time-series data for the above variables were obtained from the CBM5 model and used in the South River watershed model

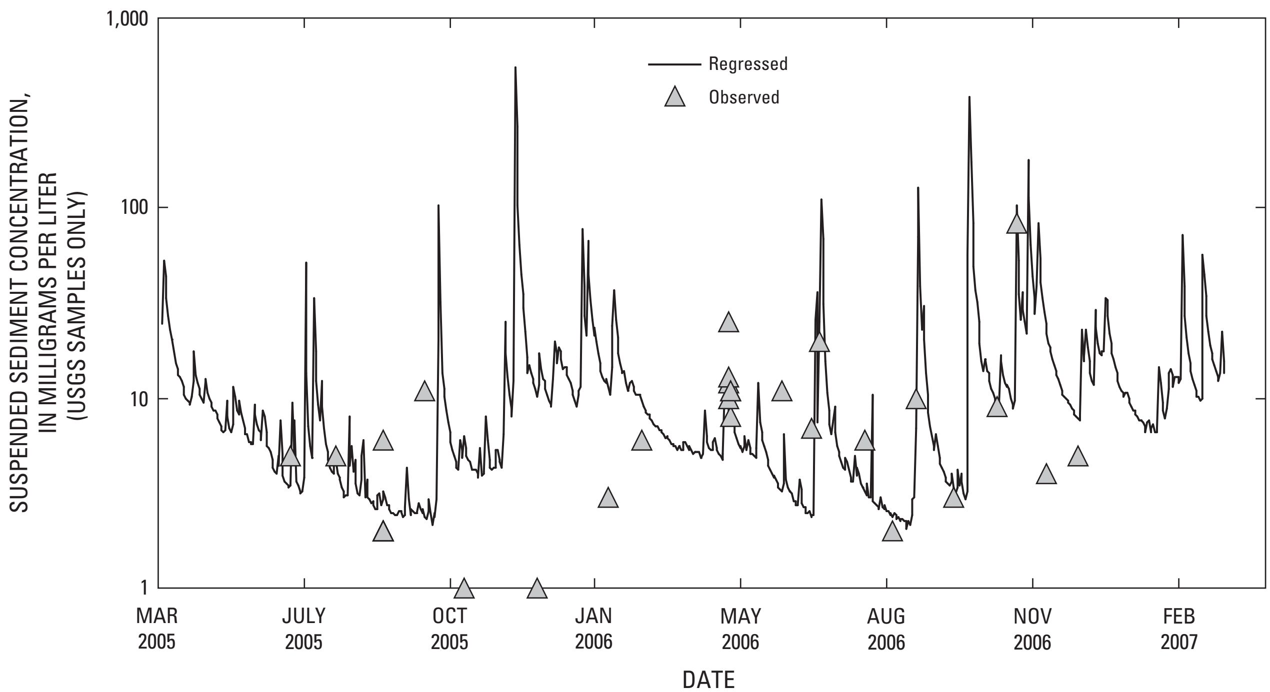


Figure 13. Time series of regressed and sampled suspended sediment concentrations, South River at Harriston, Virginia (USGS station number 01627500), April 1, 2005, through March 31, 2007.

without modification, except for scaling potential evapotranspiration time-series data to improve the overall simulated water balance. The CBM5 climatic and meteorological time-series data were developed from observational data provided by the National Climatic Data Center of the National Oceanic and Atmospheric Administration. Observational data from over 200 hourly weather monitoring stations in the Chesapeake Bay watershed were integrated using statistical techniques to account for spatial and temporal gaps in the data, and to create continuous hourly time series (Chesapeake Bay Program, 2006). Only those time series applicable to the five land segments found in the South River watershed (A51015, A51165, A51820, B51015, and C51015) were used in this study.

Hourly climatic and meteorological time series for all areas of the model were extended through March 31, 2007, using the data from U.S. Air Force meteorological monitoring station 724105 at the Shenandoah Valley Regional Airport in Weyers Cave, 14 mi north of Waynesboro (fig. 11). Hourly surface observations at the Shenandoah Valley Regional Airport were obtained from the National Climatic Data Center website (http://www.ncdc.noaa.gov/oa/ncdc.html) for precipitation, dew point, wind speed, and air temperature. Cloud cover was estimated from hourly observations of sky cover (SKC), converting the observation codes as follows: clear (CLR) = 0.0, scattered clouds (SKT) = 3.0, partial obscuration (POB) = 6.0, broken (BKN) = 7.0, overcast (OVC) = 10.0, and obscured (OBS) = 10.0. Hourly solar radiation values were calculated from cloud cover and latitude using WDMUtil software (Hummel and others, 2001). The Hamon method (Hamon, 1961) was applied within WDMUtil to calculate potential evapotranspiration using latitude and daily minimum and maximum air temperatures.

Additional sources of precipitation data were available for 2005–07. Daily precipitation data were provided by Invista for its wastewater treatment plant in Waynesboro at the former DuPont plant site (Brenda Kennell, Invista, written commun., 2007), and daily precipitation data were downloaded from the National Climatic Data Center website for the City of Waynesboro sewage treatment plant (STP) (cooperative station ID# 448941). Daily precipitation totals recorded at the Waynesboro STP and at the Invista wastewater treatment plant were not used in compiling the CBM5 data (Chesapeake Bay Program, 2006) and differ from precipitation totals recorded at the Shenandoah Valley Regional Airport during the same period. The calibrated watershed model in this study uses precipitation data from all of these sources, with CBM5 data through August 2005 as the base and the additional data included where available to modify CBM5 values.

Observed precipitation for the period April 1, 2005, through March 31, 2007, at the three monitoring stations in the study area, as well as CBM5 estimated precipitation, is shown in figure 14. All of the observation data shown were collected using different procedures and in the case of the Waynesboro

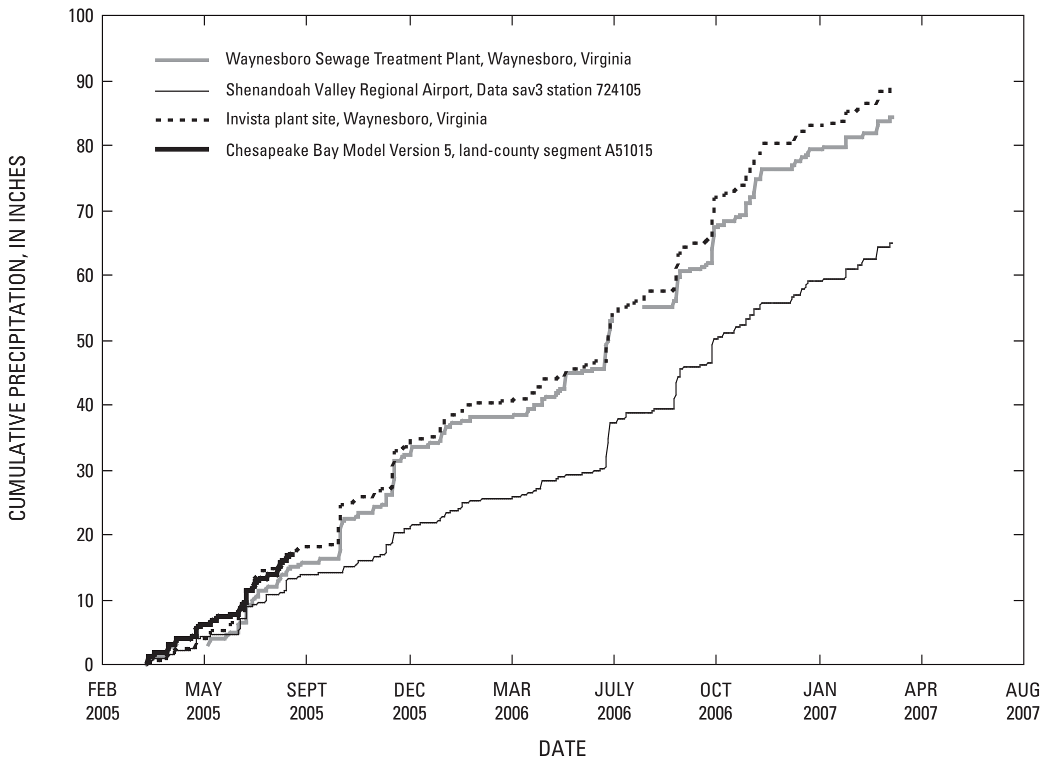


Figure 14. Cumulative precipitation at sites in and near the South River watershed, Virginia, for the period April 1, 2005, through March 31, 2007. (Chesapeake Bay Watershed Model Version 5 data obtained from the U.S. Environmental Protection Agency Chesapeake Bay Office, Annapolis, Maryland, 2006).

STP and the Invista site, were recorded on a daily, rather than hourly, basis. In addition to both the Waynesboro STP and Invista data showing an additional 20 in. of rain during the 2-year period, the storm patterns also show differences when compared to the Shenandoah Valley Regional Airport data. The most extreme example occurred during a storm on October 9, 2005, which shows up in the Invista and Waynesboro STP data as about 6 in. of precipitation, but only about 0.7 in. are observed in both the Shenandoah Valley Regional Airport and CBM-A51015 data. These differences indicate the potential for input errors to the HSPF model and are discussed in more detail later in the report.

Point Sources

In the South River watershed model, point sources are flows of water and associated constituents that discharge directly to the river. A typical example is discharge from a wastewater treatment plant.

Data describing point-source discharges to the South River were compiled from the Virginia Pollutant Discharge Elimination System database that is maintained by the VDEQ for discharges in the State of Virginia. Of the 12 individually permitted facilities in the South River, 5 industrial or major municipal facilities were included in the model. Other smaller discharges were determined to contribute insignificant amounts of mercury to the South River. A detailed listing of data used to compile point-source discharge time series is given in Appendix 1.

Because data in the Virginia Pollutant Discharge Elimination System typically have monthly time steps, whereas the time series input to the South River watershed model have daily time steps, point-source data were disaggregated assuming constant daily rates within each month. Additional data with shorter time steps were collected, where possible, from discharge facility operators and used to supplement the Virginia Pollutant Discharge Elimination System data. When only annual data were available, these were disaggregated to daily intervals assuming seasonal patterns by month and constant daily rates within each month.

Additional Model Flows to the River

Two discharges to the South River, specified in the model but not subject to permit regulations, are treated in the model as point-source flows to the river. These flows are from Frew Pond/Baker Spring and from Loth Spring, which are adjacent to the South River in Waynesboro, and are known to have large water flow rates (Brenda Kennell, Invista, written commun., 2007). Baker Spring flows into Frew Pond, which is a reservoir adjacent to the river at the plant site and managed by Invista. From Frew Pond, water flows over a weir and discharges to the South River. Loth Spring is adjacent to the river on its north side across from Frew Pond and flows directly to the river. Frew Pond/Baker Spring and Loth Spring are assigned monthly flow rates in the model on the basis of observed flows (DuPont Corporate Remediation Group, 2006a) and an assumed seasonal variation of 30 percent.

Conceptual Model of Mercury Fate and Transport in the Watershed

As a foundation for building a numerical watershed model, a conceptual model for mercury fate and transport in the watershed was developed first. The conceptual model summarizes the primary paths by which mercury enters the South River water column and the fate of the mercury once it is in the river (fig. 15).

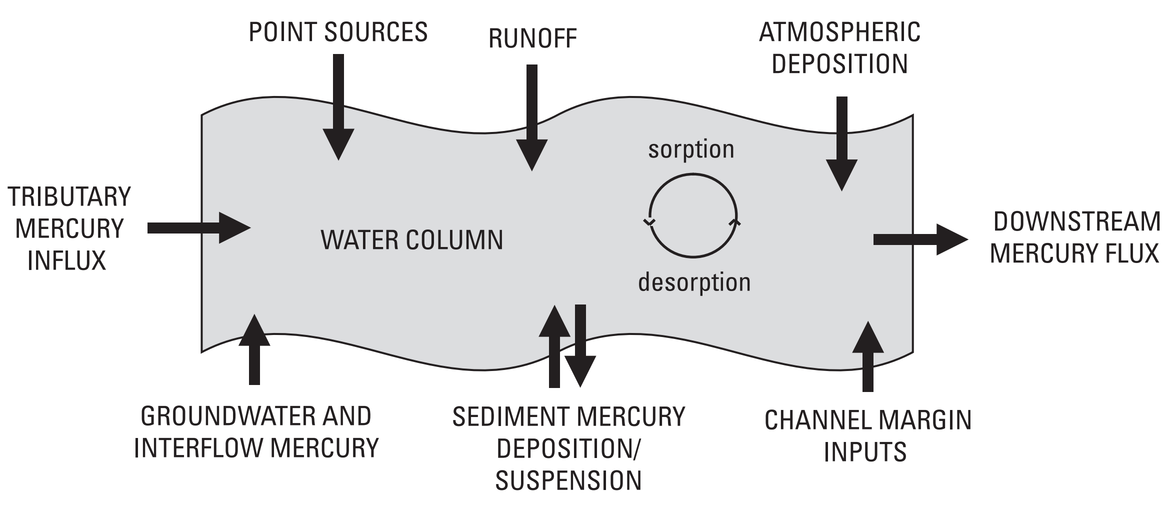


Figure 15. Conceptual model of total mercury sources, sinks, and transport in the South River, Virginia.

Mercury concentrations in all media are markedly higher downstream from the plant site than upstream, and it is presumed that most mercury currently (2009) entering the South River originated from the plant site at some time since 1929. It is known that the flood plain contains legacy mercury from the plant site and that contaminated sediment from the flood plain is currently entering the river. The Waynesboro monitoring station (01626000) is the only one of the three monitoring stations upstream from the plant site, and serves as a background reference station in this study.

At all three monitoring stations, filtered mercury concentrations in the water column increased with increasing streamflow as shown in figure 8. This observation is consistent with the hypothesis that contaminated sediments are the primary source of mercury in the water column. If point-source discharges were the primary Hg load, then river concentrations would be more likely to decrease with increased streamflow due to dilution effects.

Total mercury in the South River exhibits a partitioning ratio between dissolved and sorbed phases of about 1,000,000 (log Kd = 6). The importance of partitioning to the TMDL is diminished by the fact that fish tissue methylmercury correlates strongly with the sum of filtered and particulate mercury, and the sum of the two concentrations is only secondarily affected by the exchange of mercury between sorbed and dissolved phases.

Several lines of evidence point to contaminated soil in the flood plain and river channel as the current greatest source of mercury to the river. Downstream surveys have shown that mercury concentrations in fish, water, and sediment rise steadily from the plant site downstream for about 12 mi (Turner and Jensen, 2006; Flanders and others, 2007). The relatively steady increase in concentrations points to mercury inputs being dispersed for many miles along the river rather than coming from discrete inputs such as point-source discharges or tributaries. Except for the sharp increase in water column mercury concentrations at the plant site, there are no abrupt THG increases that would indicate a major input of mercury from point sources. The accounting of mercury loads to the river also requires that a large percentage of mercury come from nonpoint sources to achieve a mass balance, as discussed in a later section, Mercury Transport Model Calibration Results.

Watershed Model Development

A numerical watershed model of the South River watershed was developed to simulate dynamic streamflow response, sediment transport, and mercury transport. The simulation model calculates mass balances for water as well as sediment and mercury in the South River for the simulation period January 1, 1985, through March 31, 2007. The simulation model also permits hypothetical conditions, such as reduced mercury source loads, droughts, floods, or long-term mercury mass balances, to be analyzed.

The software used to implement the numerical model is Hydrological Simulation Program–FORTRAN (HSPF), a watershed-based modeling package widely used for TMDL development (Donigian and others, 1995; Bicknell and others, 2001). The hydrologic component of HSPF generates time series of streamflow in response to precipitation, evapotranspiration, and movement of water from the land surface through various routes to streams. Simulations are transient and require extensive input data describing land use and hydraulic characteristics, climatic conditions, river geometry, and sediment and mercury transport characteristics.

The first 6 years of the South River watershed model simulation (1985 through 1990) bring the model to relative steady state conditions, dampening perturbations from initial conditions. A 10-year period, from October 1, 1990, through September 30, 2000, was used to calibrate the hydrologic and sediment parts of the model. The 5 years from October 1, 2000, through September 30, 2005, were used to verify the calibrated hydrologic and sediment parts of the model. The mercury transport model was calibrated for the period April 2005 through March 2006, and verified for the period April 2006 through March 2007.

The South River watershed model has a 1-hour time step, which is sufficiently small to represent important hydrologic changes, but not so small as to make model run times impractical. The calibrated watershed model has run times of about 4 minutes.

Functional Description of Hydrological Simulation Program–FORTRAN (HSPF)

HSPF is a mathematical model designed to simulate the hydrology and movement of contaminants in a watershed. As applied to the South River watershed, the HSPF model simulates streamflow, sediment transport, and mercury transport. HSPF calculates water, sediment, and contaminant loads following mass conservation principles of water, with inflow equaling outflow plus or minus any change in storage (Bicknell and others, 2001). In HSPF, a watershed is represented by a collection of hydrologically similar areas, referred to as hydrologic response units (HRUs), which drain into a network of stream or lake segments. Each HRU represents land having characteristic hydrologic controls, such as land use, soil, subsurface geology, and other factors deemed important in controlling hydrology. Each stream segment represents a river reach or lake. For each HRU and stream segment, the model computes a water budget (inflows, outflows, and changes in storage) for each time step.

HRUs represent either pervious or impervious land areas. Both pervious and impervious land areas can retain precipitation on the surface. On pervious land areas, excess precipitation can infiltrate to the subsurface, where storages and fluxes are calculated for upper and lower groundwater zones, or can run off to a river reach. On impervious area, all water that is not evaporated from the surface produces runoff to a river reach. The downstream end of each river reach is referred to as a node. Nodes are typically placed to define channel segments with similar physical properties, or at other locations where estimates of streamflow or contaminant concentrations are desired. The hydrologic characteristics used for kinematic wave routing of water in a river reach are defined in a function table that is specified in the model input. The SCHEMATIC and MASS-LINK blocks define the physical layout of the watershed, linking river reaches together and assigning the acres to each pervious and impervious land area.

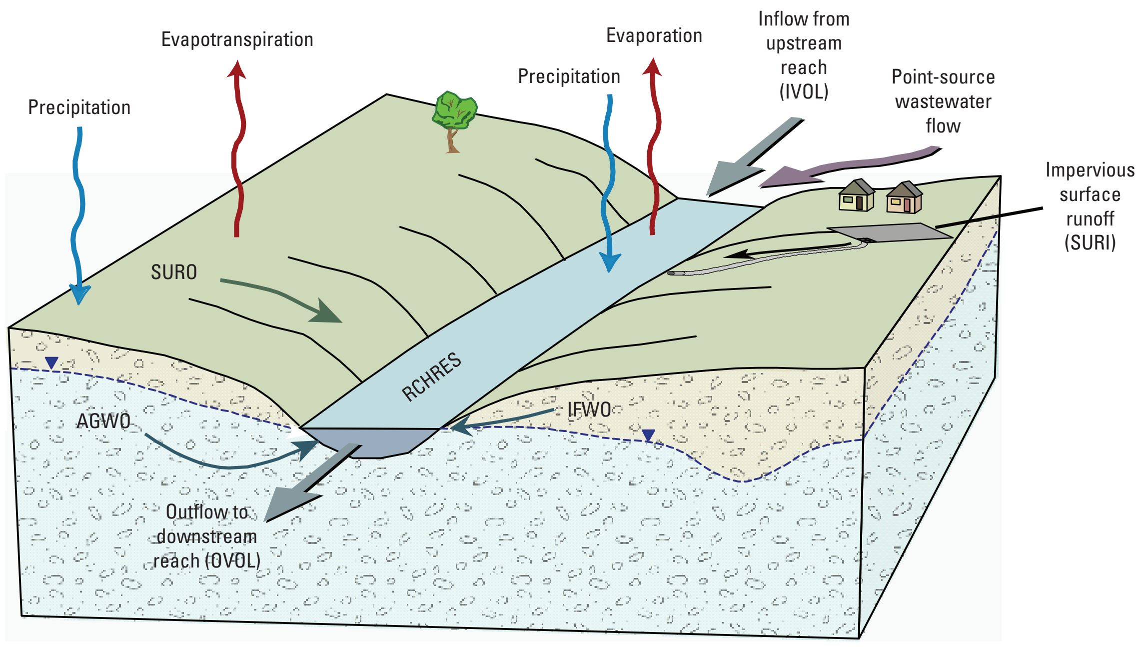
The inflows to and outflows from a river reach in the South River watershed model are shown in figure 16 (modified from Zarriello and Bent, 2004, fig. 9). Surface runoff can discharge to a reach from impervious surfaces and pervious surfaces. Infiltrated water can discharge to a reach through the subsurface as interflow, a fast-responding shallow subsurface flow, or from active groundwater, a slow-response base-flow component. Inflow to a reach can also come from upstream reaches, direct precipitation, and other user-specified sources such as treated point-source discharges.

HSPF requires two primary input files for its operation—the user control input file and the watershed data management file. The user control input file directs the model-process algorithms and sets user-specified input variables. The watershed data management file holds a time-series database. Time-series datasets are organized in the South River watershed data management file as shown in table 16. A more complete description of the HSPF software is given in the "HSPF User's Manual" (Bicknell and others, 2001).

Table 16. Organization of dataset numbers in the watershed data management file for the South River watershed model, Virginia.

[DSN, dataset number; AGWO, active groundwater flow; IFWO, interflow]

DSN	Purpose
1101–1523	Simulated daily AGWO output, last 3 digits are hydrologic response unit number.
2101–2523	Simulated daily IFWO output, last 3 digits are hydrologic response unit number.
3000–3999	Observed/calculated meteorological inputs.
4000–4999	Simulated hydrologic and sediment outputs.
5000–6015	Simulated mercury concentration, storage, and load outputs.
6101–6999	Point-source flow and load inputs.
7000–7999	Simulated daily sediment runoff output, last 3 digits are hydrologic response unit number.



SURI–Surface runoff from impervious areas
SURO–Surface runoff from pervious areas
IFWO–Interflow
AGWO–Active groundwater flow (base flow)
RCHRES–Stream reach or reservoir segment
IVOL–Inflow volume
OVOL–Outflow volume

Figure 16. Schematic showing hydrologic routing in the South River numerical watershed model (modified from Zarriello and Bent, 2004, figure 9).

Representation of the Watershed

The South River watershed is represented in the HSPF model as a combination of HRUs, consisting of pervious and impervious land surfaces. Each HRU has an assigned contributing area to each stream reach. The stream reaches are linked to each other in downstream order. Basin and subbasin boundaries in the model study area were initially obtained from the Chesapeake Bay HSPF model Phase 5.14, referred to here as “CBM5”, developed by the USEPA, the USGS, and other partners (Martucci and others, 2005; Chesapeake Bay Program, 2006).

The South River watershed is divided into five model subbasins that each contains a single river reach (fig. 17). The nodes defining the subbasins were selected to correspond with monitoring locations along the South River so that output from the model could be compared to field observations at the same locations. Each subbasin is composed of multiple HRUs, which send their output (water, sediment, and mercury) to the river reaches. The CBM5 model has four subbasins within the South River watershed (PS2_6730_6660, PS2_6660_6490, PS2_6490_6420, and PS2_6420_6360). For this study, an additional subbasin was needed to produce simulation results at the location of streamflow-gaging station 01626920. Using

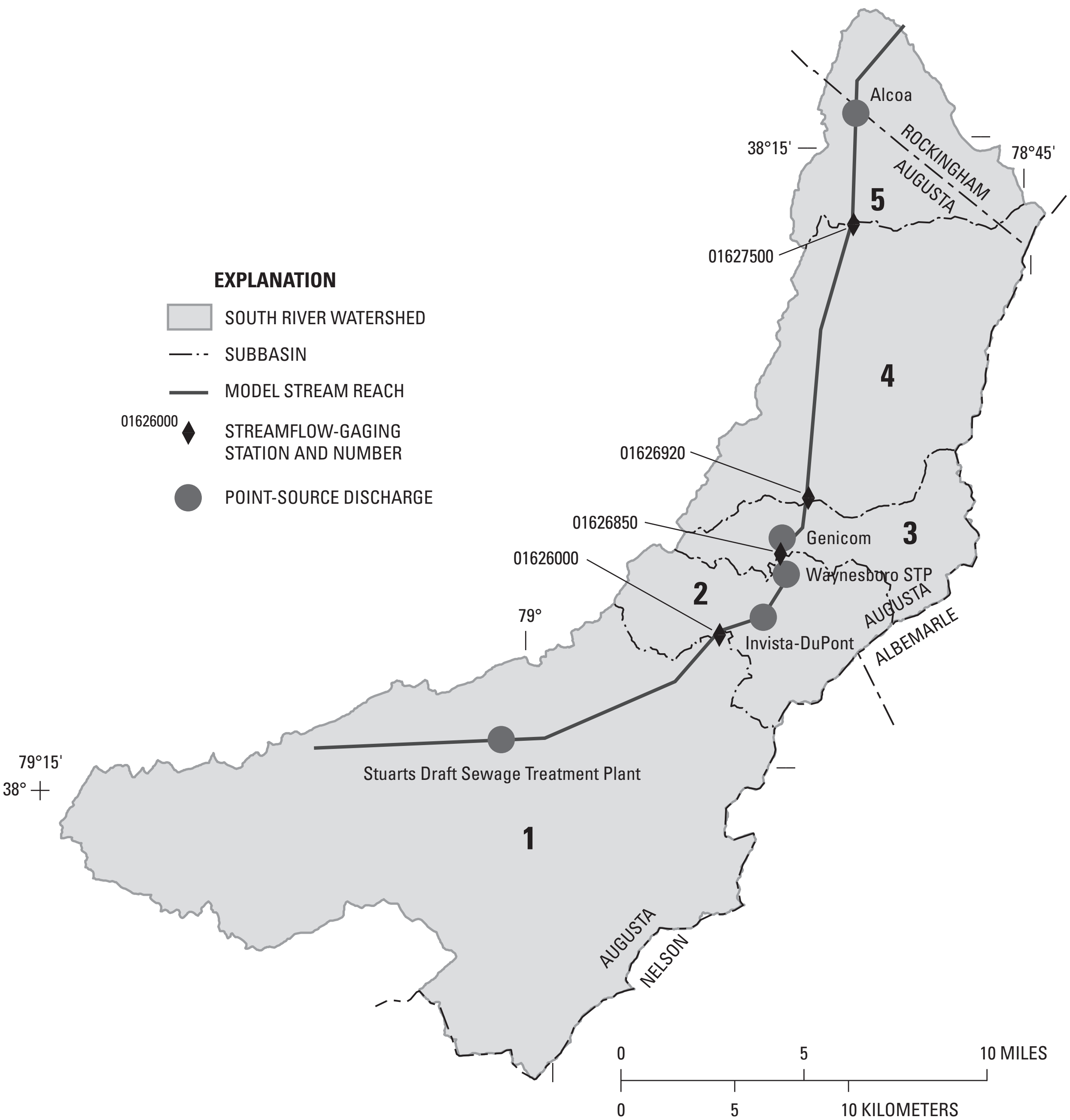


Figure 17. Location of South River watershed model subbasins.

geographic information system (GIS) software, one of the CBM5 subbasins (PS2_6490_6420) was divided into subbasins 3 and 4 in the South River watershed model (fig. 17). River reach parameters and HRU areas contributing to each reach were then recalculated.

Parameters describing hydrology, sediment transport, and mercury transport were assigned to each HRU. Initial parameter values were set equal to those in the calibrated CBM5 model. The CBM5 model parameters had already been calibrated to streamflow values from 1985 through 2005, including streamflow on three of the South River streamflow-gaging stations (01626000, 01626850, and 01627500). Some model parameters were then modified in this study to improve the match between simulated and observed streamflow, sediment concentrations, and mercury concentrations. These changes are discussed in the following sections describing calibration of the model.

Development of Hydrologic Response Units (HRUs)

The smallest HSPF model component is the HRU. Within a single HRU, climatic conditions, hydrologic responses, and contaminant transport are assumed to be uniform. The HRUs in the South River watershed model are nearly identical to those used in the CBM5 model (Martucci and others, 2005). These HRUs are based on county boundaries, land use, and valley or mountain geography. Five land-county segments developed for the CBM5 model are present in the South River (fig. 18). Climatic variables and precipitation vary according to land-county segment. There are 25 CBM5 land-use types in the watershed, and an additional land use, mercury-contaminated flood plain, was added for this study (table 17). The five land-county segments combined with the 26 land uses result in 130 different HRUs in the South River watershed. Fifteen of the HRUs are impervious land areas, and 115 are pervious areas.

Table 17. Land-use representation in the watershed model, South River, Virginia.

[HRU, hydrologic response unit; IMPLND, impervious land area; PERLND, pervious land area]

HRU type	Land use	Subbasin area (acres)					Total (acres)
		1	2	3	4	5	
IMPLND	animal feeding operations	20	7	1	13	51	92
IMPLND	low intensity impervious urban	352	865	53	76	99	1,444
IMPLND	high intensity impervious urban	113	263	3	25	32	436
PERLND	forest	48,816	5,885	5,862	15,817	6,090	82,470
PERLND	harvested forest	493	64	63	175	73	868
PERLND	alfalfa	1,221	0	162	520	76	1,979
PERLND	natural grass	1,865	1	3	13	11	1,892
PERLND	high till without manure	18	1	2	8	5	33
PERLND	high till with manure	259	11	36	114	125	544
PERLND	hay without nutrients	538	22	59	254	152	1,026
PERLND	hay with nutrients	2,371	98	261	1,118	626	4,475
PERLND	low till with manure	1,293	54	178	574	439	2,537
PERLND	nutrient management alfalfa	262	61	43	137	251	754
PERLND	nutrient management high till with manure	176	7	24	78	57	342
PERLND	nutrient management high till without manure	12	1	2	5	3	22
PERLND	nutrient management hay	1,611	67	232	704	333	2,946
PERLND	nutrient management low till	879	36	97	414	217	1,642
PERLND	nutrient management pasture	453	380	87	375	1,103	2,397
PERLND	pasture	16,042	302	1,727	7,401	2,287	27,759
PERLND	bare-construction	369	548	26	101	95	1,138
PERLND	extractive	92	3	0	7	2	103
PERLND	trampled	83	3	12	34	17	149
PERLND	nursery	210	9	32	90	31	372
PERLND	high intensity pervious urban	2,541	956	225	606	404	4,732
PERLND	low intensity pervious urban	1,230	3,484	513	538	810	6,576
PERLND	mercury-contaminated flood plain	0	493	378	1,412	1,105	3,388
	Total acres	81,316	13,619	10,082	30,606	14,493	150,115

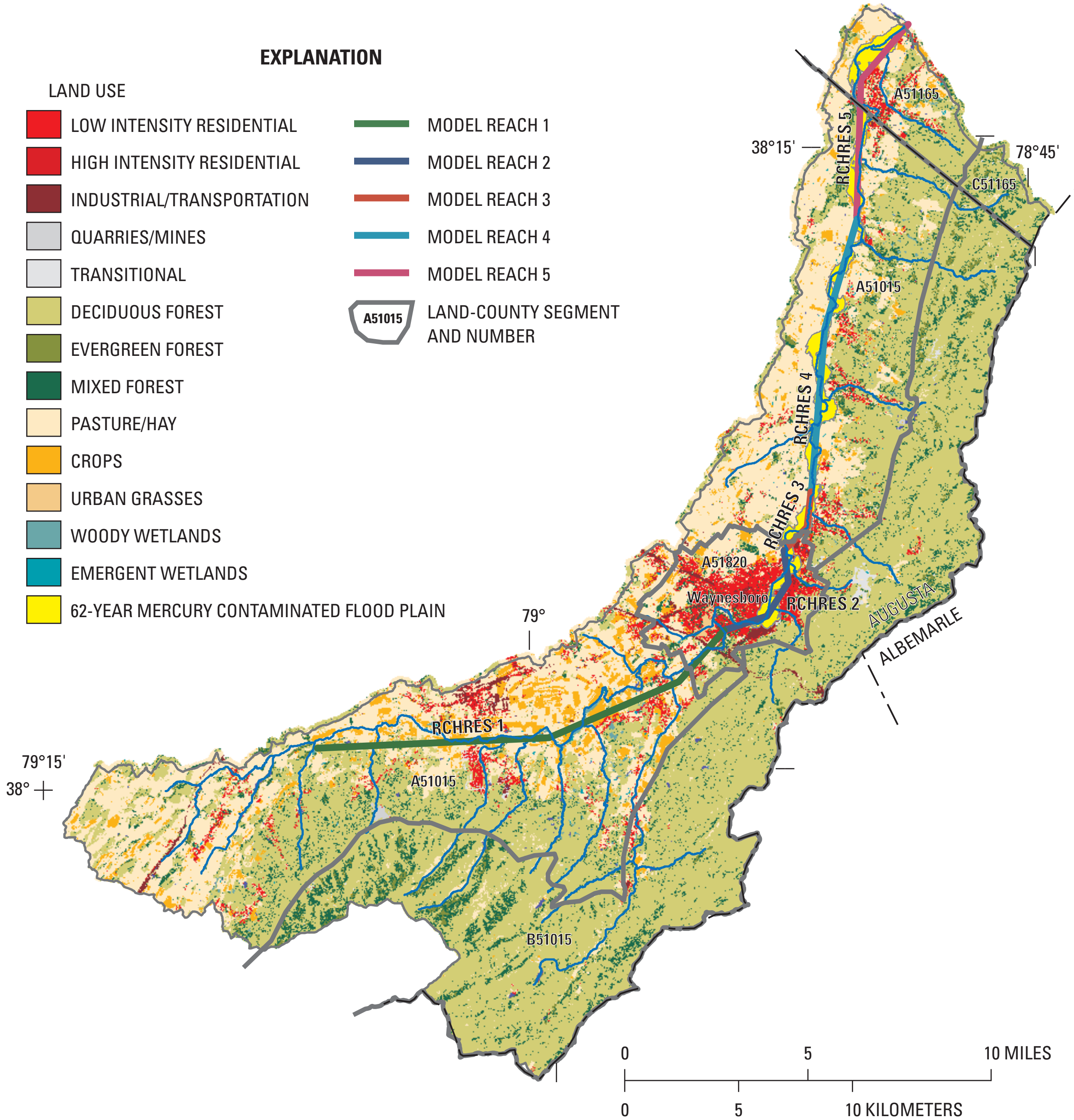


Figure 18. Land use in the South River watershed (National Land Cover Dataset, April 27, 1999; DuPont Corporate Remediation Group, 2007, South River 62-year flood-plain data layer).

Pervious areas occupy 98.7 percent of the watershed. Forestry and agriculture are the dominant land uses, representing 55.5 percent and 31.2 percent, respectively of the total watershed area. Impervious surfaces in the watershed consist primarily of developed urban areas with dense building and pavement cover and make up 1.3 percent of total watershed area. All pervious and impervious areas in the model contribute their outflows directly to a stream reach.

All HRUs were defined according to the CBM5 scheme, with one exception. Five pervious land areas were created to represent mercury-contaminated flood plains. Areas for the five pervious land areas representing mercury-contaminated flood-plain areas were calculated from spatial data outlining the 62-year flood plain. The 62-year flood plain represents the maximum extent of the flood plain inundated since mercury was originally released from the former DuPont plant site. The largest daily flow recorded since release of mercury was determined by flood frequency analysis to have a return period of 62 years. Hydraulic analysis was then conducted to delineate the flood-plain area inundated by a flood of this magnitude (DuPont Corporate Remediation Group, 2007).

Stream Reaches

River reaches receive their input from pervious land areas, impervious land areas, atmospheric deposition, and upstream reaches, while discharging either to a downstream reach or to the model exit (fig. 15). The watershed model contains five stream reaches, one for each subbasin. Model parameter values for each reach were initially set to be the same as those in the CBM5 model. Reach PS2_6490_6420 in the CBM5 model was divided into reaches 3 and 4 of this study's model, so that simulation results at streamflow-gaging station 01626920 could be obtained.

The physical characteristics of the five South River watershed model river reaches are listed in table 18. Parameters were adjusted during the calibration process, including the length and elevation drops, to reflect additional observation data and to improve hydrologic and sediment transport simulations. These parameters were reset to values determined by GIS analysis of 10-m digital elevation model data. The FTABLES, which specify channel geometry, were not changed from the CBM5 model.

Hydrologic Model

The hydrologic component of the model simulates water movement and storage in the South River watershed. Precipitation and point-source discharges to the river are the only hydrologic inputs to the model domain whereas actual evapotranspiration and streamflow are the only outputs. Precipitation that falls on the land surface but does not evaporate or transpire is routed to the river. Once in the river, water moves downstream and exits the model from the last river reach (number 5). Major components of the hydrologic cycle simulated by HSPF for pervious land areas and river reaches are shown in figure 19. More detailed descriptions of the storage and flow terms can be found in Bicknell and others (2001).

Table 18. River reach characteristics in the calibrated South River watershed model.

[mi, miles; ft, feet; USGS, U.S. Geological Survey]

Model river reach number	Extent		Upstream reach number	Length (mi)	Elevation drop (ft)	Slope
	From	To				
1	headwaters	USGS station no. 01626000	none	14.3	164	0.0022
2	USGS station no. 01626000	USGS station no. 01626850	1	5.1	46	0.0017
3	USGS station no. 01626850	USGS station no. 01626920	2	3.0	20	0.0013
4	USGS station no. 01626920	USGS station no. 01627500	3	11.3	98	0.0017
5	USGS station no. 01627500	South Fork Shenandoah River	4	7.7	105	0.0026

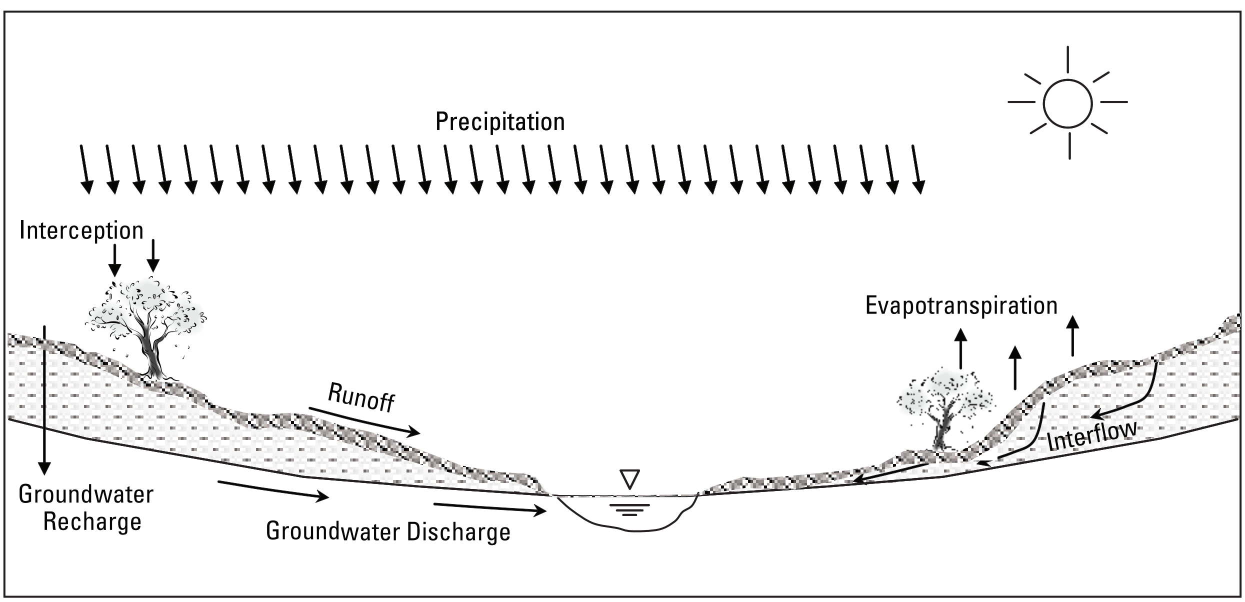


Figure 19. Major hydrologic components for pervious land areas and river reaches simulated in the South River numerical watershed model.

Point-Source Discharges

Reaches 1, 2, 3, and 5 receive discharges from point sources. The discharges come from a variety of permitted facilities, listed in table 19 and Appendix 1. Other small facilities discharge to the South River but were not included in the model because they have flows of less than 0.5 Mgal/d (million gallons per day) and discharge insignificant amounts of mercury. Discharge rates, suspended sediment concentrations, and mercury concentrations were assigned outside of the model and input to the model as time series with daily time steps. The data available to describe each point source varied widely and were from a variety of sources. Time series describing the point-source discharges were developed in collaboration with Invista, DuPont, and the VDEQ.

Sediment Transport Model

Sediment transport was incorporated into the watershed model because most mercury transport occurs in association with suspended sediment. At both the Dooms and Harriston monitoring stations, water-sample analyses indicate that over 95 percent of the mercury in the water column is sediment-associated, with suspended sediment defined as material not passing a 1.5-µm filter.

In the watershed model, sediment moves to the river from impervious and pervious land areas during surface runoff events (fig. 20). Sediment loads from land surfaces vary according to land use and location in the watershed. The South River watershed model simulates sediment transport in the river using the same parameterization as the CBM5 model

Table 19. Point sources in the South River watershed model, average flow, sediment loads, and mercury loads for the period April 1, 2005, through March 31, 2007.

[VPDES, Virginia Pollutant Discharge Elimination System; Hg, mercury; g, grams; ft^3/s, cubic feet per second; STP, sewage treatment plant; na, not applicable]

Model ID	Point sources in model		Model reach	VPDES permit number	Annual mean (2005–2007)		
	Facility name	Downstream order			Flow (ft^3/s)	Sediment load (ton)	Hg load (g)
101	Stuarts Draft STP		1	VA0066877	1.671	1.5	1.0
222	Loth Spring		2	na	1.756	1.5	6.4
—	Invista/ former DuPont		—	—			
201		outfall 001	2	VA0002160	6.523	17.2	402.9
203		outfall 003	2	VA0002160	0.066	0.4	2.8
204		outfall 004	2	na	0.014	0.3	0.5
208		outfall 008	2	na	0.374	4.2	89.0
209		outfall 009	2	na	0.111	0.8	8.1
210		outfall 010	2	na	0.040	1.9	8.2
211		outfall 011 (after 08/02)	2	VA0002160	0.020	0.4	21.8
212		outfall 012	2	na	0.000	0.0	0.0
213		outfall 013	2	na	0.007	0.0	0.3
214		outfall 014	2	na	0.005	0.0	0.3
221		Frew Pond, Baker Spring	2	na	7.025	5.9	25.4
231		Plant site groundwater discharge	2	na	0.501	0.0	1.5
—	*Invista/ former DuPont*		*Plant Site Totals*		*15*	*31*	*561*
241	Waynesboro STP		2	VA0025151	5.497	42.2	37.1
301	Genicom		3	VA0002402	0.196	0.0	0.0
501	Alcoa		5	VA0001767	2.486	12.7	40.6
				Totals	26	89	646

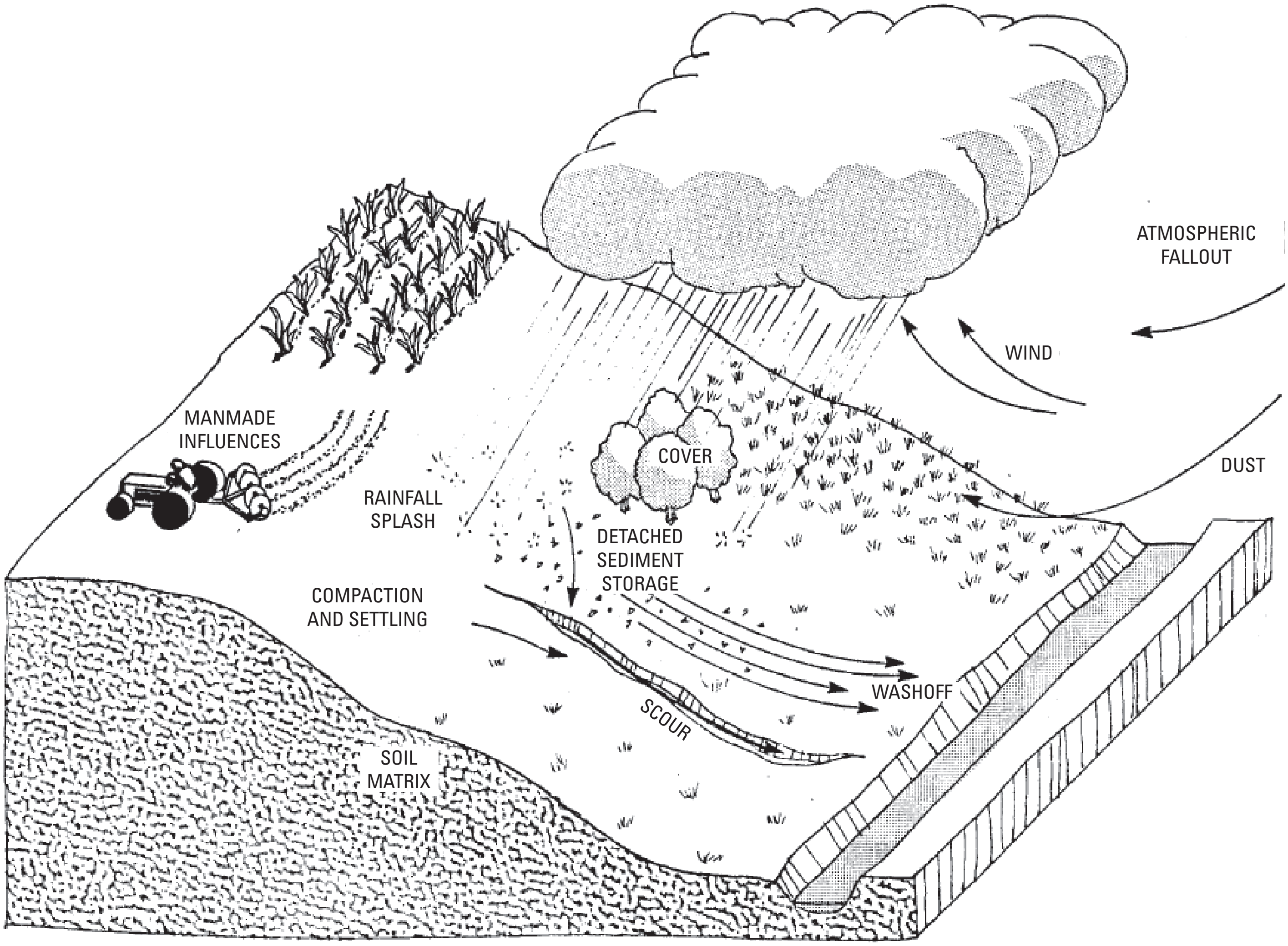


Figure 20. Sediment transport processes for pervious land areas (from Bicknell and others, 2001).

(Chesapeake Bay Program, 2006); with a power function governing sand transport and critical stress levels controlling silt and clay transport. Sediment transport parameter values were initially assigned to be the same as those in the CBM5 model and were then modified during the calibration process. Sediment transport is handled differently for impervious land areas, pervious land areas, and river reaches as described in the next section(s) (fig. 21).

Impervious Land Area Sediment Transport

Sediment transport from impervious land surfaces to river reaches is simulated using the IMPLND-SOLIDS module. At each hourly time step, solids accumulate or are removed, by street cleaning for example, from the land surface at the user-specified rates listed in Appendix 2 (available only online at http://pubs.usgs.gov/sir/2009/5076/). Solids are transported from impervious land areas to river reaches, at user-specified exponential rates, when overland flow occurs. Parameters governing sediment production from each impervious land area were initially assigned CBM5 values, and then calibrated by matching simulated to observed suspended sediment concentration values, as described in a later section of this report, Sediment Transport Model Calibration Results.

Pervious Land Area Sediment Transport

Simulation of sediment transport to the river from each pervious land segment is performed by the PERLND-SEDMNT module. Only detached sediment is available to be transported to the river, therefore, no scouring is simulated. Sediment can be detached by soil drying, rainfall splash, or other processes at detachment rates specified by the user. Detached sediment is transported to the river during overland flow runoff events at exponential rates controlled by user-specified coefficients. Sediment transport from the five pervious land areas representing mercury-contaminated flood-plain areas is simulated using the same processes and simulation modules. Final calibrated values for sediment transport parameters are listed in Appendix 2.

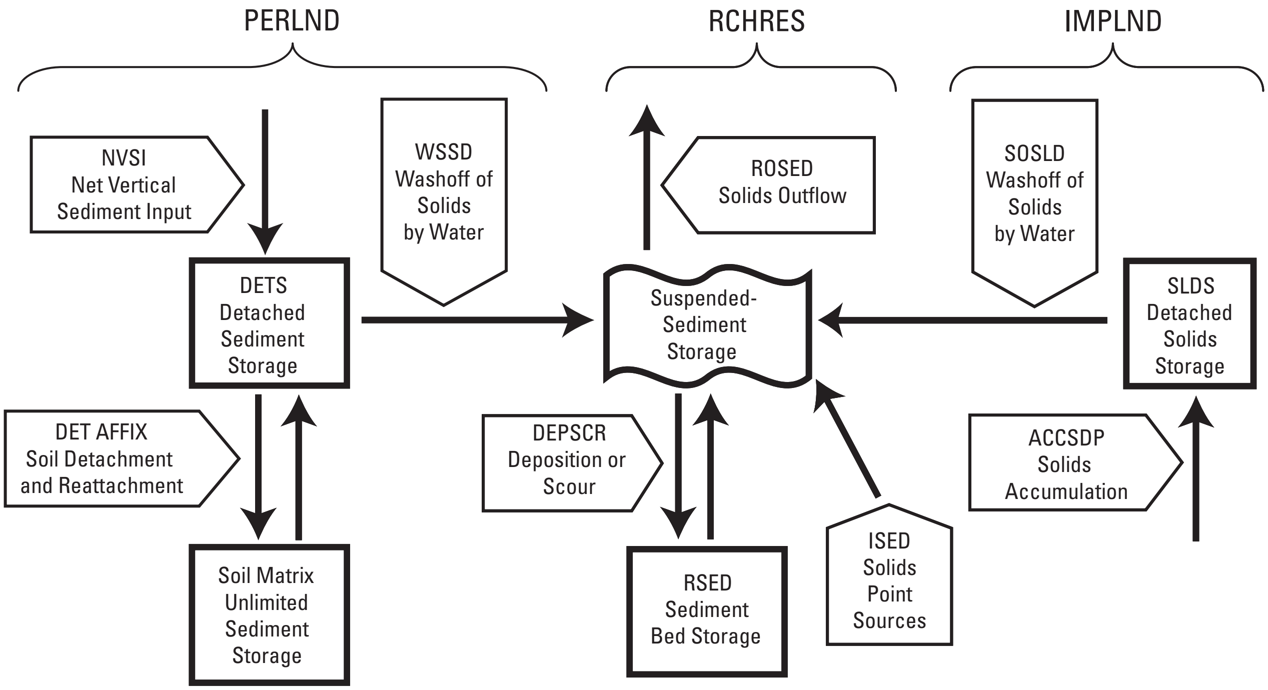


Figure 21. Sediment routing processes in the South River numerical watershed model.

Sediment Point Sources

Municipal and industrial discharges to the river generally contain suspended sediment. These point sources are treated in the model as direct inputs to the river with sediment loading rates specified outside of the model. These rates were determined from data collected by discharge permit owners and stored in the Virginia Pollutant Discharge Elimination System database. Point sources contribute only a very small percentage (less than 1 percent) to the total sediment load of the South River. Summaries of the sediment point-source loads are listed in table 19 and Appendix 1.

Sediment Transport in the River

Sediment entering a river reach can be deposited and remain stationary on the channel bed or travel downstream in suspension. Transport, deposition, and resuspension of sediment within a river reach are handled in HSPF by the modules shown in figure 21. At each hourly time step, HSPF recalculates all sediment storage and load terms. Suspended sediment present in a river reach can settle to the channel bottom, exit downstream, or remain in the reach. Sediment deposited on the channel bottom can be resuspended by increased flow velocities. Initial conditions are user-specified for initial suspended sediment concentration and for depth of sediment on the bed of each river reach.

Sediment within a river reach is divided by HSPF into three sediment size classes—sand, silt, and clay. Transport of each size class is simulated separately. Non-cohesive particles (sand) and cohesive particles (silt and clay) have different algorithms controlling transport within the river. There were insufficient data from the South River to accurately calibrate to suspended sediment size, so sediment size fractions in the model were assigned to be 33.3 percent sand, 33.3 percent silt, and 33.3 percent clay. The capacity of each river reach to transport sand downstream is calculated using an exponential equation (Bicknell and others, 2001) with user-specified rates. When transport capacity exceeds the rate of sand transport, resuspension of bed sand occurs. Conversely, when sand load exceeds transport capacity, deposition of sand on the channel bed occurs. Silt and clay transport are simulated with a different algorithm that controls scour and deposition according to user-specified settling rates, critical stress thresholds for deposition and suspension, and erodibility coefficients. Values for sand, silt, and clay transport parameters used in the calibrated South River watershed model are listed in Appendix 2.

Mercury Transport Model

The third component of the South River watershed model simulates mercury transport on the basis of the conceptual model described earlier. Total mercury is the only form of mercury that was simulated. Other forms of mercury such as methylmercury were not simulated, not because they are absent or unimportant, but because the dynamics of methylmercury cycling and bioaccumulation in the South River system are currently not well understood. Modeling of total mercury in the South River was performed because fish tissue methylmercury concentrations correlate more strongly with total mercury than with any other form of mercury in the water column, including methylmercury (Virginia Department of Environmental Quality, 2008b). The model is constructed so that future studies can incorporate methylmercury cycling, bioaccumulation, or other processes if desired.

Mercury is transported to the river along multiple hydrologic pathways: direct precipitation to the river surface, point-source discharges, groundwater and interflow, land-surface sediment runoff, channel margin inputs, and downstream advection. The HSPF modules used to simulate these pathways are listed in table 20 and shown in figure 22. Once mercury enters a river reach, it partitions between dissolved and sorbed phases. The model simulates the storage of mercury in channel bed sediment and the reintroduction of mercury to the water column when bed sediment is resuspended by higher flows.

Silt and clay particles are assigned the same mercury transport parameters and initial THG_{SS} concentrations. Sand is assumed to have a mercury sorption capacity 1,000 times lower than that of silt or clay

Table 20. Modules in Hydrological Simulation Program–FORTRAN used to simulate mercury transport.

[Hg, mercury; PERLND, pervious land area; IMPLND, impervious land area; RCHRES, river reach]

Mercury source/Process	HSPF module(s)
Groundwater	PERLND>PQUAL>QUALGW
Interflow	PERLND>PQUAL>QUALIF
Sediment Hg in runoff	PERLND>PQUAL>QUALSD and IMPLND>IQUAL>WASHSD
Precipitation Hg on river	RCHRES>CONS
Hg point sources	EXT SOURCES
Instream sorption/desorption	RCHRES>GQUAL>ADSDES
Downstream advection	RCHRES>GQUAL>ADVECT (Dissolved Hg) RCHRES>GQUAL>ADVQAL (Sediment associated Hg)
Channel margin inputs	PERLND>PWAT and MASS-LINK

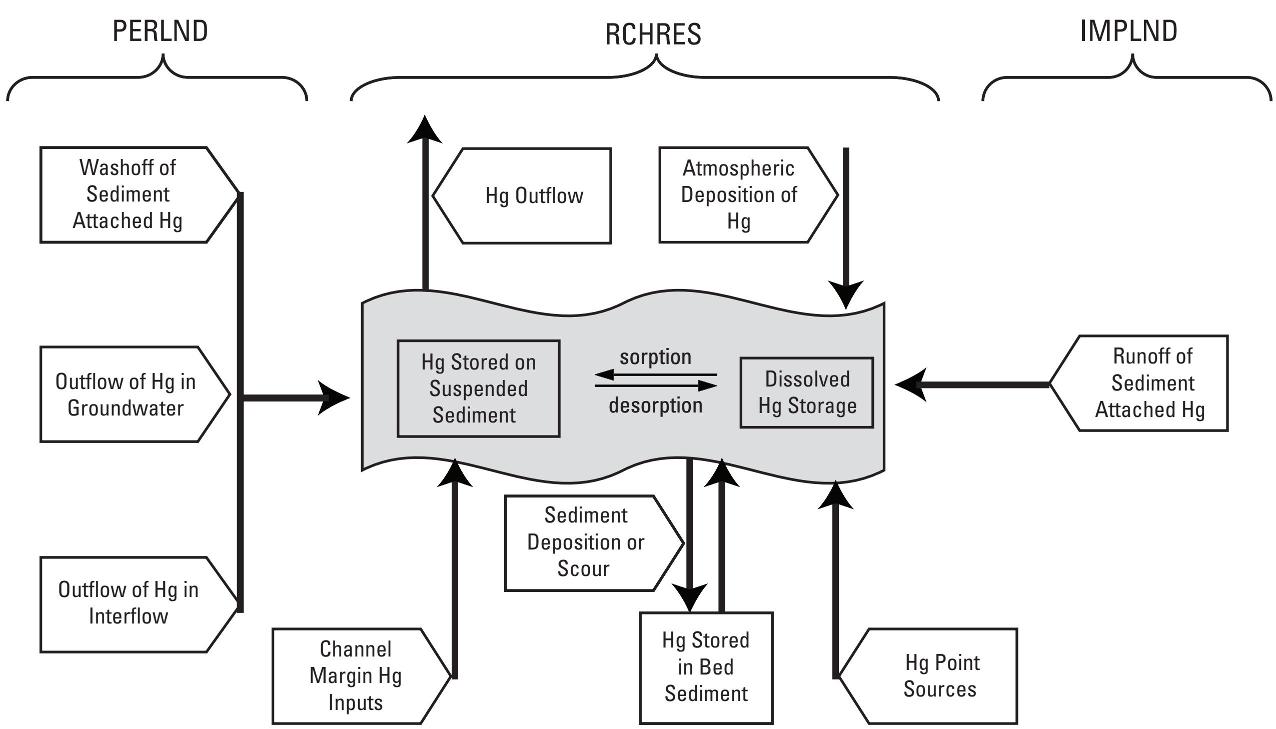


Figure 22. Mercury (Hg) routing in the South River numerical watershed model.

Mercury Sources to the River

Mercury sources to the South River that were known as of April 1, 2007, were included in the watershed model. The sources are listed in table 21 and discussed separately below. For mercury sources that are relatively well described by observation data, model concentrations were either held constant or were minimally adjusted during the calibration process. Relatively well-described sources include point sources and direct precipitation to the river. Other mercury sources that are less well described by data include groundwater, interflow, concentrations on runoff sediment, and channel margin inputs, all of which had greater adjustments during the model calibration process.

Atmospheric Deposition

It is assumed that precipitation falling directly on the river has a dissolved mercury (THG_F) concentration equal to 21.8 ng/L, which is the average HG concentration in precipitation discussed earlier in this report. The model indirectly accounts for atmospheric mercury deposited on land surfaces by assigning mercury concentrations to hydrologic and sediment loads leaving the land surface. This approach allows more accurate mass balancing of mercury, and indirectly accounts for the processes of mercury cycling through soils, vegetation, animals, and atmospheric evasion.

Land-Surface Runoff

All land surfaces in the model have runoff sediment with associated mercury. Runoff sediment THG_{Sed} concentrations varied by reach and HRU. Sediment from uncontaminated areas was initially assigned a THG_{Sed} value = 0.127 µg/g, the average mercury concentration on suspended sediment at the Waynesboro monitoring station. During the calibration process, this value was lowered to 0.07 µg/g. Land surfaces known to be contaminated with mercury (such as 62-year flood-plain areas downstream from the plant site) were assigned higher runoff sediment THG_{Sed} mercury concentrations, between 7.6 and 16.7 µg/g, to correspond with the observational data shown in table 13. These THG_{Sed} concentrations for runoff sediment from contaminated areas were not changed during the calibration process, but loading coefficients controlling the amount of runoff sediment reaching the river were adjusted.

Model river reach 1 receives no runoff from contaminated flood-plain land areas. Model river reaches 2–5 are all at least partially downstream from the plant site, and receive sediment from both contaminated flood plains (determined from the 62-yr flood plain) and uncontaminated land surfaces. The watershed model accounts for the acreage of each HRU contributing to each model river reach.

Table 21. Mercury sources to the South River in the watershed model.

[Hg, mercury; THG, total mercury; THG_F, aqueous filterable total mercury; THG_{Sed}, total mercury on soils or surface sediment; USEPA, U.S. Environmental Protection Agency; VPDES, Virginia Pollutant Discharge Elimination System; ng/L, nanograms per liter; µg/g micrograms per gram; HRU, hydrologic response unit]

Hg source to South River	Data used to determine initial concentrations	Model input
Atmospheric deposition on river surface	USEPA (U.S. Environmental Protection Agency, 2007)	Precipitation Hg concentration = 21.8 ng/L
Groundwater from uncontaminated land areas	THG_F concentrations at Waynesboro gage (01626000)	Groundwater dissolved Hg concentration = 0.7 ng/L
Groundwater from Hg contaminated flood plain	Flood-plain groundwater samples, plus calibration	Groundwater dissolved Hg concentration = 1.3–2.9 ng/L
Interflow	Precipitation THG_F (U.S. Environmental Protection Agency, 2007) and calibration	Calibrated values from 10.0 to 16.7 ng/L
Sediment attached Hg runoff from uncontaminated pervious and impervious land surfaces	Sediment samples from uncontaminated areas	THG_{Sed} concentration = 0.07 µg/g for all uncontaminated HRUs
Sediment attached Hg runoff from contaminated pervious land surfaces	Sediment samples within respective reaches	THG_{Sed} concentration varies by reach and HRU (from 7.6 to 16.7 µg/g)
Point-source discharges	VPDES flow data, grab sample analyses for minor sources, routine base-flow and stormflow monitoring of former DuPont plant site	Point-source flow rates and concentrations to river (model river reaches 1, 2, 3, and 5)
Channel margin inputs	THG concentrations at Waynesboro (01626000), Dooms (01626920), and Harriston (01627500)	Input of sediment attached Hg to water column of each model river reach, using MASS-LINK block

Groundwater and Interflow

Pervious land areas contribute mercury to river reaches through groundwater and interflow discharge (AGWO and IFWO). All mercury in AGWO and IFWO is assumed to be in the dissolved phase (THG_F). Impervious land areas have no groundwater or interflow discharge.

Groundwater from all uncontaminated pervious land areas was assumed to have the same THG_F concentration value. This was initially assigned to be 0.49 ng/L, the average base-flow THG_F concentration at the Waynesboro monitoring station above the plant site. In the final calibrated model, this value was adjusted to 0.7 ng/L. Groundwater from contaminated pervious land areas was assigned THG_F concentrations of 2.9 ng/L for model river reaches 2, 3, and 4, and 1.3 ng/L for model river reach 5. Interflow THG_F concentrations were assigned initial values between those of precipitation, 21.8 ng/L, and AGWO THG_F concentrations. During calibration these were slightly adjusted, and final IFWO THG_F concentrations ranged from 10.0 to 16.9 ng/L.

Point-Source Discharges

All point-source discharges in the model were assigned dissolved mercury concentrations. The actual point sources in most cases do carry sediment-associated mercury, but limited monitoring data did not permit distinguishing between dissolved and sorbed phases for most of the point sources. Mercury point-source inputs are partitioned by the model between dissolved and sorbed phases within a single time step once they enter the river. Mercury loads from point sources and the data used to assign flow rates and concentrations are listed in table 19 and Appendix 1.

There were extensive monitoring data describing discharges from the former DuPont plant site and the other discharge facilities (DuPont, 2003a, 2006a, b; Brenda Kennell, Invista, written commun., 2007). These data, which were collected at irregular intervals, were disaggregated and extrapolated to produce daily discharge values over the full simulation period. These data and the statistical treatments applied are summarized in Appendix 1.

Riverbank and Channel Margin Inputs

During model calibration, it was observed that the model could not reproduce high observed THG concentrations during low and moderate flow periods, when little or no runoff was entering the stream reaches. An additional mercury load of roughly 100–200 kg/yr to the river was needed to calibrate the model. Model results discussed later in this report indicate that groundwater and interflow discharge to the river could not provide 100–200 kg/yr of mercury to the river without assigning them unreasonably high concentrations of mercury. The additional mercury entering the South River is most likely coming from contaminated channel margin sediment deposits. A variety of possible mechanisms could move mercury in these contaminated channel margin sediments to the river: bank erosion, bank collapse, disturbance of sediment by animals or fishermen or boaters, diffusion of mercury from contaminated sediment in contact with the water column, tree falls, ecological extraction of mercury from channel sediment, sediment displacement by interflow and groundwater discharge, hyporheic flow, desorption due to changed pH or oxidative state, another unknown mechanism, or some combination of these, all of which could operate along the length of the river.

Bank retreat could account for much of the missing mercury load. Rhoades and others (2009) found that, on average, 109 kg/yr of mercury enters the South River from bank retreat, based on long-term erosion profiling and sampling of bank sediment. Bank collapse may work in concert with other mechanisms to produce mercury load to the river. Collapsed riverbank sediment could release mercury to hyporheic flow or groundwater discharge passing through it, for example. Sampling of pore water in surface sediment adjacent to the river during this study found elevated THG_F concentrations at several locations downstream from the plant site (table 11). Evidence of mercury input to the river from banks was also seen by Turner and Jensen (2007), who found river reaches where water column mercury concentrations were higher near the bank than in the center of the river, implying an active source of dissolved mercury close to the banks.

The exact mechanism responsible for the additional mercury source along the South River is not known. Therefore, a relatively simple approach was taken in the model. MASS-LINK tables were added to create Hg-contaminated sediment inputs to the river reaches. Inputs were scaled with groundwater discharge (AGWO) and interflow (IFWO) from HG-contaminated pervious land areas. Groundwater and interflow rates provide signals of hydrologic conditions that are responsible for at least some of the wetting and hydraulic stress factors controlling bank collapse (Knighton, 1998). Loading coefficients were adjusted during the calibration process so that simulated THG concentrations in the river at the Dooms and Harriston monitoring stations matched observations. Channel margin inputs are treated separately from dissolved Hg groundwater and interflow inputs and separately from sediment-associated Hg in pervious land area and impervious land area runoff.

Mercury Transport Within the River

In the simulations, mercury in the water column moves downstream both in the dissolved phase and sorbed to suspended sediment. When suspended sediment with sorbed mercury settles out of the water column onto the channel bed, the sorbed mercury remains with the sediment until it is resuspended. When sediment exits a reach, the associated mercury also exits.

HSPF partitions mercury in the water column by transferring it between dissolved and sorbed phases so that dissolved and sorbed concentrations approach an equilibrium ratio. The phase transfer is limited by a user-specified rate coefficient so that equilibrium partitioning is not instantaneous. A finite difference expression of the mercury continuity equation (equation 1) is solved for each reach at each time step to calculate the mass transfer between phases. The phase transfer is calculated separately for each size fraction (sand, silt, clay) of the suspended sediment. No transfer is simulated between sediment of different size classes, between bed sediment and groundwater, or between bed sediment and the water column. Decay or production of mercury from other constituents are likely negligible, and therefore they were not simulated.

$$-d(RSED*SQAL)/dt + RSED*KT*(KD*DQAL-SQAL) = 0 \quad (1)$$

where:

RSED	=	quantity of sediment in the model river reach (mass);
SQAL	=	concentration of constituent on sediment (mass Hg/mass sediment);
DQAL	=	concentration of dissolved constituent (mass Hg/volume water);
KD	=	distribution coefficient; and
KT	=	rate transfer coefficient.

A single distribution coefficient of 1,000,000 L/kg (liters per kilogram) is used to partition mercury between the aqueous phase and sorbed phase on suspended silt and clay. This value is based on ratios of THG_{Sed} and THG_F concentrations listed in tables 7 and 8 and batch tests results from Mason (2006). HSPF also requires a distribution coefficient for mercury sorption to sand, and a lower coefficient of 1,000 L/kg is assumed. To ensure nearly instantaneous transfer of mercury between phases, a high rate transfer coefficient of 25.0 was used for partitioning between all suspended sediment size fractions and the water column. Mercury partitioning between channel bed sediment and the water column was slowed to almost zero by assigning a low rate transfer coefficient (0.0001) for all sediment-size fractions. This was done because *in-situ* partitioning of mercury between channel bed sediment and pore water is not well understood for the South River.

Watershed Model Results

After compiling input data, the numerical watershed model was tested and calibrated. Model calibration, or the adjustment of model parameter values to achieve better agreement between observed and simulated values, was performed sequentially for streamflow, suspended sediment transport, and mercury transport. The streamflow and sediment transport calibration covered the period from water year 1991 through water year 2000 (October 1, 1990, through September 30, 2000). For mercury, the model calibration covered the period from April 2005 through March 2006, which corresponds with the period of intense mercury data collection. Model verification, in which results from the calibrated model are compared to observations for a separate period with the same model fit targets as used for calibration, was also performed. For streamflow and sediment transport, verification covered the period from water years 2001 through 2005, whereas for mercury, verification covered the period from April 2006 through March 2007.

As described in a previous section, Representation of the Watershed, all hydrologic and sediment model parameters were initially assigned values from the calibrated CBM5 model and were then adjusted to achieve a closer fit between simulated and observed values. Most of these changes were relatively minor because the CBM5 model parameters were previously calibrated. The CBM5 model does not simulate mercury; therefore, mercury transport parameters were assigned according to observations.

Improvements to the South River watershed model hydrology and sediment parameters were made by using additional data that were not available during the CBM5 calibration effort. CBM5 parameter values were calibrated using observed streamflow both outside and within the South River watershed. In the CBM5 model, for example, evaporation coefficients for land-county segment A51015 were optimized using streamflow observations from the South River streamflow-gaging stations (0162600, 01626850, 01627500) as well as stations on the Middle River (01624800, 01625000). Because this study focuses on the South River, parameter values were changed to obtain a better fit for only the South River observed streamflow values. Additional justification for modifications to the CBM5 parameters include the division of CBM5 RCHRES PS2_6490_6360 into reaches 3 and 4 in this model, and the availability of more recent streamflow and suspended sediment concentration data.

Streamflow Model Calibration Results

The ability of the model to accurately simulate streamflow was evaluated by statistically comparing simulated and observed streamflow with respect to annual and seasonal water budgets, high-flow and low-flow distribution, and stormflow volumes. These comparisons were performed primarily using Expert System for the Calibration of the Hydrological Simulation Program–FORTRAN (HSPEXP) (Lumb and others, 1994).

The hydraulic component of the South River watershed model simulates the period January 1, 1985, through March 31, 2007, using hourly time steps. The 10-year calibration period includes the wettest year (1998) and the fourth driest year (1999) on record for the Harriston streamflow-gaging station. Observed mean annual flows at the Harriston streamflow-gaging station for years with complete data are shown in figure 23. A 2-year verification period from April 1, 2005, through March 31, 2007, was used to verify that the calibrated hydrology model can accurately simulate other time periods.

Hydraulic parameter values were adjusted during calibration to match observed and simulated water volumes. Changes to initial CBM5 parameter values were made to reduce the

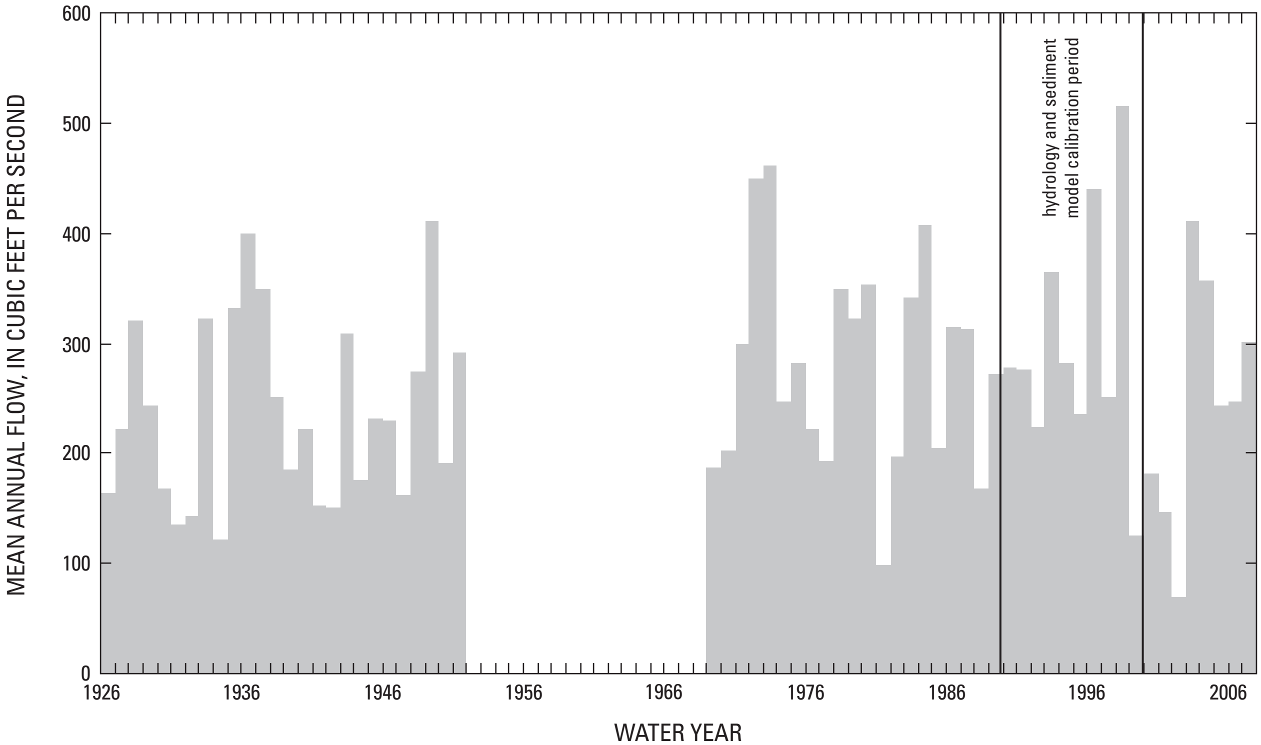


Figure 23. Observed mean annual flow, South River at Harriston, Virginia (USGS station number 01627500), water years 1926–2007.

amount of runoff (table 22). Changes were made to the actual evapotranspiration coefficients that scale the External Source EVAP time series to improve simulated runoff volumes and to parameters INFILT and AGWETP to improve the distribution of runoff volumes between high- and low-flow periods. Final calibrated values for these parameters are listed in Appendix 2. The actual evapotranspiration multiplier coefficients used to scale evaporation input time series were increased by an average of 16 percent to better match observed total runoff. Parameter values for INFILT, which controls infiltration capacity, were reduced uniformly by 50 percent to reduce runoff in the 40–60 percent streamflow duration range. Values for AGWETP, which control how much actual evapotranspiration can come from base flow, were set to zero to increase runoff during periods of low flow.

Two streamflow-gaging stations were used for calibrating streamflow, South River near Waynesboro (01626000) and South River at Harriston (01627500). These two streamflow-gaging stations are the only ones on the South River with complete daily streamflow data for the calibration period. Station 01626000 is the most upstream stream reach node in the model, whereas 01627500 is the penultimate downstream node.

Simulated streamflow exhibits annual, seasonal, and daily patterns similar to those in observed streamflow (figs. 24–31). Calibrated model simulation results compared to calibration goals are shown in tables 23 and 24 (Bicknell and others, 2001). There is a good overall mass balance for the simulation period, and the distribution of high and low simulated flow matches well with observed values. The frequency distribution of simulated streamflow values matches the observed distribution, as shown by the flow duration curves in figures 32 and 33. High streamflows caused by storms, which occur infrequently but account for the majority of total discharge, show a close match between simulated and observed values. The lowest 20 percent of daily streamflows, from 80 percent to 100 percent exceedance in figures 32 and 33, are less accurately simulated; however, at Harriston, they account for just 4.9 percent of total discharge volume.

Observed daily-mean and simulated daily flows do not match in all cases, as can be seen in the 1:1 plots of observed to simulated streamflow, (figs. 34–35). The R^2 value for figure 34 is 0.39, and 0.41 for figure 35. The mismatch between daily values is, in many cases, caused by an offset in timing of a day or two between simulated and observed stormflows. The primary reason for differences between simulated and observed stormflows in most cases is probably differences between modeled and actual precipitation. As described in an earlier section, Meteorological and Climatic Data, the hourly precipitation data used in the South River watershed model were taken from the CBM5 model and were derived by spatial averaging of records from nearby meteorological monitoring stations, which for water years 1991 through 2000 were all outside the watershed. Although there are no hourly precipitation records from stations within the watershed during the calibration period, differences between actual precipitation

Table 22. Primary model transport parameters changed from Chesapeake Bay Model Phase 5 values during calibration of the South River watershed model.

[HSPF, Hydrological Simulation Program–FORTRAN; ET, actual evapotranspiration; PERLND, pervious land area; IMPLND, impervious land area; RCHRES, model river reach]

HSPF module	Parameter name	Description
	Hydrologic	
PERLND	INFILT	Controls infiltration capacity
	ET coefficients	Scale evaporation rate input time series
	AGWETP	Controls ET rate from base flow
	Sediment transport	
IMPLND	Loading factors	Control fraction of sediment runoff from PERLND to RCHRES
	KEIM	Controls solids wash-off rate
PERLND	Loading factors	Control fraction of sediment runoff from PERLND to RCHRES
	NVSI	Represents external application of detached soil
	KRER	Controls rate of soil detachment
	KSER	Controls rate of transport of detached soil
RCHRES	W	Particle settling velocity
	TAUCD	Critical bed shear stress for deposition
	TAUCS	Critical bed shear stress for scour
	M	Erodibility of bed sediment

Table 23. Simulation results for the calibration period water years 1991 through 2000, calibrated model, South River, Virginia.

[in., inches; %, percent]

Runoff category	Criterion (percent)	South River near Waynesboro 01626000			South River at Harriston 01627500		
		Observed (in.)	Simulated (in.)	% Error	Observed (in.)	Simulated (in.)	% Error
Total annual runoff	±10	186.9	182.2	–2.5	185.1	194.6	5.2
Highest 10-percent flow	±10	84.7	86.5	2.0	81.5	87.8	7.7
Lowest 50-percent flow	±15	28.0	25.6	–8.4	31.5	31.4	–0.2
Winter runoff	±15	64.3	61.6	–4.3	63.0	64.7	2.6
Spring runoff	±15	65.9	63.4	–3.9	63.6	66.5	4.5
Summer runoff	±15	26.1	26.7	2.2	26.2	29.7	13.4
Fall runoff	±15	30.8	30.5	–1.1	32.2	33.7	4.7
Total storm volume	±20	19.6	17.1	–13.0	19.0	17.4	–8.5

Table 24. Simulation results for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia.

[in., inches; %, percent]

Runoff category	Criterion (percent)	South River near Waynesboro 01626000			South River at Harriston 01627500		
		Observed (in.)	Simulated (in.)	% Error	Observed (in.)	Simulated (in.)	% Error
Total annual runoff	±10	35.5	32.5	–8.6	35.3	34.9	–1.0
Highest 10-percent flow	±10	14.0	13.2	–5.5	13.8	13.4	–2.8
Lowest 50-percent flow	±15	6.4	6.1	–4.4	7.0	7.3	3.5
Winter runoff	±15	11.4	9.8	–13.5	10.8	10.5	–3.3
Spring runoff	±15	7.8	7.2	–7.8	7.6	7.9	3.2
Summer runoff	±15	3.8	5.7	51.9	4.2	6.3	50.5
Fall runoff	±15	12.7	9.8	–23.1	12.7	10.3	–18.7
Total storm volume	±20	9.8	9.6	–2.0	9.9	9.7	–1.7

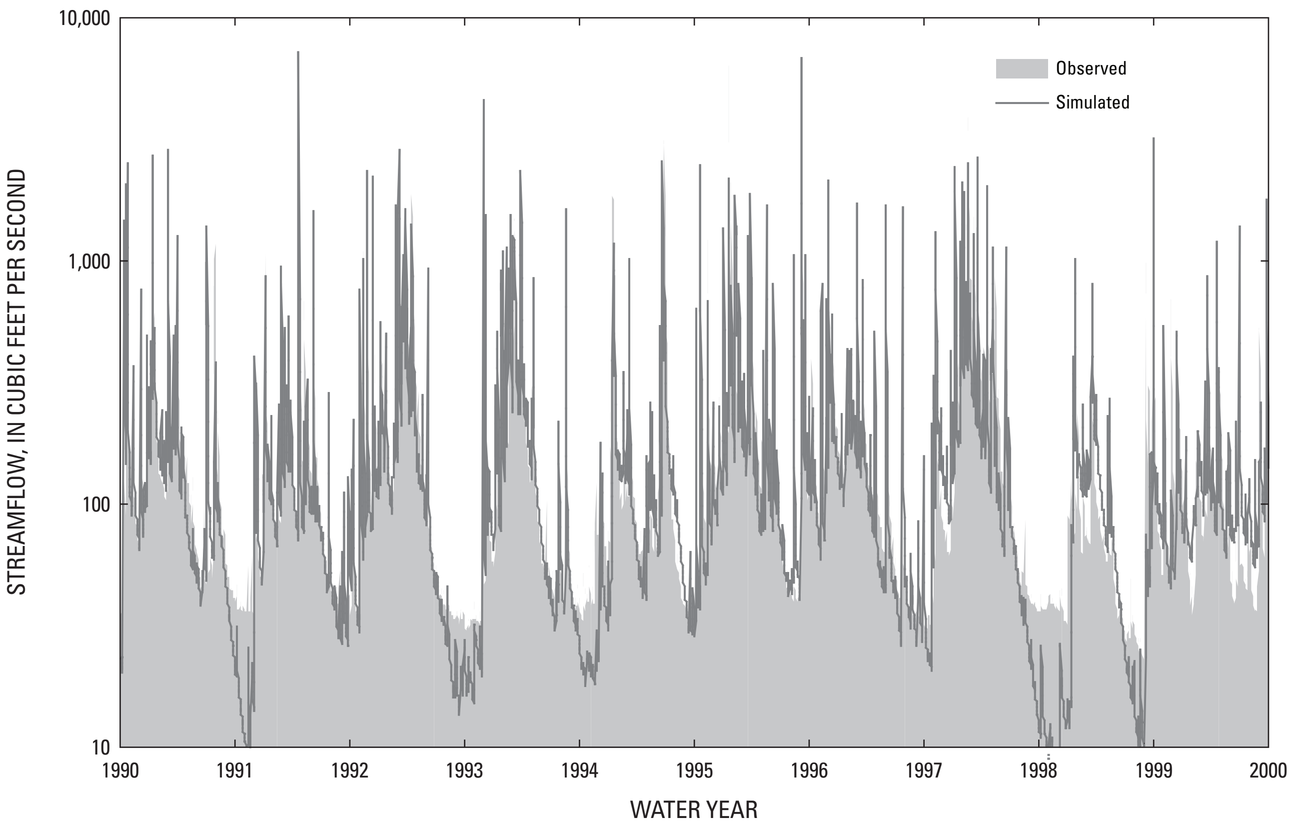


Figure 24. Simulated and observed daily streamflow for the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

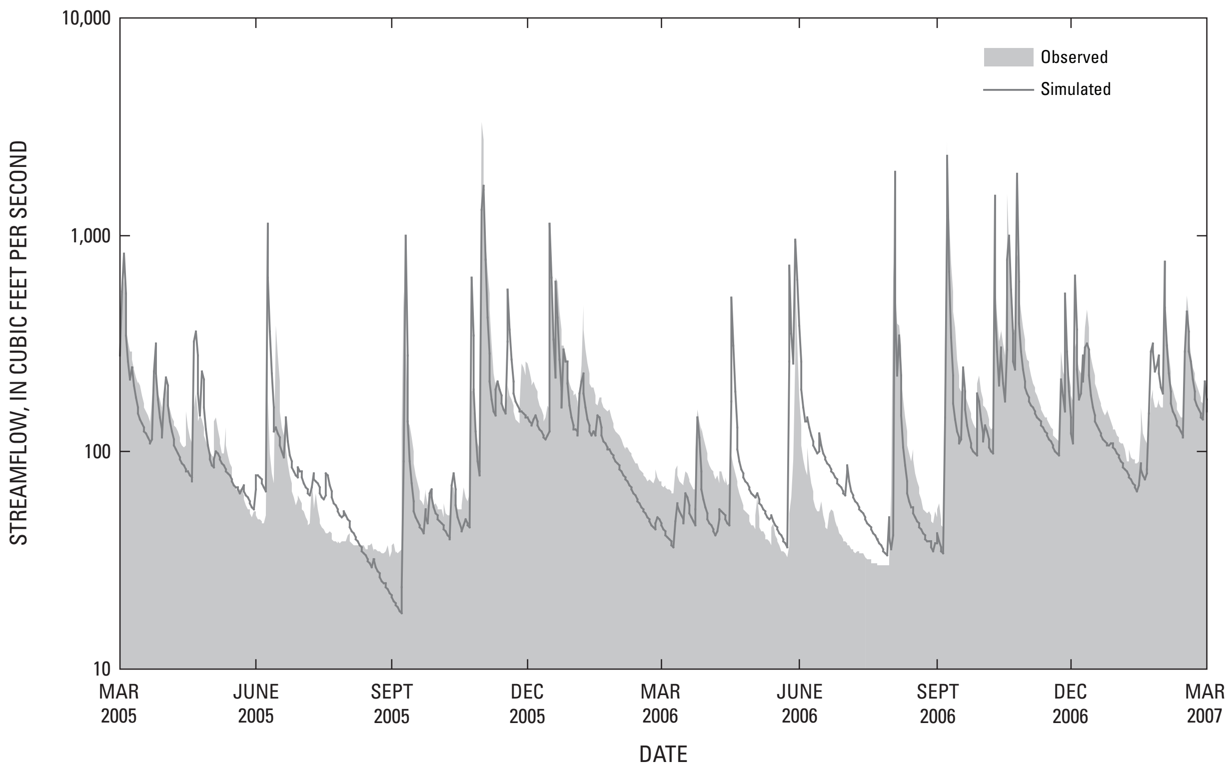


Figure 25. Simulated and observed daily streamflow during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

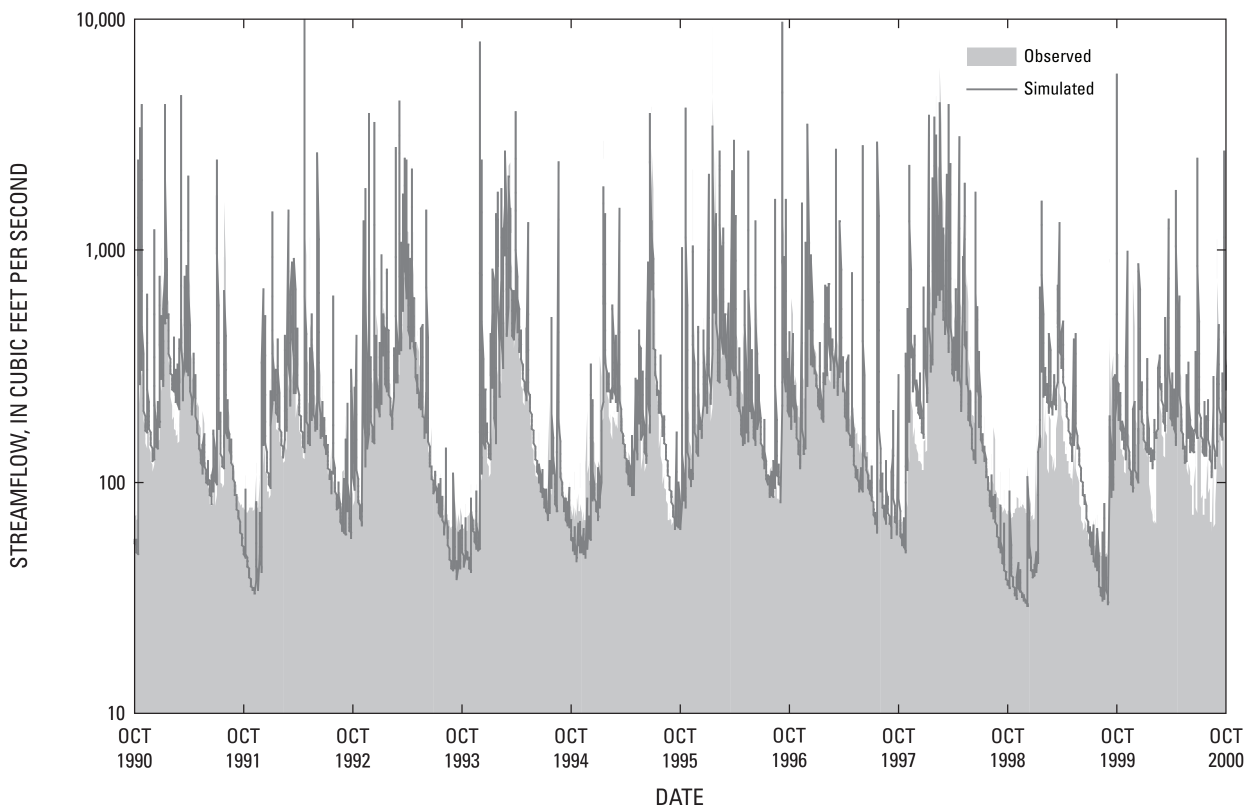


Figure 26. Simulated and observed daily streamflow during the calibration period water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

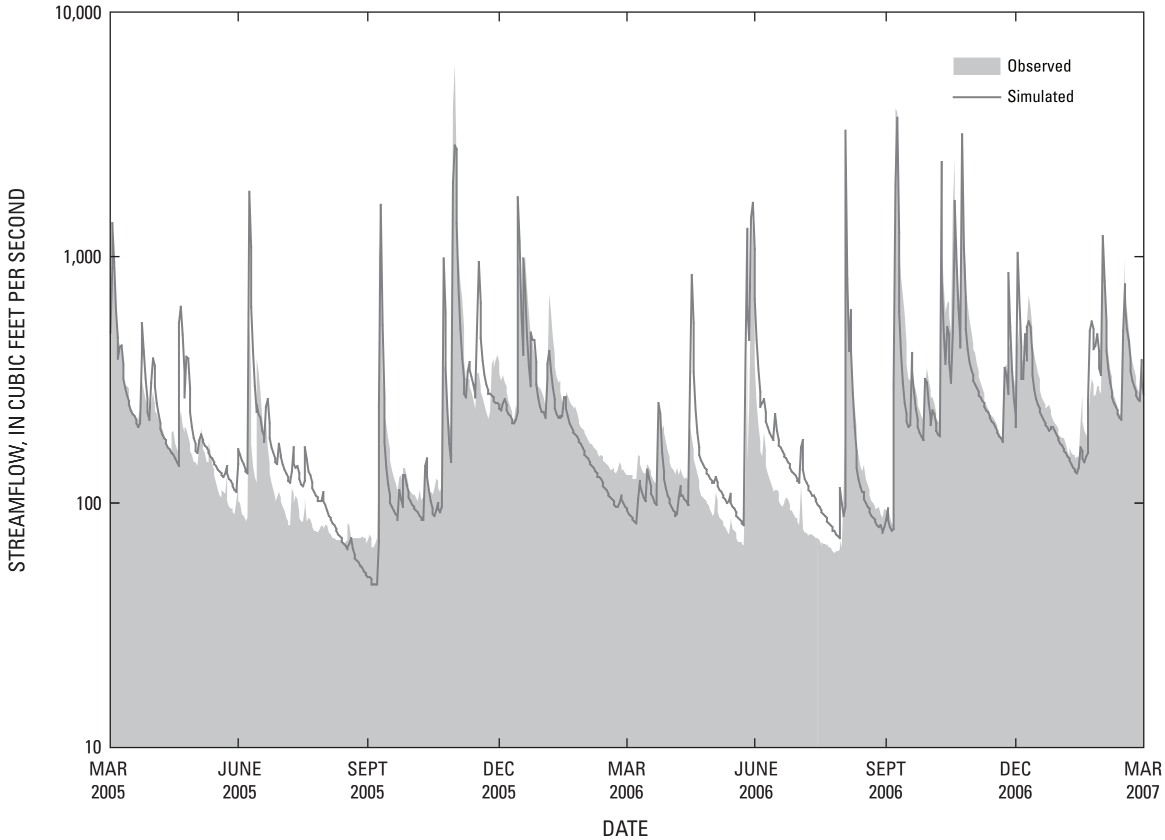


Figure 27. Simulated and observed daily streamflow for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

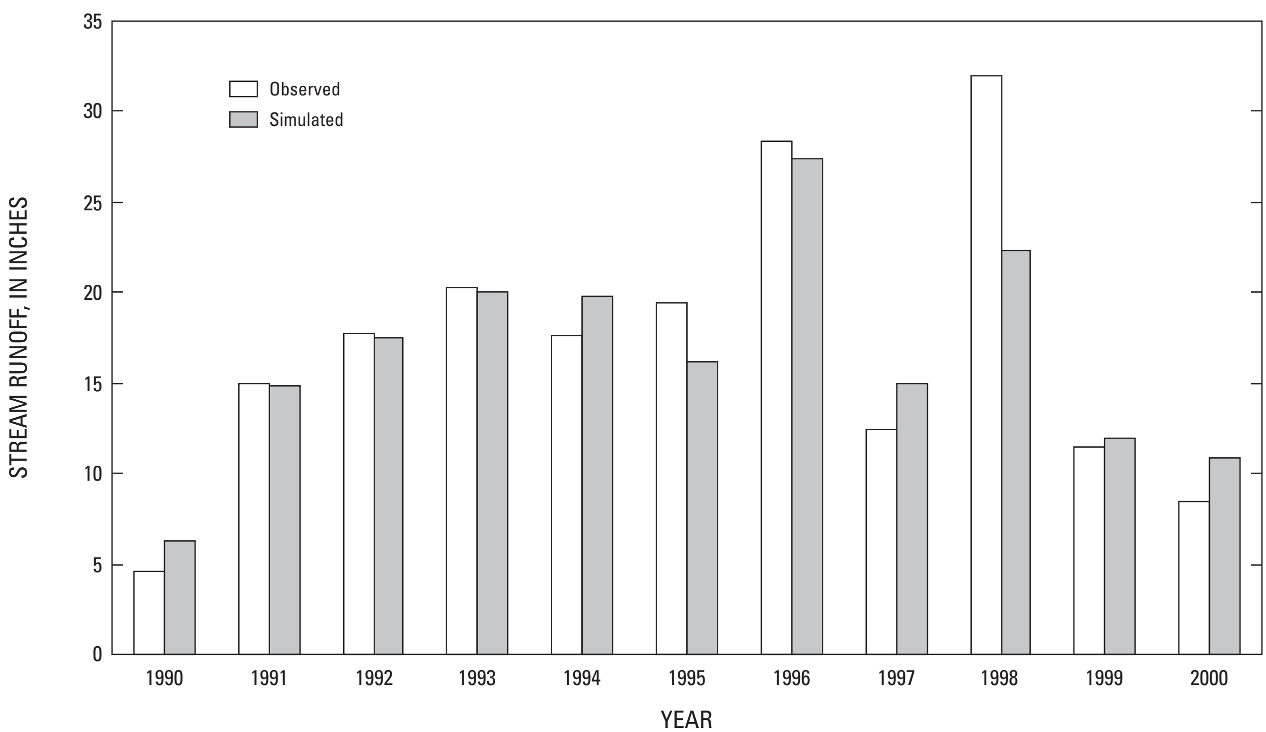


Figure 28. Simulated and observed annual runoff during the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

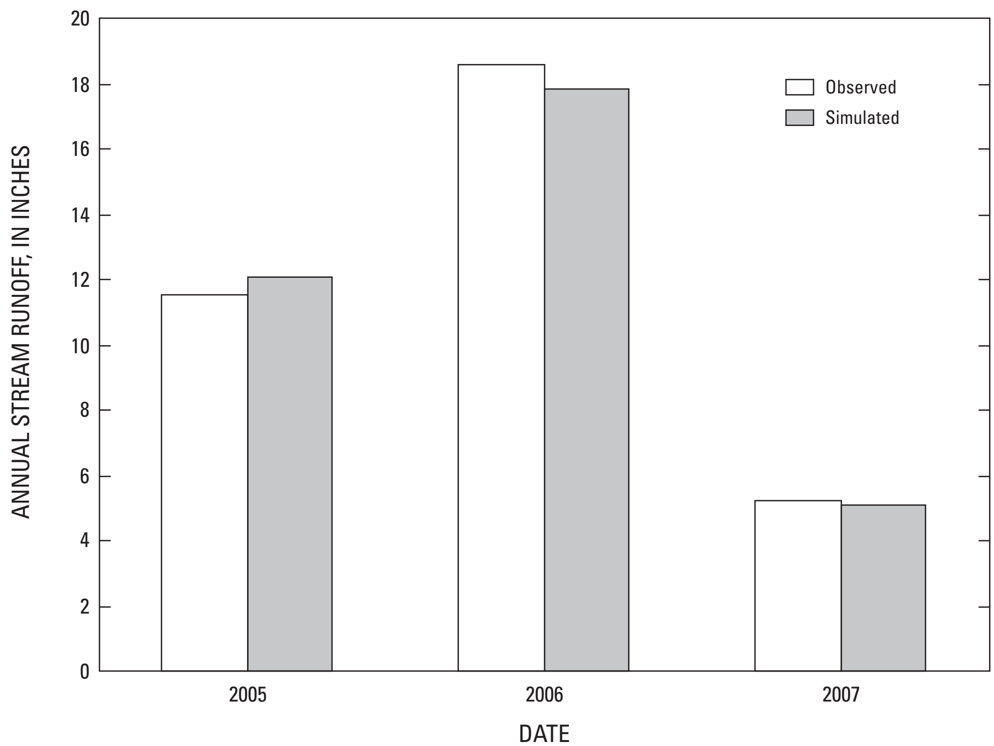


Figure 29. Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

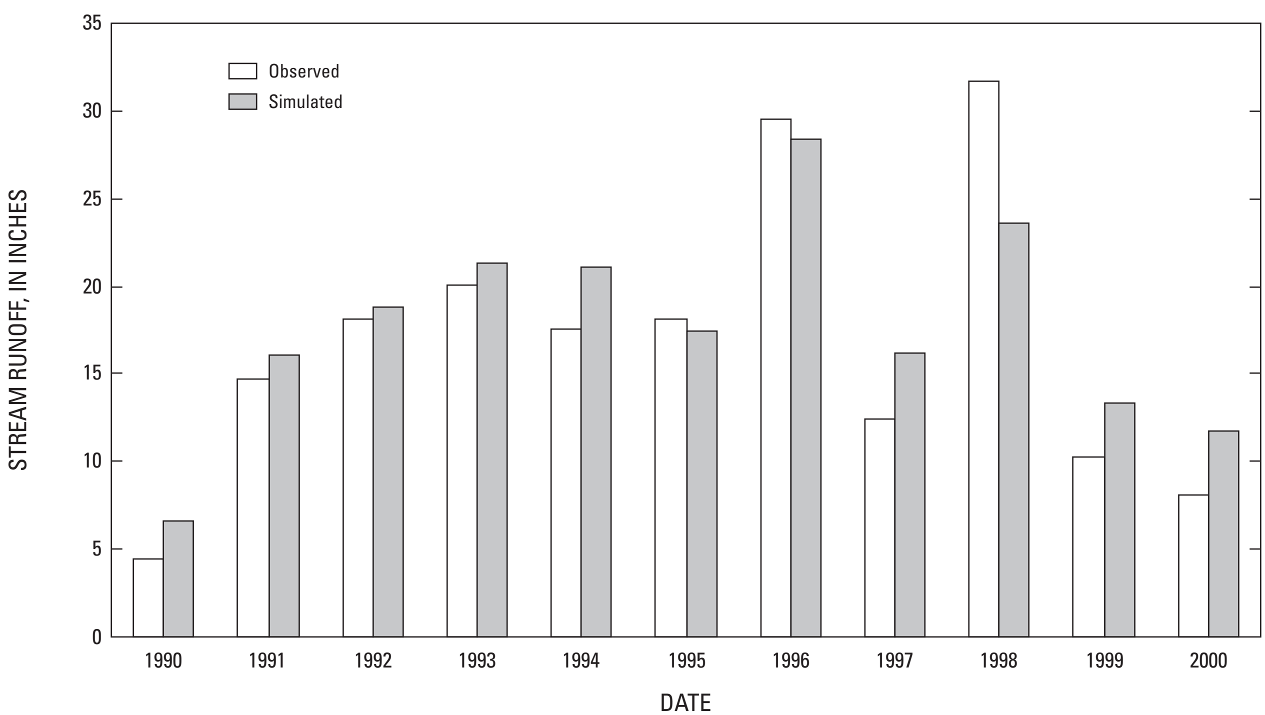


Figure 30. Simulated and observed annual runoff during the calibration period water years 1991–2000, calibrated, South River at Harriston, Virginia (USGS station number 01627500).

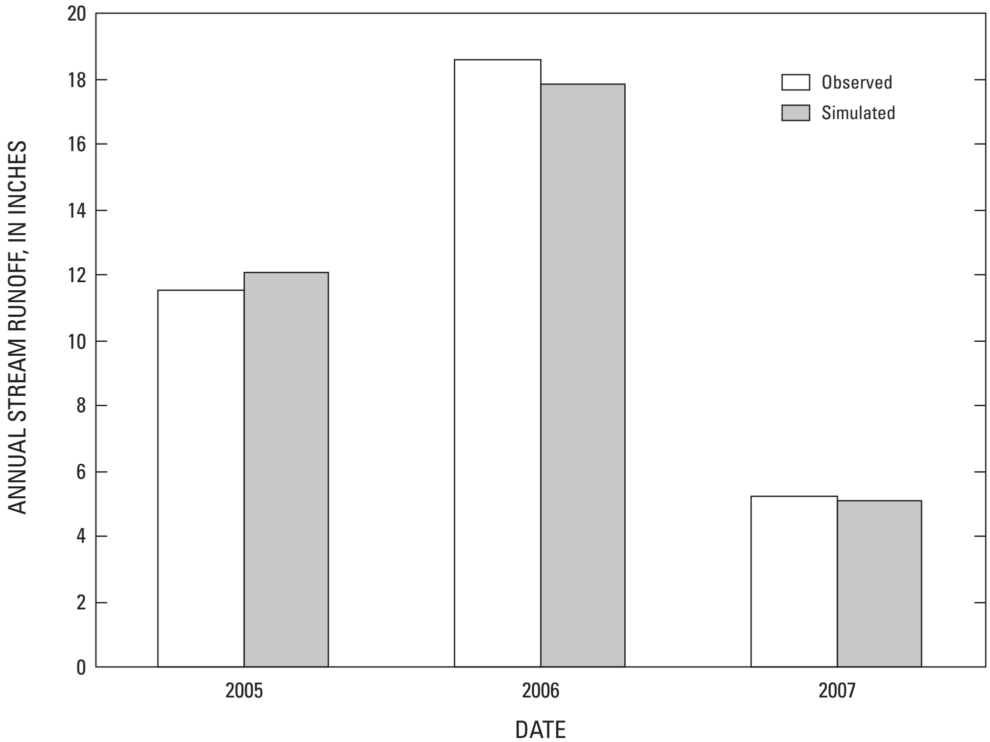


Figure 31. Simulated and observed total runoff during the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

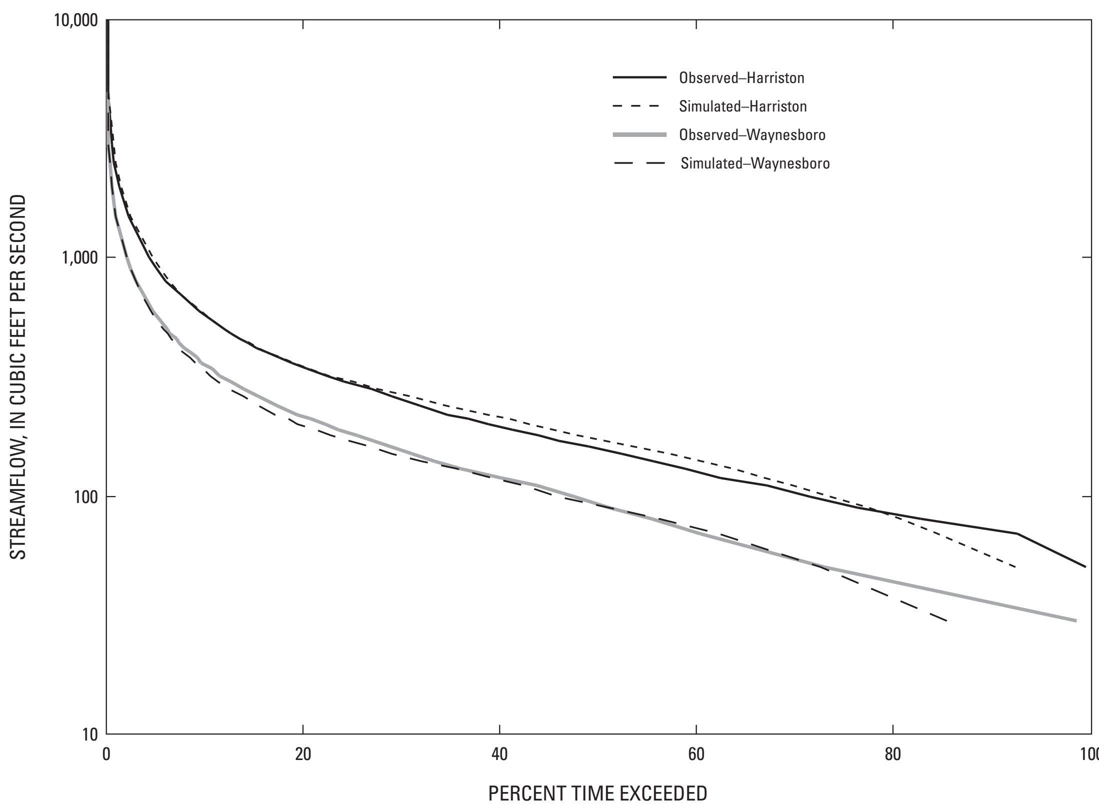


Figure 32. Flow duration curves for observed and simulated streamflow, calibration period water years 1991–2000, calibrated model, for the South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500).

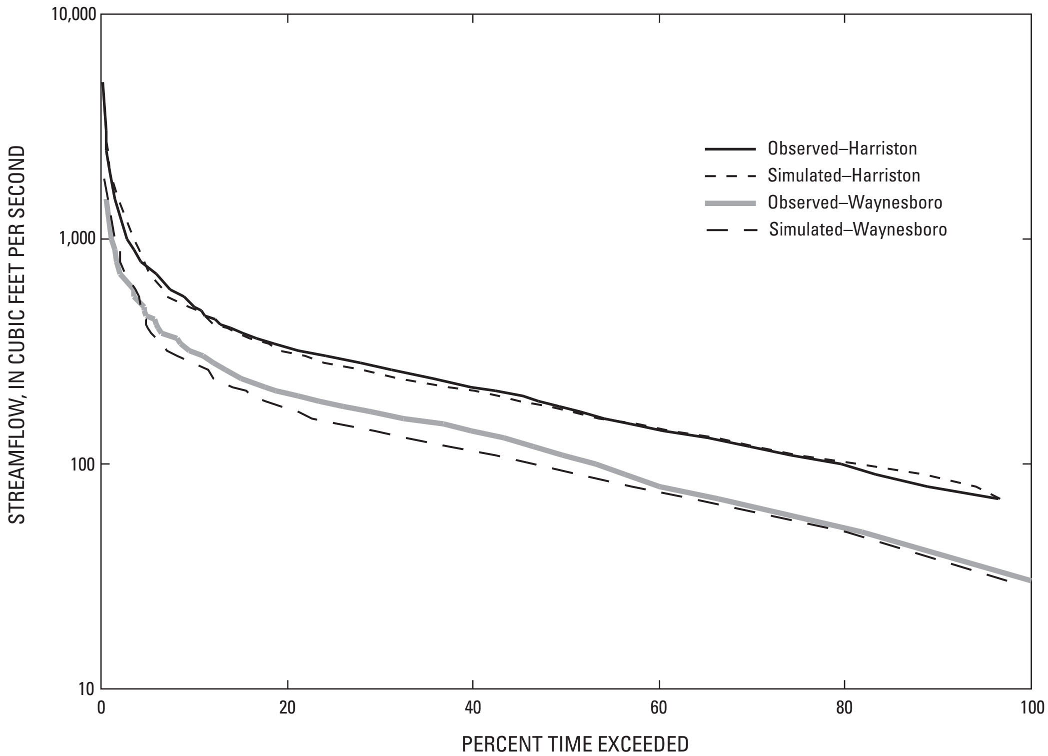


Figure 33. Flow duration curves for observed and simulated daily streamflow, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000) and at Harriston, Virginia (USGS station number 01627500), verification period April 1, 2005, through March 31, 2007.

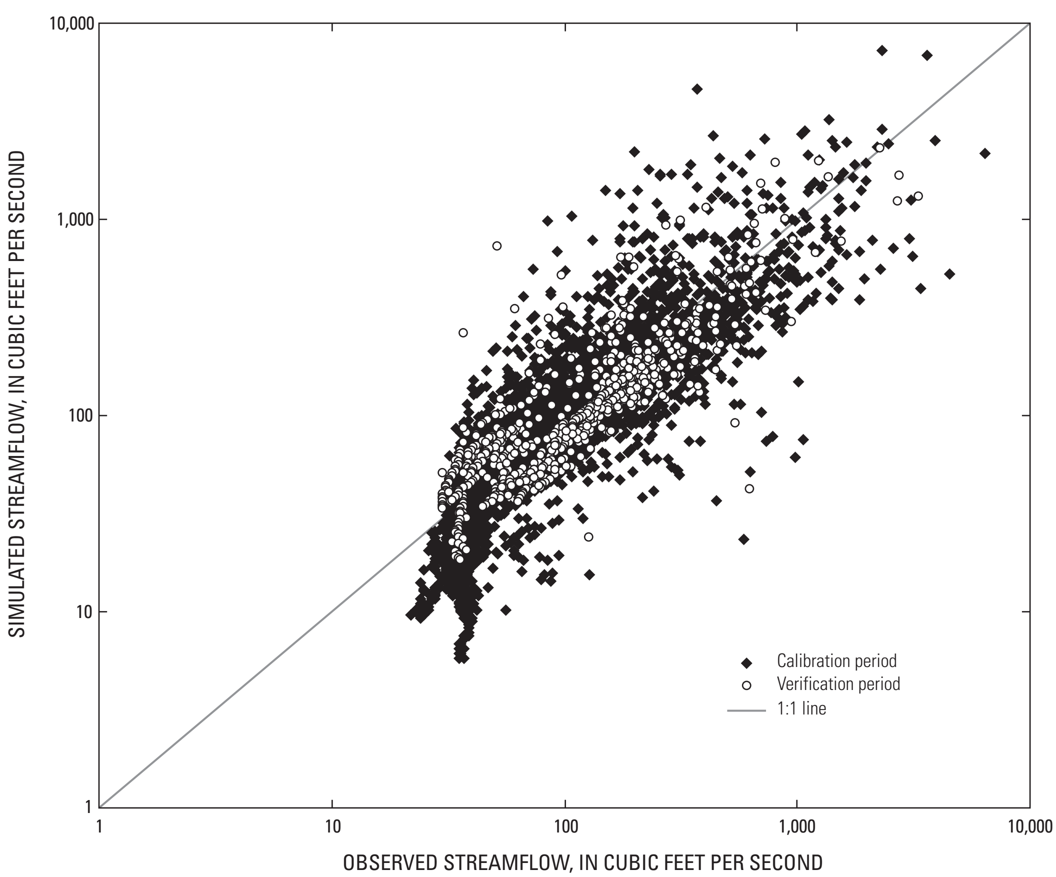


Figure 34. 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000), water years 1991–2000 and April 2005 through March 2007.

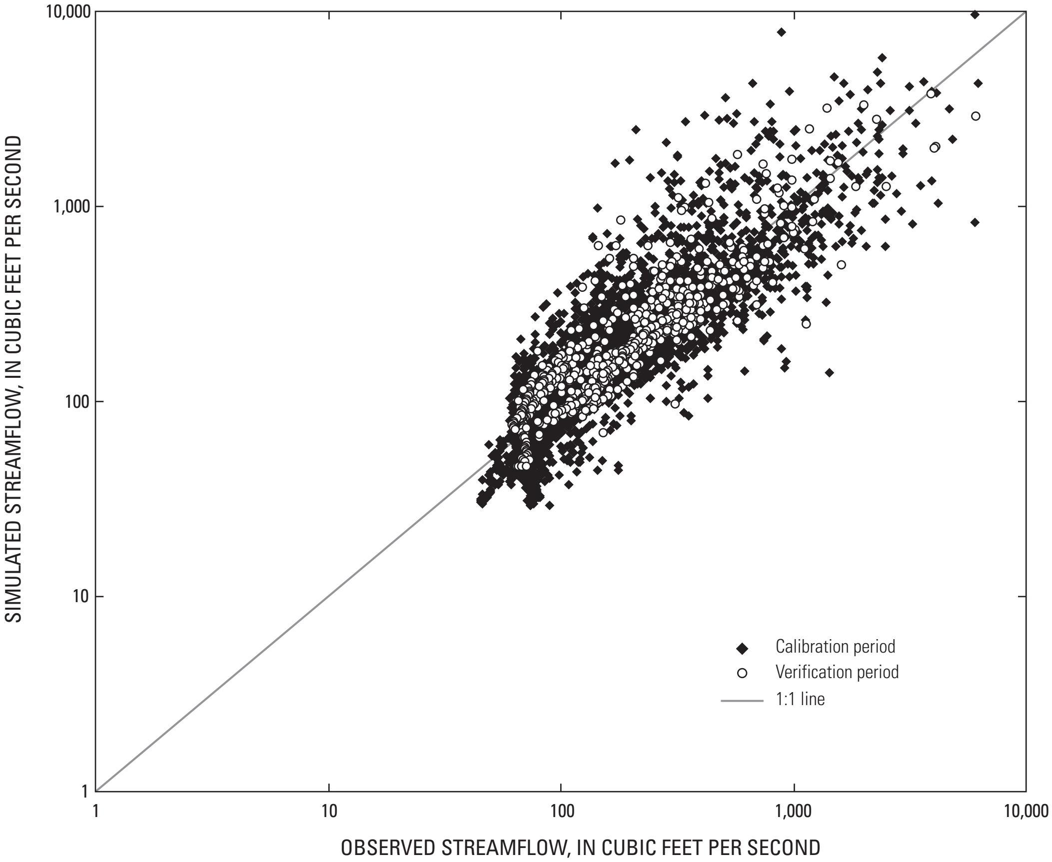


Figure 35. 1:1 comparison of simulated and observed daily streamflow, calibrated model, South River at Harriston, Virginia (USGS station number 01627500), water years 1991–2000 and April 2005 through March 2007.

on the basin and the precipitation time series in the model can be inferred from the fact that some observed storms had total storm discharge that exceeded the model precipitation volumes for the same period. Similarly, some simulated storms have discharge volumes that exceeded observed precipitation volumes for the same period based on daily precipitation data collected within the watershed.

Sediment Transport Model Calibration Results

The sediment transport component of the South River watershed model was calibrated using a “weight-of-evidence” approach (Donigian and Love, 2003), in which multiple numeric and qualitative calibration goals were assessed. Comparisons were made between simulated and observed suspended sediment concentration, suspended sediment loads, and depth of bed sediment. Comparisons were made using the same calibration period (water year 1991 through 2000), the same verification period (April 1, 2005, through March 31, 2007), and the same two calibration sites (Waynesboro 01626000 and Harriston 01627500) as were used for the calibration of streamflow. Only USGS suspended sediment concentration values were used for quantitative calibration of the sediment transport model. Suspended sediment values from the VDEQ (reported as total suspended solids as discussed earlier) were used only for qualitative and supplemental checks during the sediment model calibration.

Time series of regressed daily suspended sediment concentration values were used as the primary “observed” values during calibration because the regressed time series have values for every time step and therefore, their statistics are unbiased towards either stormflow or base flow. The regressed suspended sediment concentration time-series data were derived from USGS grab samples and multiple linear regression, as described earlier. So that a consistent regression model was used throughout the entire simulation period, regressed suspended sediment concentration values were used from estimation model number 7 in table 15, which derived suspended sediment concentration from normalized streamflow and streamflow increase. Observed suspended sediment loads were calculated by multiplying observed daily flow values with regressed suspended sediment concentration values, whereas simulated loads were calculated by HSPF using its mass balance formulas.

The South River watershed model has coarse spatial discretization relative to channel morphology and sediment distribution patterns. Riffle spacing in the South River is typically less than 0.2 mi, for example (Pizzuto and others, 2006, p. 24), whereas river reaches in the model are about 8.0 mi long. Due to the coarse discretization and the limited sediment transport algorithms available in HSPF, the accurate simulation of any single observed suspended sediment concentration value was not the primary focus of the calibration. Rather, the goal was to match simulated and observed suspended sediment concentration statistics and suspended sediment loads.

The multiple calibration goals were defined as follows:

1. Simulated suspended sediment concentration ranges match observed suspended sediment concentration ranges, and simulated 50-percent and 10-percent duration suspended sediment concentration values are within 30 percent of observed values.
2. Simulated and observed suspended sediment concentration duration plots show no major differences.
3. Total simulated suspended sediment loads are within 10 percent of observed loads for the calibration period.
4. The total of the bottom 50 percent of daily simulated sediment loads and the top 10 percent of daily simulated sediment loads are within 30 percent of observed values.
5. Simulated annual sediment loads show patterns similar to observed annual loads.
6. Simulated depth of bed sediment does not show a long-term increasing trend.

Calibration goal 6 is based on the results of a study by Pizzuto and others (2006), who found that very little fine-grained sediment is stored on the channel bed of the South River, an amount that is “3 orders of magnitude less than the annual suspended sediment load of the South River, and is volumetrically insignificant.” They found that average depth of sediment in the channel was less than 0.04 inch downstream from the plant site. On the basis of this observation, the model was calibrated so that depth of deposited sediment in each model river reach did not show long-term increasing trends. This goal was met in the calibrated model as shown in figure 36.

Selected sediment transport parameters for each impervious land area, pervious land area, and river reach were adjusted during the calibration process to obtain a better fit to observations (table 22). Changes to initial CBM5 parameter values were made to reduce the amount of sediment entering the river, to redistribute sediment loads across flow regimes, and to prevent sediment building up on the river bed. For impervious land areas, sediment transport coefficients KEIM were reduced by 50 percent. For pervious land areas, the coefficients NVSI, KRER, and KSER were reduced by 80 percent. For each impervious and pervious land area, coefficients used to adjust sediment loads reaching the river (sediment load factors) were reduced from CBM5 values (Chesapeake Bay

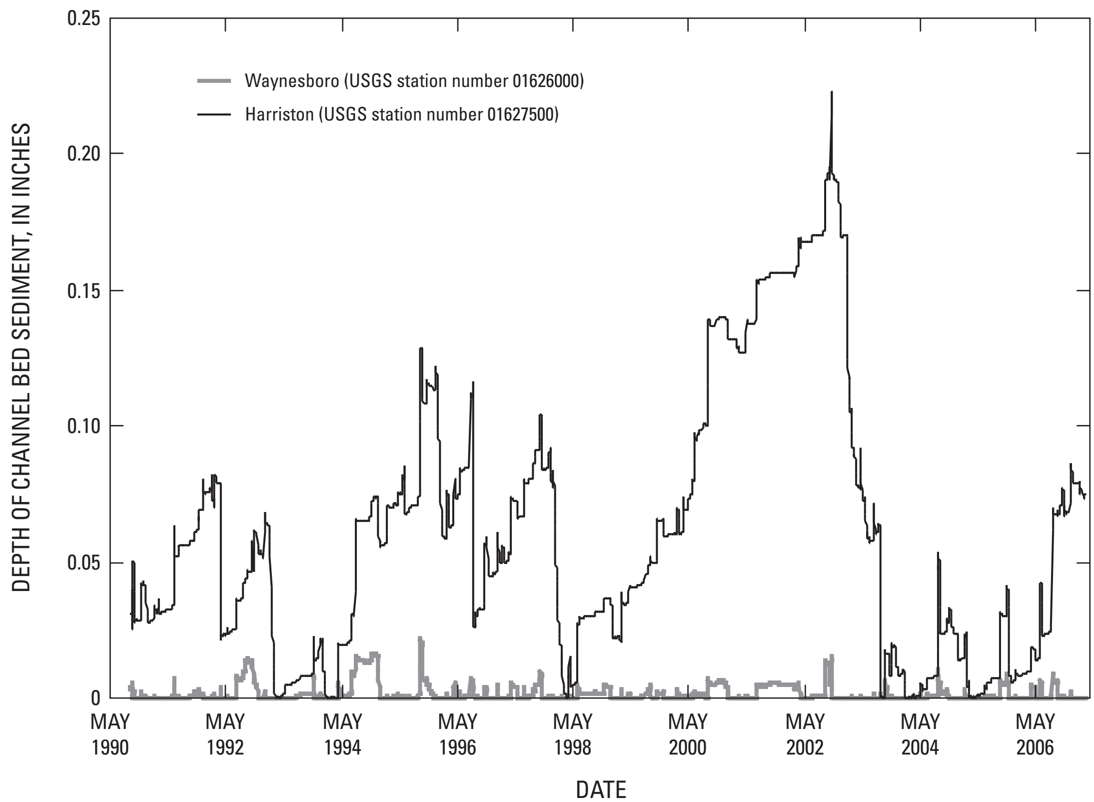


Figure 36. Simulated depth of sediment in model river reaches 1 and 4, calibrated South River model, water years 1991–2000.

Program, 2002, Appendix F; Gary Shenk, Chesapeake Bay Program, written commun., 2007) to achieve better sediment mass balance. Sediment load factors are multiplied into overland runoff sediment loads before they enter the river to improve mass balances. The calibrated South River watershed model uses the same sediment load factor value for all pervious and impervious land areas contributing to a reach. The load factor for reach 1 is 15.6 percent, reduced from the equivalent CBM5 value of 21 percent. For reaches 2–5, the load factor is 21 percent, reduced from the equivalent CBM5 value of 23 percent.

As can be seen in figures 37–44 and tables 25–26, the watershed model does a reasonable job of recreating observed grab samples, suspended sediment concentration ranges, and regressed concentrations and annual loads. The simulated annual sediment load at Harriston for the calibration period is 22,400 tons, of which 98 percent comes from pervious land area surfaces, 2 percent from impervious land area surfaces, and 0.1 percent from point-source discharges. Total simulated loads during the calibration period have an error of +2.1 percent at Harriston and –3.0 percent at Waynesboro, when compared to loads calculated from the regressed suspended sediment concentration time series. Yearly loads for Waynesboro and Harriston are shown in figures 41–44.

Time series of simulated and observed (regressed) suspended sediment concentration values are shown in figures 37 and 38 for the Waynesboro station and in figures 39 and 40 for the Harriston station. Simulated suspended sediment concentration values have an overall good match to observed values. All but one of the six numeric calibration goals was met (tables 25 and 26). The goal not met was the lowest 50 percent of suspended sediment concentration at the Waynesboro station, which had –46.5 percent error.

Simulated annual sediment loads (figs. 41–44) have the same temporal pattern of change as observed (regressed) annual loads, but show less range of variation. The difference between simulated and observed (regressed) loads in 1996 is due primarily to a storm on January 19 that had a daily

Table 25. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, calibration period water years 1991 through 2000, calibrated model, South River, Virginia.

[mg/L, milligrams per liter; %, percent]

		Criterion (percent)	South River near Waynesboro (01626000)			South River at Harriston (01627500)		
			Observed (Regressed)	Simulated	% Error	Observed (Regressed)	Simulated	% Error
Suspended sediment concentration (mg/L)	90th percentile	±30	29.4	26.1	–11.4	30.3	33.2	9.5
	50th percentile	±30	6.6	6.5	–1.2	6.8	7.5	9.7
Sediment load (tons)	Total	±10	125,500	125,000	–0.2	231,700	224,300	–3.2
	Top 10%	±30	113,600	116,100	2.2	212,600	204,500	–3.8
	Lowest 50%	±30	1,000	1,200	15.7	2,100	2,600	26.6

Table 26. Comparison of simulated and observed (regressed) daily sediment concentrations and loads, verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia.

[mg/L, milligrams per liter; %, percent]

		Criterion (percent)	South River near Waynesboro (01626000)			South River at Harriston (01627500)		
			Observed (Regressed)	Simulated	% Error	Observed (Regressed)	Simulated	% Error
Suspended sediment concentration (mg/L)	90th percentile	±30	23.7	23.9	0.8	24.5	25.7	4.8
	50th percentile	±30	7.8	4.1	–46.5	7.6	5.5	–28.5
Sediment load (tons)	Total	±10	19,100	18,100	–5.5	29,900	32,800	9.8
	Top 10%	±30	16,800	16.600	–1.1	26,300	29,800	13.4
	Lowest 50%	±30	300	200	–16.9	500	500	–13.5

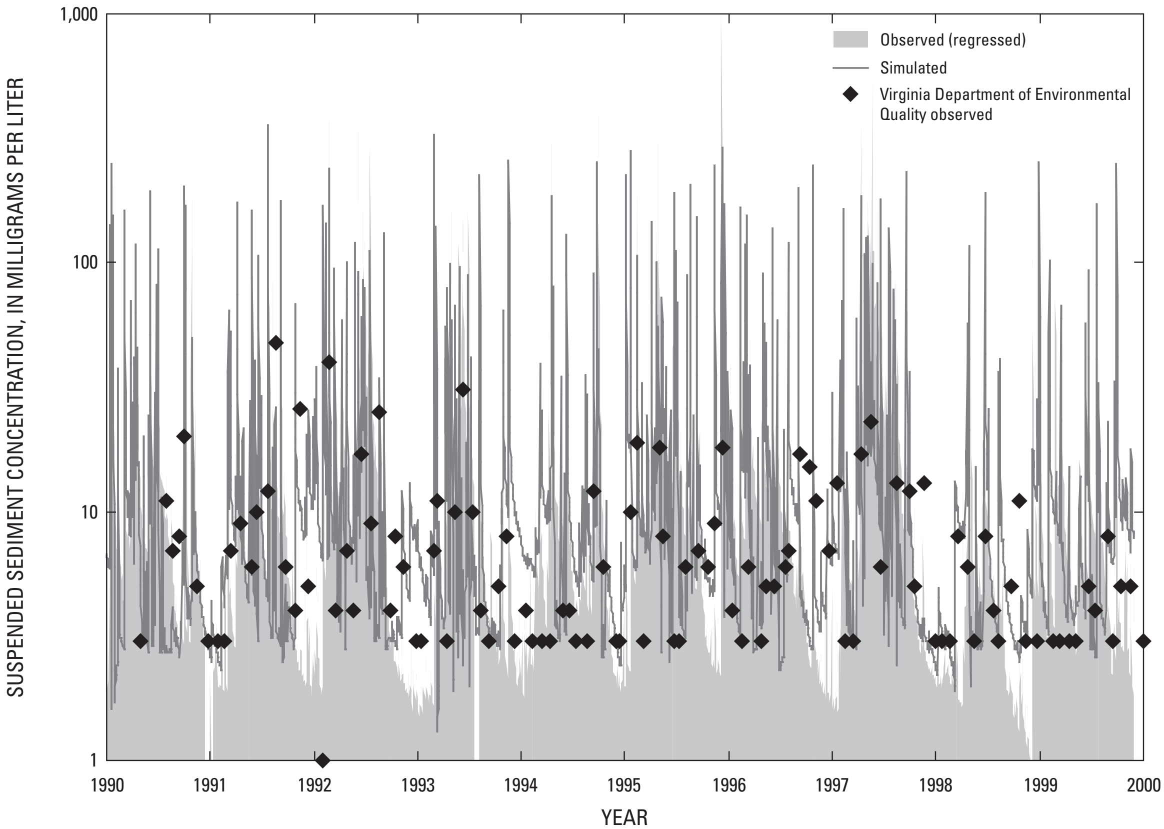


Figure 37. Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the calibration period, water years 1991–2000, South River near Waynesboro, Virginia (USGS station number 01626000).

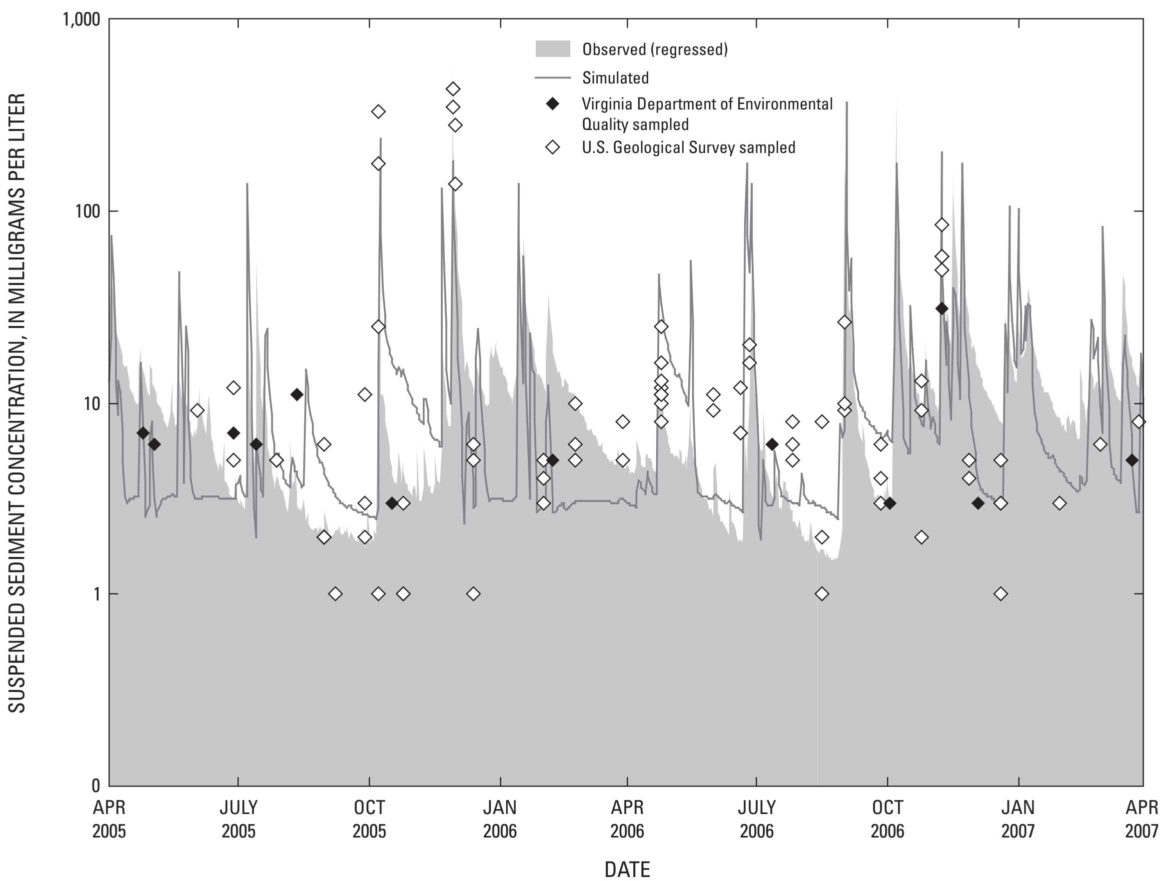


Figure 38. Simulated daily, observed (regressed), and sampled suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

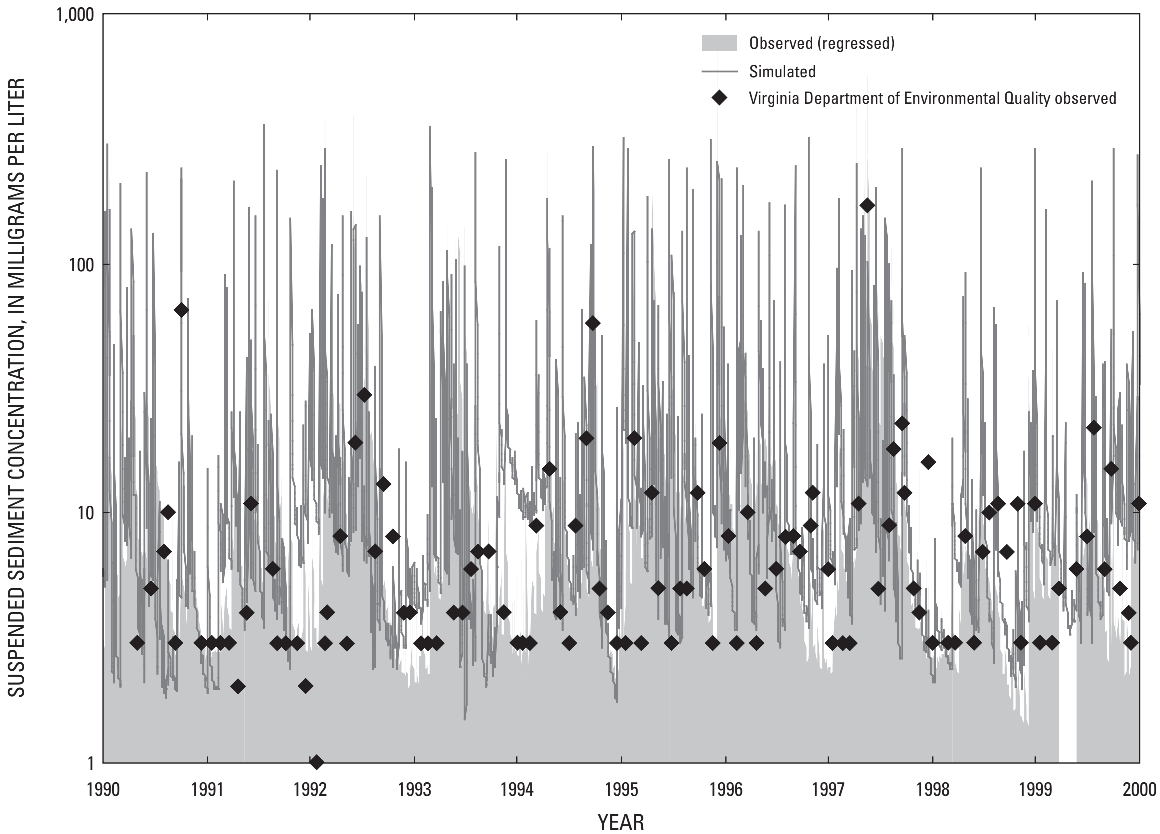


Figure 39. Simulated and observed (regressed) suspended sediment concentrations for the calibration period water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

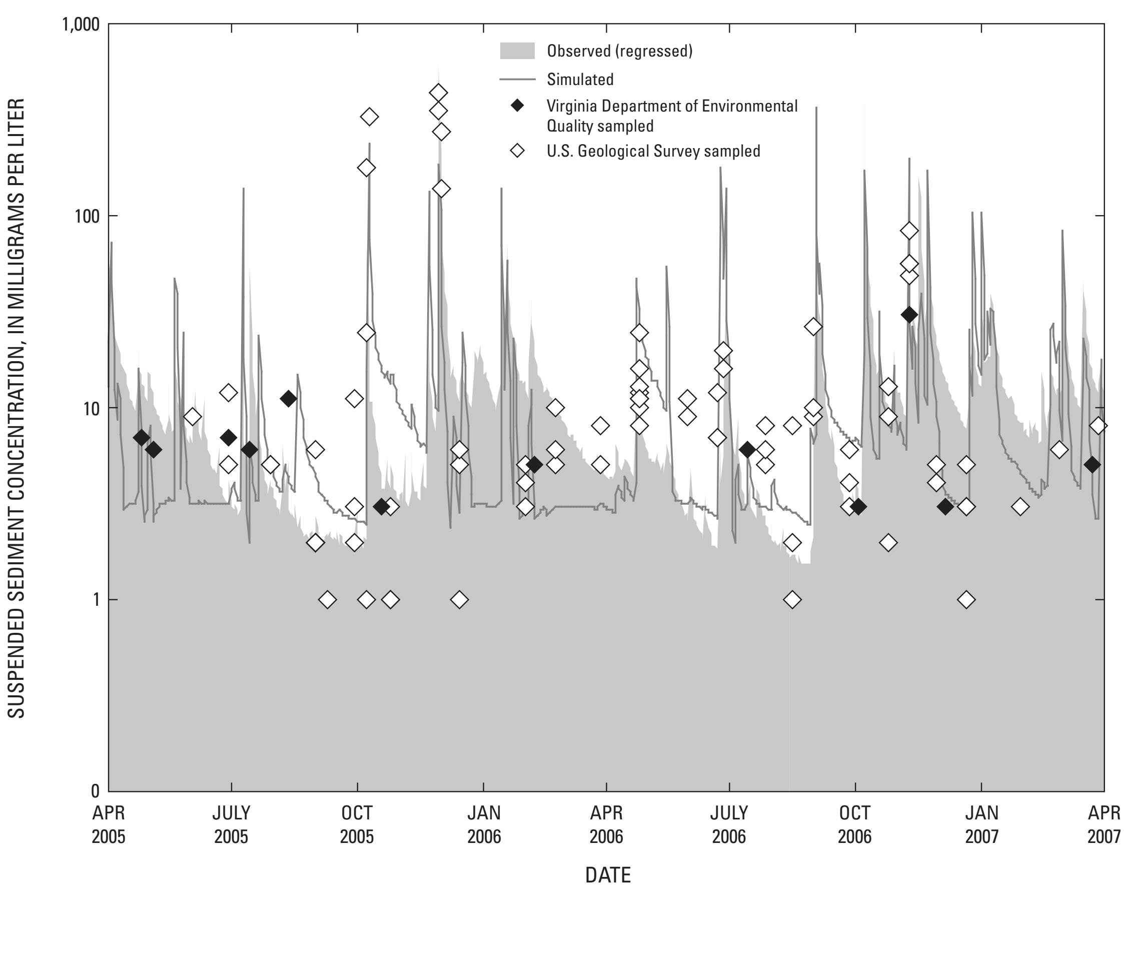


Figure 40. Simulated and observed (regressed) suspended sediment concentrations for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

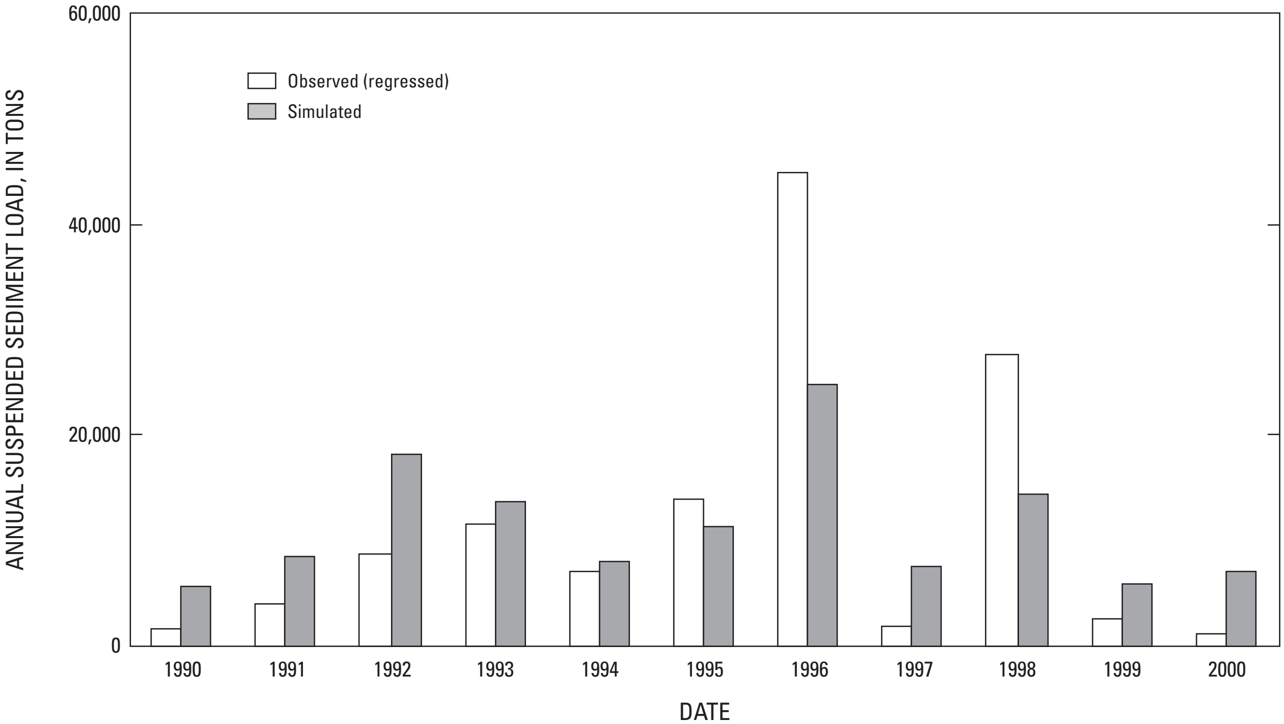


Figure 41. Annual simulated and observed (regressed) suspended sediment loads for the calibration period water years 1991–2000, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

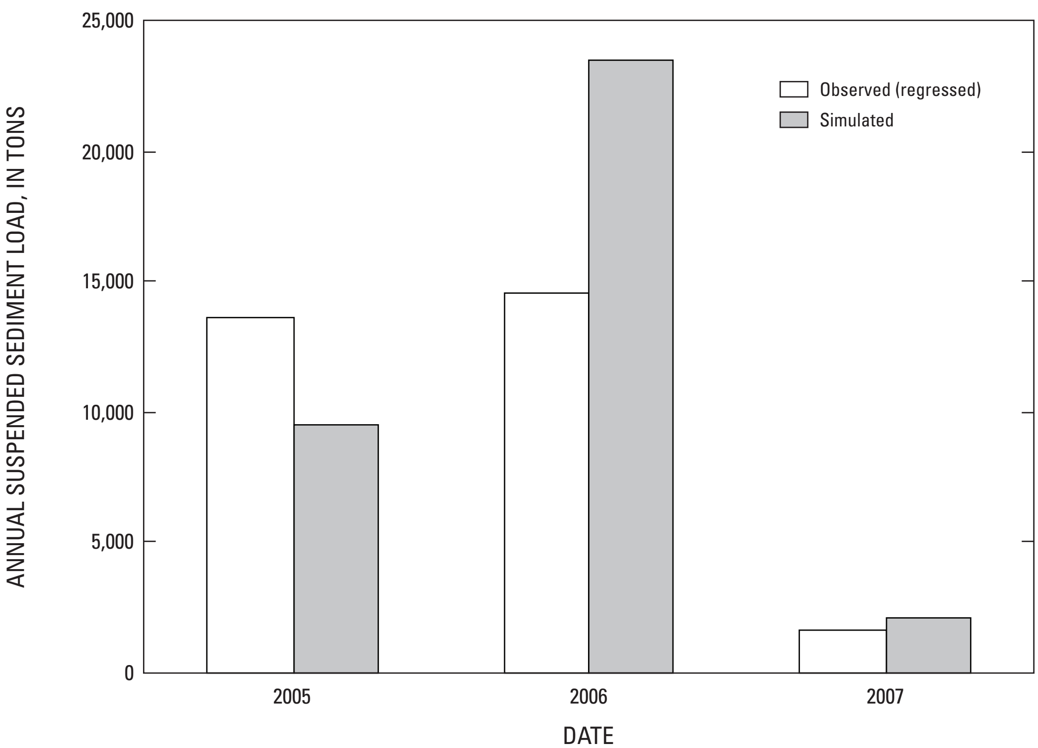


Figure 42. Annual simulated and observed (regressed) suspended sediment loads for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River near Waynesboro, Virginia (USGS station number 01626000).

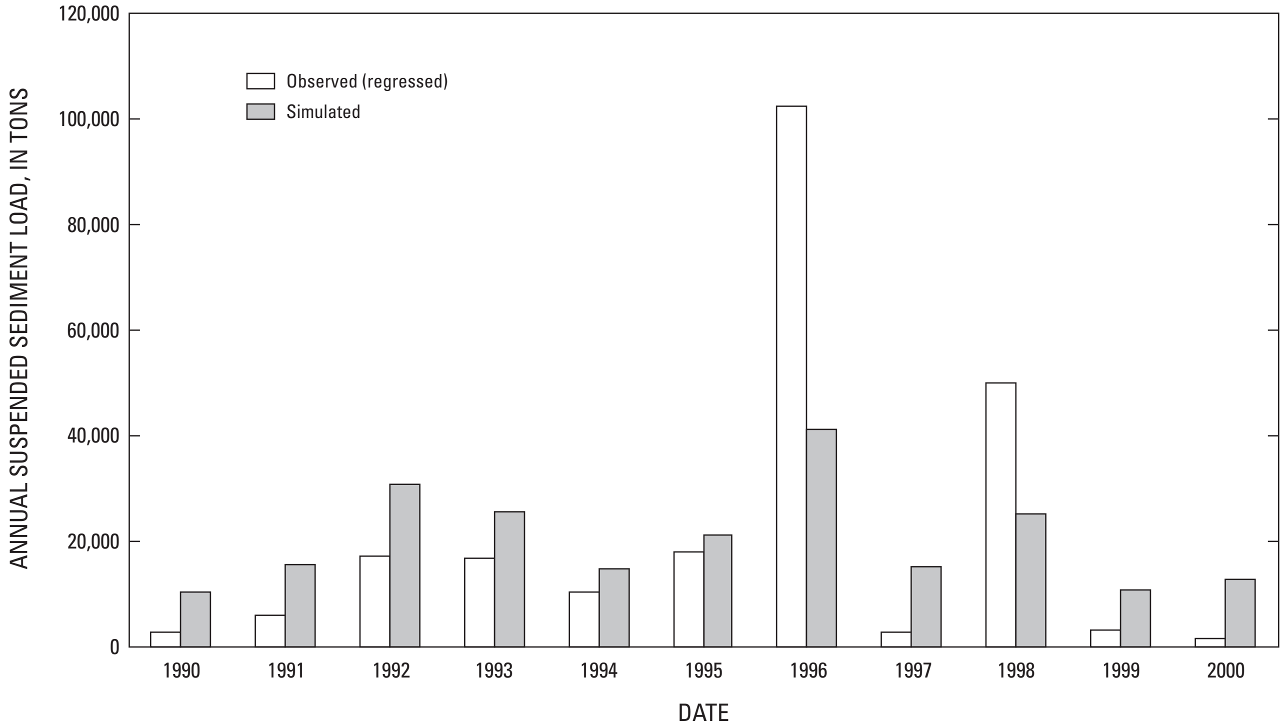


Figure 43. Annual simulated and observed (regressed) suspended sediment loads for the calibration period, water years 1991–2000, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

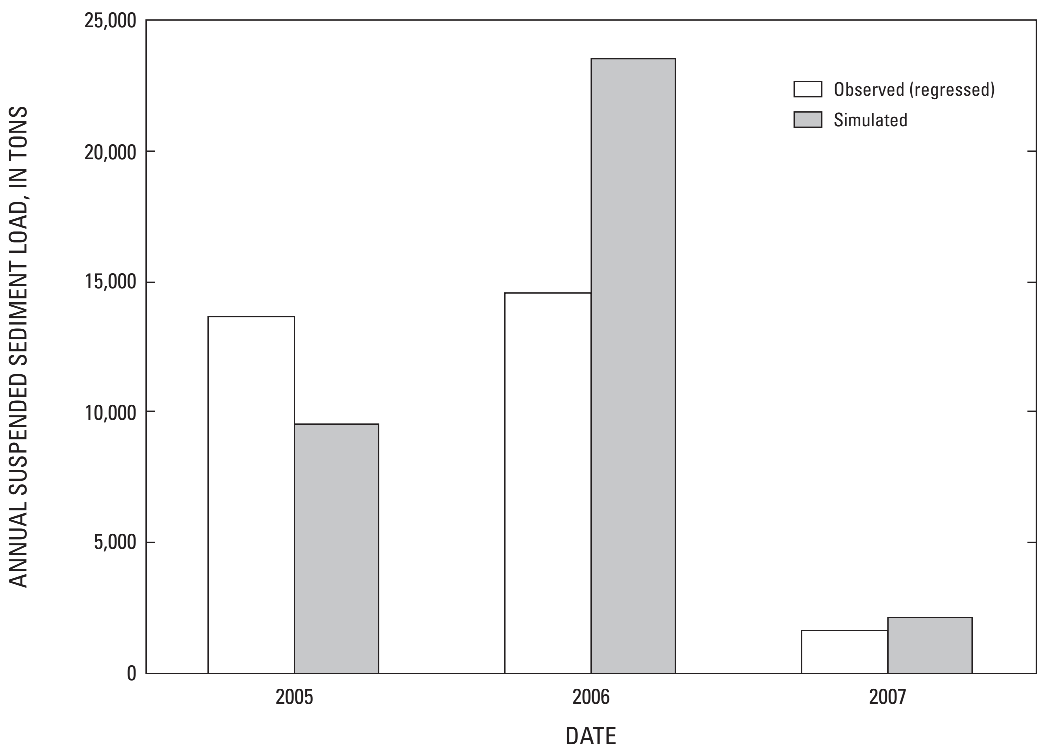


Figure 44. Annual simulated and observed (regressed) suspended sediment loads for the verification period, April 1, 2005, through March 31, 2007, calibrated model, South River at Harriston, Virginia (USGS station number 01627500).

observed (regressed) load of 40,400 tons but a simulated load of only 1,600 tons (figs. 41 and 43). Streamflow also was undersimulated for this storm in both cases due to differences between modeled and actual precipitation. Similarly, the difference between simulated and observed (regressed) loads in 1998 occurred primarily during two February storms in which streamflow, and therefore sediment load, were undersimulated. Sediment transport is dominated by infrequent high-flow events, and individual storms can have a large effect on annual sediment loads.

The mean observed (regressed) annual sediment load from 1991 through 2000 at monitoring station 01627500 is 23,170 tons/yr (tons per year). This compares to an annual mean load calculated in the Pizzuto and others (2006) study of 10,100 tons at the same location for the period 1967 through 2003 using different estimation methods. Both the Pizzuto load estimate and the "observed" load estimate calculated for this study are subject to considerable uncertainty. The uncertainty in simulated loads results from uncertainty in the suspended sediment concentration regression, sampling errors propagating through the calibration, uncertainty in flow estimates, use of daily average rather than instantaneous flow values, and the inherent uncertainty of representing low frequency high load events based on periodic data and linear estimation methods.

Sediment results for the calibrated model during the calibration and verification periods are shown in tables 25 and 26. Simulated loads are comparable to those reported in other studies of Chesapeake Bay watersheds (Langland and others, 2003; Phillips, 2007).

Duration plots for simulated and observed (regressed) suspended sediment concentrations are shown in figure 45 for the calibration period and in figure 46 for the verification period. Duration plots are comparable to cumulative distribution functions and express the percent of time that a variable (suspended sediment concentration in this case) exceeds a given value. The simulated and observed (regressed) suspended sediment concentration duration plots are visually similar at both the Waynesboro and Harriston monitoring stations.

Mercury Transport Model Calibration Results

The mercury transport component of the South River watershed model was calibrated by adjusting parameters so that hourly simulated total mercury concentrations match observed concentrations in grab samples from the river. Unlike water and sediment, there are no continuous time series of observed mercury concentrations to use as a calibration goal. Calibration of mercury transport also differed from water

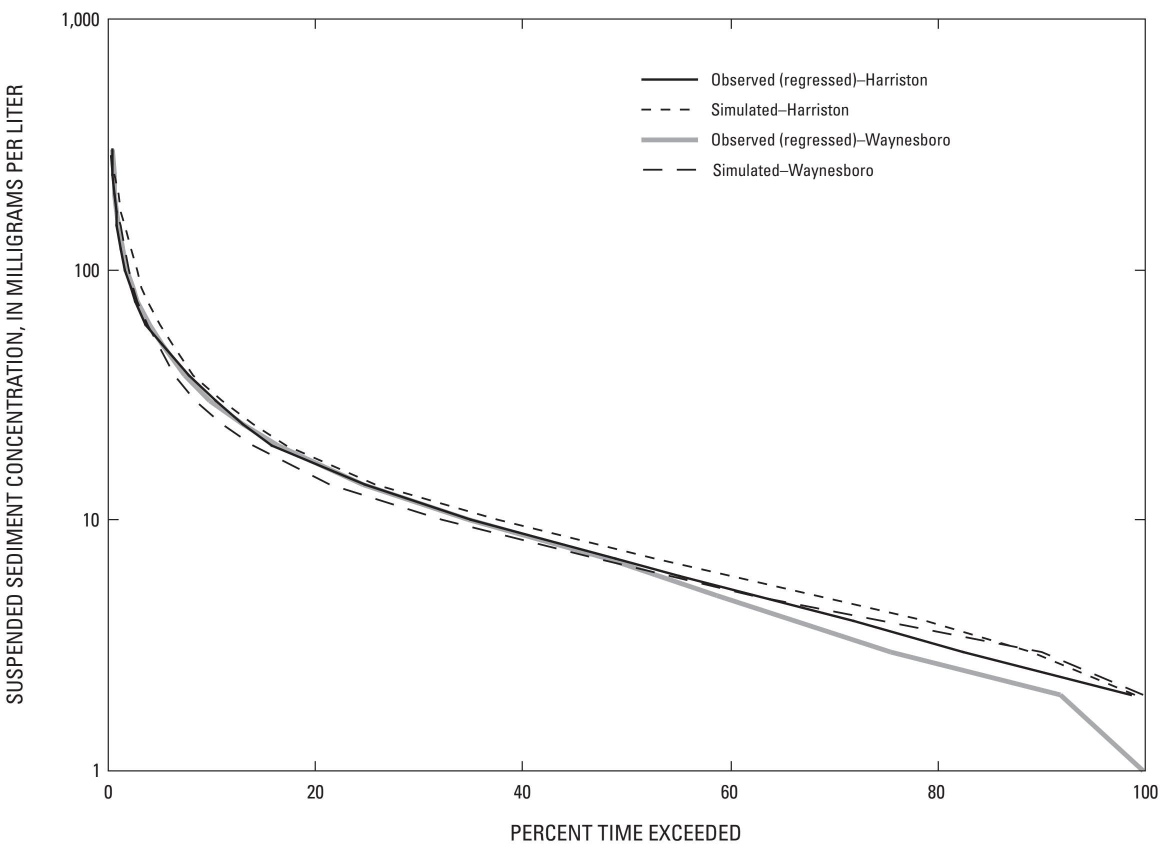


Figure 45. Duration plots for simulated and observed (regressed) daily suspended sediment concentrations, calibration period water years 1991–2000, calibrated model, South River, Virginia.

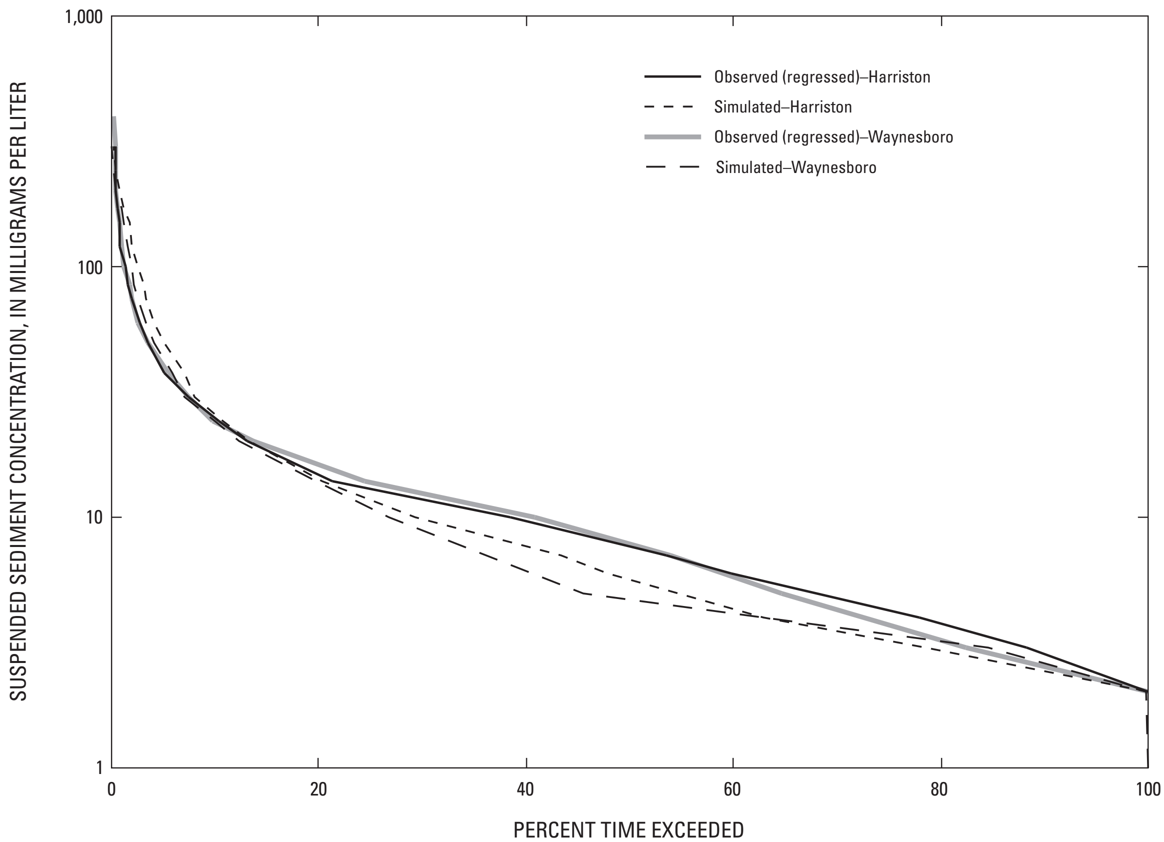


Figure 46. Duration plots for simulated and observed (regressed) daily suspended sediment concentration for the verification period April 1, 2005, through March 31, 2007, calibrated model, South River, Virginia.

and sediment in that it used a 1-year calibration period, from April 1, 2005, through March 31, 2006, and a 1-year verification period, from April 1, 2006, through March 31, 2007. Three monitoring sites were used for calibration—01626000 (Waynesboro), 01626920 (Dooms), and 01627500 (Harriston). As with sediment calibration, USGS mercury concentration data were used for quantitative comparison to simulated results, and data from the VDEQ were used for additional visual checks.

Although the calibration process compared observed and simulated concentrations, these values have somewhat different characters. Hourly simulated concentrations represent average conditions in a river reach over a 1-hour period and do not capture variability occurring within a reach or at time intervals less than 1 hour. Observed THG concentration values represent instantaneous vertically averaged conditions at the centroid of flow at a single point along the river. In the actual river, there likely is substantial variation of THG concentrations within a reach and within an hour time span, therefore simulated concentrations are not expected to match observed concentrations exactly. Instead, the goal was to recreate observed THG statistics and spatial and temporal patterns.

Initial calibration efforts indicated that downstream from the plant site, the model had insufficient sources of mercury to the river during stormflow recession periods and during other times of declining streamflow when there was no surface runoff. This was true despite the fact that hydrology and sediment transport were well calibrated, incorporating all explicitly known mercury sources, and using assigned model input mercury concentrations that matched observed values. Results from an example simulation with sediment runoff mercury adjusted to match storm peak values are shown in figure 47. When mercury on runoff sediment was assigned unrealistically high concentrations, simulated THG values could be raised to match observed values at the low end, but then simulated high end values were much too high.

To calibrate the mercury model, an additional mercury source was added to the model to mimic channel margin inputs of mercury to the river, as discussed in the earlier section of this report describing the mercury transport model. Channel margin mercury loads are linked to groundwater discharge (AGWO) and interflow (IFWO), and therefore occur during low and moderate flow and during periods of no surface runoff. The coefficients multiplied into IFWO and AGWO time series were adjusted during calibration to match simulated to observed THG concentrations. No channel margin inputs were used for model river reach 1 because they were not needed to achieve good calibration, and because model river reach 1 is upstream from the historic mercury source.

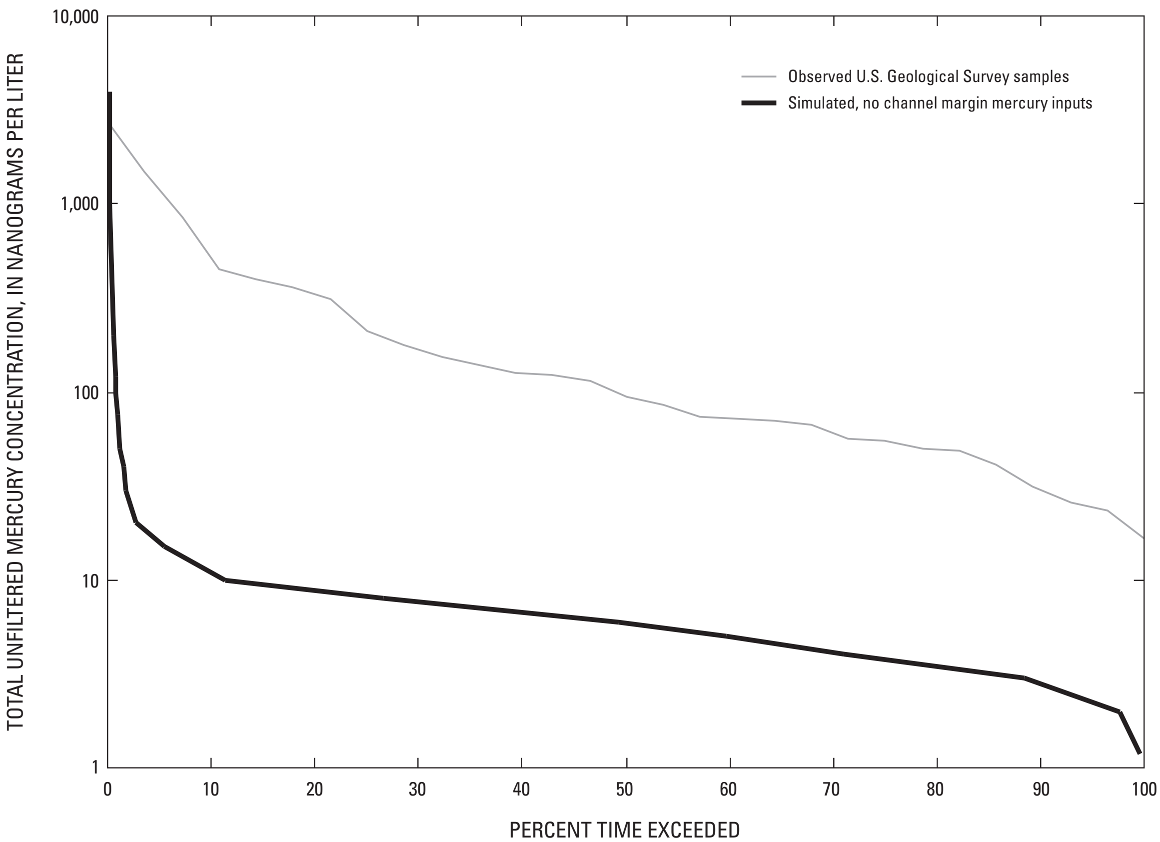


Figure 47. Simulated and observed (USGS samples only) total unfiltered mercury concentration distributions showing poor calibration obtained with no channel margin inputs, simulation period April 1, 2005, through March 31, 2007, South River at Dooms, Virginia (USGS station number 01626920).

Final calibrated concentrations for mercury sources to the river are shown in table 27. These concentrations are within the range of observed concentrations. Although there are no observations of interflow (THG_F), the calibrated value of 10.0 ng/L is reasonable because interflow is conceived as precipitation traveling through the shallow subsurface for a few days or less before discharging to the river. Therefore it is expected that interflow would have a THG_F concentration between that of groundwater and precipitation (0.07 ng/L and 21.8 ng/L), respectively.

With the channel margin inputs added to the model, it was possible to successfully calibrate the model to match observed THG concentrations in the river. The time series of calibrated THG values are shown in figures 48*A*–*C* for the Waynesboro, Dooms, and Harriston stations, respectively. For all three monitoring stations, the model produces reasonably accurate simulations of water column THG concentrations. Simulated THG concentrations from the calibrated model have a slightly wider range than observed concentrations because grab samples are unlikely to capture the very highest and lowest concentrations. Simulated high concentrations during storm events agree well with observed storm sample concentrations in figures 48*A*–*C*.

Table 27. Input mercury concentrations to the calibrated watershed model.

[THG_F, aqueous filterable total mercury; THG_{SS}, total mercury on solids suspended in water; ng/L, nanograms per liter; µg/g, micrograms per gram]

Mercury source and hydrologic response unit type	Calibrated model concentration value
Groundwater THG_F concentrations (ng/L)	
Uncontaminated pervious land areas	0.7
Contaminated flood-plain areas	2.9
Interflow THG_F concentrations (ng/L)	
Uncontaminated pervious land areas	10.0
Contaminated flood-plain areas	10.0 to 16.7
Precipitation THG_F concentrations (ng/L)	21.8
Runoff sediment associated mercury THG_{SS} concentrations (µg/g)	
Uncontaminated pervious land areas	0.061
Contaminated flood-plain areas	7.6 to 16.7

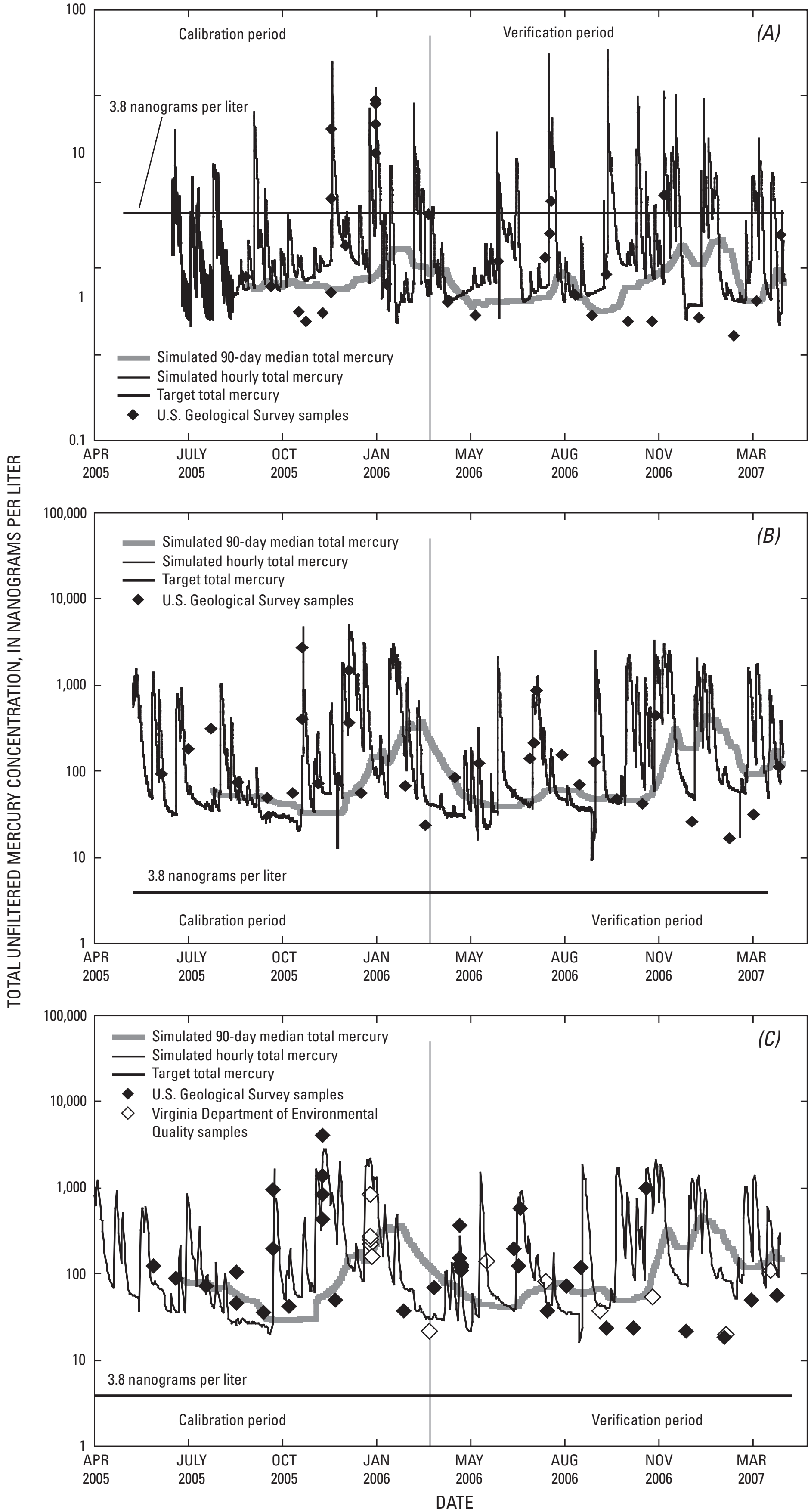


Figure 48. Simulated total unfiltered mercury concentration time series and observed concentrations, calibrated model, existing conditions, April 2005 through March 2007, *(A)* South River near Waynesboro, Virginia (USGS station number 01626000), *(B)* South River at Dooms, Virginia (USGS station number 01626920), and *(C)* South River at Harriston, Virginia (USGS station number 01627500).

Simulated mercury concentration values do not match all observed values, however. These discrepancies may result from a variety of factors including errors in the sediment or hydrologic components of the model, errors in mercury component input or parameterization, or real world variability at scales below model discretization. During periods of extended low flow, when THG concentrations are low, the simulated hourly THG concentrations for both Waynesboro and Harriston (figs. 48*A* and 48*C*) exhibit spurious numerical oscillations. These oscillations have an hourly period driven by a corresponding oscillation in suspended sediment concentration. As a result of numerical dispersion and(or) rounding errors, the model at each hourly time step alternately deposits or resuspends a large percentage of the suspended sediment that is present in the water column. Most mercury in the water column is attached to sediment, and this causes the total water column mercury concentrations to oscillate as well. This is clearly a numerical artifact of the model simulation and was not observed in South River sample data. These oscillations do not affect the mass balance of total mercury at periods of a day or more, and do not significantly affect the TMDL calculations because the 1-hour oscillation period is much shorter than the 90-day averaging period used to determine the TMDL.

Statistics for simulated THG concentrations from the calibrated model and for USGS observed concentrations at the three primary South River monitoring stations are listed in table 28. Results for the calibration and verification periods have been combined to produce the statistics in table 28. Simulated mercury statistics closely approximate observed mercury statistics. Undersimulation of the 90th-percentile THG concentration value at Waynesboro is at least partially the result of multiple storm samples being collected at that monitoring station in October and November 2005 (fig. 48*A*), causing bias in the sample population towards the high end. Similarly at Dooms, where a smaller percentage of storm samples were collected, the 90th-percentile value is oversimulated (fig. 48*B*).

Duration plots for simulated and observed (USGS samples only) mercury concentrations are shown in figures 49*A*–*C* for the Waynesboro, Dooms, and Harriston stations. Curves for the simulated THG duration show a reasonable match to observed duration curves at all three monitoring stations.

Simulated mercury loads to the river are listed by source in table 29. Nonpoint sources account for 99.7 percent of the mercury load to the South River. The largest of the nonpoint sources are channel margin inputs, accounting for about 84 percent of all mercury entering the river. Runoff from land surfaces, primarily contaminated flood-plain areas, accounts for most of the rest. Point sources, groundwater discharge, interflow discharge, and precipitation on the river surface collectively account for less than 1 percent of the mercury load to the South River.

Table 28. Statistics for hourly simulated and observed total mercury concentrations, calibrated watershed model, South River, Virginia, calibration and verification periods combined, April 1, 2005, through March 31, 2007.

[Observed values from U.S. Geological Survey samples only; %, percent; ng/L, nanograms per liter; THG, total unfiltered mercury]

THG concentration (ng/L)	Waynesboro (01626000)			Dooms (01626920)			Harriston (01627500)		
	Observed	Simulated	% Error	Observed	Simulated	% Error	Observed	Simulated	% Error
90th percentile	14.9	7.1	–52	568.3	988.0	74	895.2	898.8	0.4
50th percentile	1.3	1.2	–9	103.6	69.6	–33	115.0	91.4	–21
10th percentile	0.7	0.7	–5	29.5	31.7	8	29.3	26.5	–10

Table 29. Simulated annual total mercury loads to the South River, calibrated model, existing conditions, April 1, 2005, through March 31, 2007.

[%, percent]

Reach	Total mercury (grams/year)						
	1	2	3	4	5	Total all reaches	
Point sources	1	608	0	0	41	650	(0.3%)
Direct precipitation to river	28	7	2	11	8	55	(0.0%)
Interflow discharge	382	46	48	151	41	667	(0.4%)
Groundwater discharge	54	8	7	24	6	99	(0.1%)
Runoff	573	144	3,998	21,205	3,316	29,237	(15.4%)
Channel margin inputs	0	59,179	82,742	14,551	2,241	158,713	(83.8%)
Totals	1,038 (1%)	59,992 (32%)	86,797 (46%)	35,942 (19%)	5,653 (3%)	189,421	(100%)

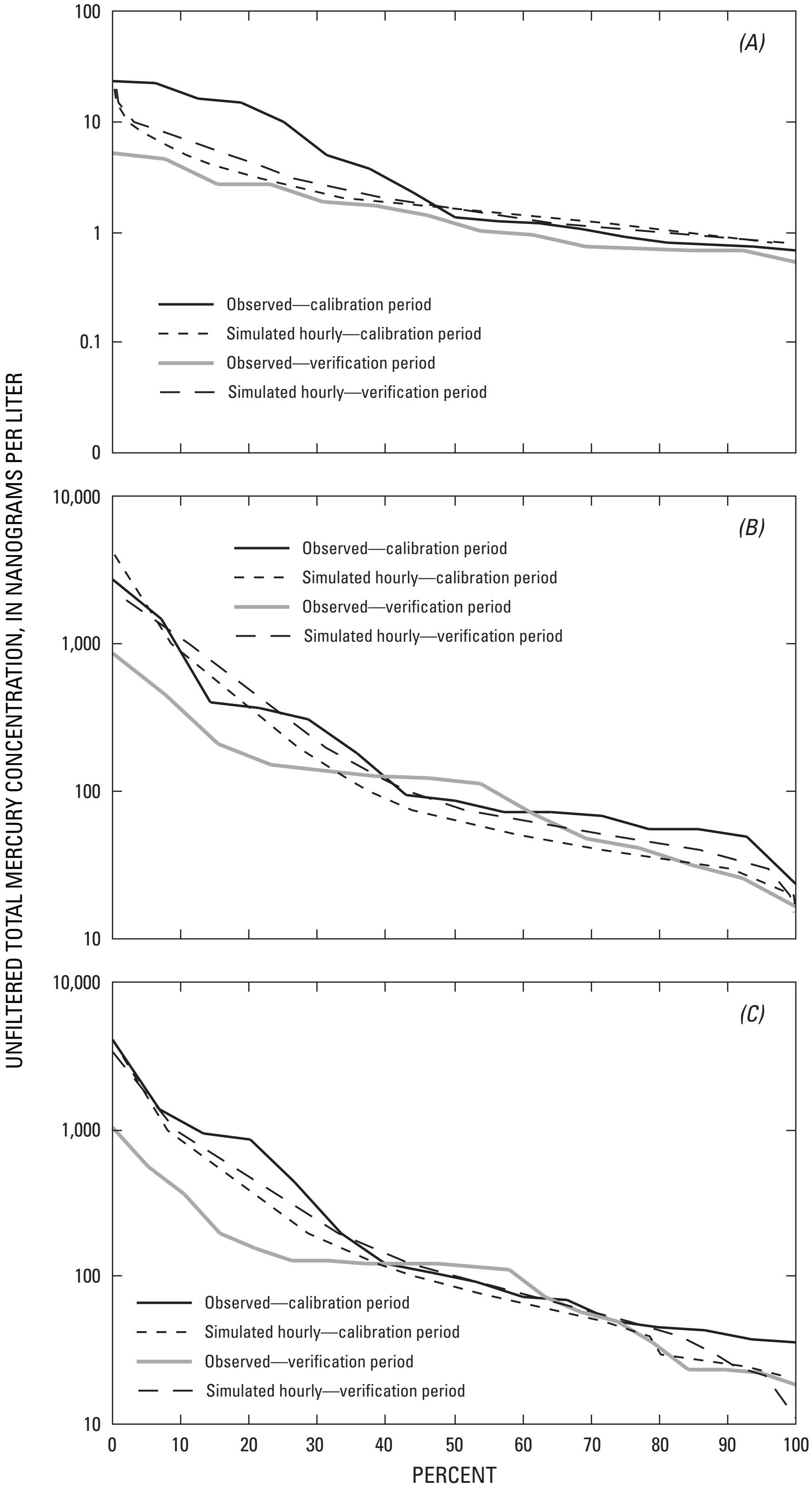


Figure 49. Duration curves for simulated and observed (USGS samples only) total unfiltered mercury concentrations, calibrated model, existing conditions, April 1, 2005, to March 31, 2007, South River *(A)* near Waynesboro, Virginia (USGS station number 01626000), *(B)* at Dooms, Virginia (USGS station number 0162920), and *(C)* at Harriston, Virginia (USGS station number 01627500).

Limitations of the South River Watershed Model and Suggestions for Future Investigations

A number of factors limit the accuracy of the HSPF South River model simulations. A primary factor is the spatial and temporal discretization within the model, particularly spatial discretization. Parameters such as water velocity, sediment depth, suspended sediment concentration, and mercury concentration exhibit a wide range of values over relatively small distances (less than 100 m) in the South River. The model treats all such variables as homogeneous within each river reach, however. Model reach lengths range from 1.5 to 24.6 mi. Temporal discretization is less of an issue because the model progresses in 1-hour time steps. During periods of flooding, however, and particularly at the beginning of a runoff event, hydrologic variations can be substantial from one hour to the next. There were not enough data to justify finer spatial discretization of the model. Collecting data at additional monitoring stations could provide the data needed for future calibration of the model at finer spatial scales.

A second limitation of the model is the exclusion of physical mechanisms that may be major controls on mercury transport. Although inputs of mercury from channel margin processes, such as bank collapse and erosion, make up more than 80 percent of the mercury load to the river in the calibrated model (table 29), these mercury inputs to the river are treated in the model as simple lumped parameter processes rather than explicit physical processes. Related to this limitation is the lack of data describing the magnitude and timing of these processes. Detailed studies of the timing and spatial extent of mercury release from channel margin sediments in response to changes in temperature, pH, and oxidative states could improve understanding of the channel margin mercury loading, for example. Ongoing studies are examining the effects of hyporheic flow and bank collapse on loading of mercury to the river. These and other future research efforts could improve the understanding of channel margin inputs of mercury and guide changes to the watershed model that could improve its accuracy and certainty in model output.

Deficiencies in model input data are an additional potential source of model error. Precipitation data are the primary hydrologic input to the model and have partially known errors, as previously discussed, that directly affect simulation results. Precipitation has spatial variation at scales smaller than the land-county segments used to assign precipitation time series. Additional precipitation data could reduce this uncertainty in the model. Because most observed mercury concentration values are high relative to background levels, model results are tied to relatively few calibration data at low concentrations. The model was designed to accurately simulate the full range of concentrations currently seen in the watershed, most of which are much greater than the TMDL target concentration of 3.8 ng/L. None of the samples collected downstream from the plant site in this study had THG concentrations below 13 ng/L. If more low concentration mercury data were available, perhaps after initial cleanup efforts, it could help reduce uncertainty associated with simulation of low mercury concentrations. This uncertainty is especially applicable to the TMDL Scenarios discussed later in this report, which examine potential clean-up efforts and their effects on THG concentrations in the river. Groundwater THG_F data are sparse, and the model value for THG_F concentrations in groundwater from contaminated pervious lands areas is assigned primarily on the basis of data from a single contaminated flood-plain area. Additional mercury concentration data for groundwater would be useful for reducing uncertainty in future modeling efforts.

Limitations that should be noted by both readers and model users are that the HSPF model in its current state relies heavily on data collected since 2004, and that data related to mercury loading to the river prior to 2004 are relatively sparse and generally not produced by low-level detection laboratory methods for measuring mercury concentrations. Before 2004, there were several early reports on fish tissue concentrations and sediment and soil concentrations, but there were few reliable and low-detection mercury concentration data for plant outfalls or the South River. Mercury sources to the river and mercury concentrations within the river may have changed significantly over the past 30 years, but the model does not reflect those changes due to insufficient data. This limitation does not apply to dates from 2004 to 2007, but should be considered if the model is used to simulate mercury transport during earlier time periods.

Simulation of Mercury Total Maximum Daily Load (TMDL)

Subsequent to calibration of the mercury transport component of the watershed model, the model was used to simulate a TMDL for mercury in the South, South Fork Shenandoah, and Shenandoah Rivers. The TMDL value is set at a level to ensure that mercury loads from point sources and nonpoint sources can be assimilated without exceeding the criterion of 0.3 mg/kg methylmercury in fish tissue. Allocations from point sources, nonpoint sources, and natural background sources are included in the TMDL. The South River TMDL includes an implicit margin of safety to account for uncertainties in calculation of the TMDL. The South River was analyzed in detail and results were then extrapolated downstream to determine a TMDL for both the South Fork Shenandoah and Shenandoah Rivers.

Designation of Endpoints

The South River model links the identified sources of mercury to water column concentrations of total mercury (THG). An empirical bioaccumulation model then relates THG concentrations to fish tissue concentrations. The watershed model, in conjunction with the bioaccumulation model, provides the basis for estimating the total assimilative capacity of the river and any needed load reductions (Virginia Department of Environmental Quality, 2008b). The mercury TMDL for the South River is then determined as a mercury loading rate that is consistent with the endpoint fish tissue methylmercury concentration of 0.3 mg/kg.

Numeric endpoint water column total mercury concentration values were determined by the VDEQ based on the 0.3 mg/kg fish tissue methylmercury level and the empirical bioaccumulation model (table 30). These target concentrations were used to evaluate attainment of acceptable water quality and represent water-quality goals that will be targeted through load-reduction scenarios. The target concentrations decrease downstream to account for variations in fish size and natural variability of bioaccumulation rates in the Shenandoah river system.

For each modeled river reach, simulated total mercury concentrations were compared to target concentrations to determine whether a violation had occurred. Simulated 90-day median THG concentrations were used in the comparison. On a daily basis, simulated 90-day median THG concentrations were compared to target concentrations for each river. If for that day, the median total mercury concentration for the preceding 90-day period was higher than the target concentration, then a violation had occurred.

Existing Conditions

The calibrated South River watershed model was run with a simulation period of April 1, 2005, through March 31, 2007, to simulate existing conditions in the South River. When 90-day median THG concentrations are below target endpoint concentrations (table 30), fish are protected from tissue mercury concentrations above 0.3 mg/kg. If 90-day median THG concentrations exceed target concentrations then fish are expected to have tissue mercury concentrations in excess of 0.3 mg/kg. Table 31 shows median hourly total mercury concentrations for the entire period, April 1, 2005, through March 31, 2007 (730 days).

Under existing conditions, median mercury concentrations in the South River are below the target concentration of 3.8 ng/L only at the Waynesboro monitoring station, upstream from the plant site. Below the plant site, median THG concentrations exceed target concentrations by a factor of 5 or more (table 31). Rolling 90-day median THG simulated concentrations from the calibrated model under existing conditions are shown in figures 48*A–C*. At the Waynesboro monitoring station, 90-day median THG concentrations are always below the target concentration of 3.8 ng/L, whereas, at Dooms and Harriston, 90-day median THG concentrations are always far above it.

Simulated mercury loads in the South River under existing conditions are summarized in table 32. Mercury loads increase dramatically below the plant site (in reach 2) as a result of a variety of point and nonpoint source inputs. The annual mercury load of 189 kg/yr at Port Republic can be compared to the estimated 109 kg/yr of mercury loading due to bank retreat estimated by Rhoades and others (2009). Although the time period for the simulations (2005 through 2007) is shorter than the averaging period (1937 through 2006) used by Rhoades and others (2009), it is noteworthy that the two values are relatively close and the total simulated load is higher than the estimated load resulting solely from bank retreat.

The results indicate that, as expected, mercury loads to the river increase dramatically in model river reach 2, which contains the plant site. Mercury attributable to releases from the plant site, including legacy mercury entering the river through channel margin inputs and contaminated runoff sediment, increases the total load of mercury to the river by a factor of more than 100 when compared to background conditions. The relative percentage of different mercury loads also changes, as shown in figure 50. Upstream from the plant site, most mercury is loaded to the river through interflow or runoff of sediment at background THG_{Sed} concentrations, whereas downstream from the plant site, channel margin inputs dominate mercury loads.

Table 30. Target total mercury water column concentrations for rivers in the study.

[g, grams; ng/L, nanograms per liter; THG, total unfiltered mercury]

Water body	Normalized fish size (g)	Target water column THG concentration (ng/L)
South River	218	3.8
South Fork Shenandoah River	253	3.2
Shenandoah River	321	2.5

Table 31. Simulated total mercury concentrations for the South River, Virginia, existing conditions, median hourly concentrations for the period April 1, 2005, through March 31, 2007.

[– indicates upstream; ng/L, nanograms per liter]

Model river reach	Reach end node	Miles downstream from plant site	THG concentration (ng/L) simulated median
1	01626000	–2.8	1.2
2	01626850	2.3	21.7
3	01626920	5.3	69.6
4	01627500	16.5	91.4
5	Port Republic	24.0	93.4

Table 32. Simulated annual mercury loads by reach in the South River, existing conditions, April 1, 2005, through March 31, 2007.

[– indicates upstream; USGS, U.S. Geological Survey; kg/yr, kilograms per year]

Model river reach	Endpoint	USGS station ID	Miles downstream from plant site	Total HG load (kg/yr)
1	Waynesboro	01626000	–2.8	1.0
2	Hopeman Parkway	01626850	2.3	61.0
3	Dooms	01626920	5.3	147.8
4	Harriston	01627500	16.5	183.8
5	Port Republic	None	24	189.4

Table 33. Mercury loading rates to watersheds and subwatersheds by model reach, calibrated model, existing conditions, South River, Virginia, April 1, 2005, through March 31, 2007.

[g/yr, grams per year; g/acre/yr, grams per acre per year]

	Model river reach				
	1	2	3	4	5
Reach subwatershed					
Subwatershed area (acres)	81,468	13,651	10,129	30,704	14,525
Reach-specific mercury loading rate (g/yr)	1,038	59,992	86,797	35,942	5,653
Reach-specific unit mercury loading rate (g/acre/yr)	0.013	4.395	8.569	1.171	0.389
Total upstream watershed					
Total upstream area (acres)	81,468	95,119	105,248	135,952	150,477
Total watershed Hg loading rate (g/yr)	1,038	61,030	147,827	183,768	189,421

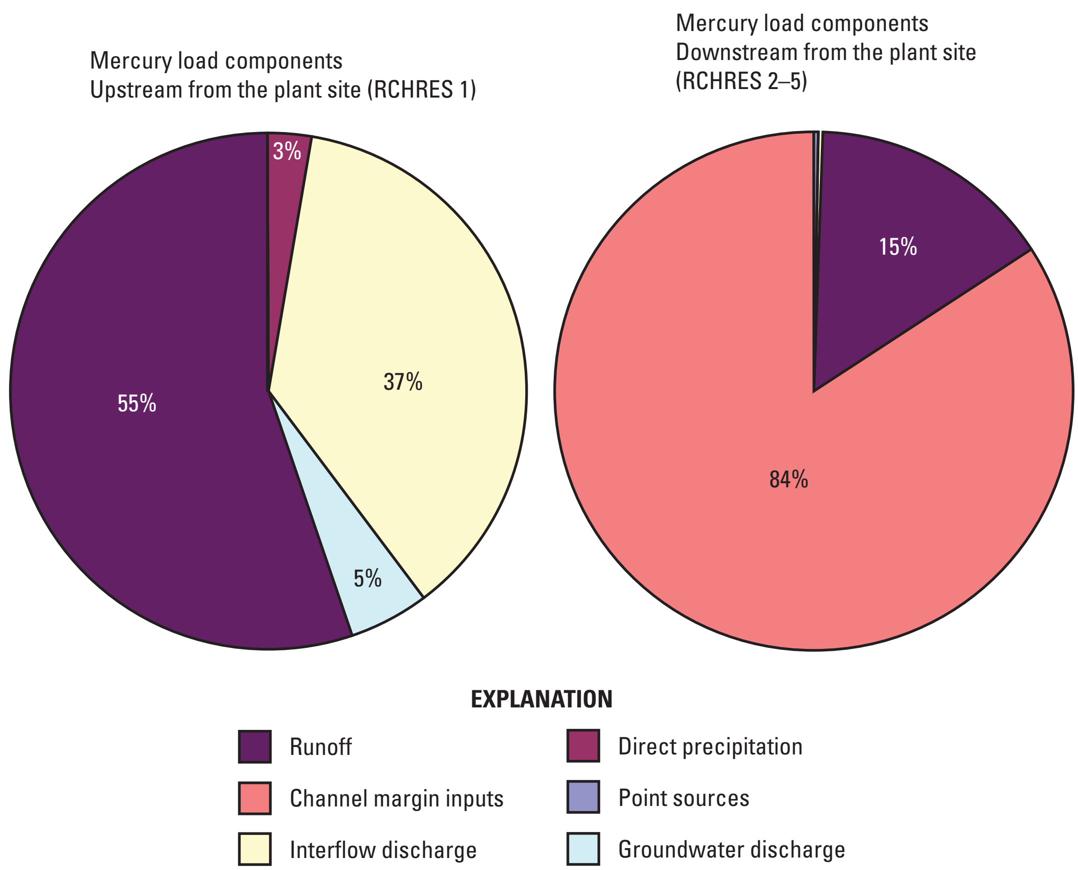


Figure 50. Percent mercury loading to the South River from sources upstream (model reach 1) and downstream (model reaches 2–5) from the plant site, calibrated model, existing conditions.

Scenarios for Mercury Load Reductions

Simulated loads to the river were modified to determine how water column THG concentrations would respond. Mercury loads were increased or decreased to simulate possible future scenarios, as shown in table 34. Scenario 1, “existing conditions,” is discussed in the previous section.

Future Conditions

Under Scenario 2, future conditions are simulated by increasing permitted point-source flows to limits set by current (2007) discharge permits. These “future conditions” are comparable to “build-out” scenarios used in other TMDL studies (Interstate Commission on the Potomac River Basin, 2004). Flow rates are increased to maximum permitted values, but concentrations of mercury are not changed, reflecting that current permits do not specify maximum concentrations. Under future conditions, Invista outfall 011 is assumed to discharge directly to the South River under monthly average flow rates. Since 2002, flow from outfall 011 has actually been routed through the Invista wastewater treatment plant, but under the current discharge permit, it is allowed to flow directly to the river. It is also assumed that THG_F concentrations in precipitation will decline by 19 percent (from 21.8 to 17.6 ng/L) as a result of USEPA’s Clean Air Interstate Rule and the Clean Air Mercury Rule (Alex Barron, Virginia Department of Environmental Quality, written commun., 2008), and that interflow THG_F concentrations will therefore also decrease by 19 percent. These changes to point-source loads, atmospheric mercury deposition rates, and interflow mercury concentrations are included in Scenarios 2 through 4B.

The results of Scenario 2 show that “future conditions” cause higher median THG concentrations in all South River reaches, with the highest increase of 43 percent just below the plant site at Hopeman Parkway (table 35). These increases are due to the higher loads from Invista outfall 011 and the somewhat higher mercury loads from point sources that come with the assumption that maximum permitted flows are in effect. Simulated total mercury loads decrease slightly at the

Table 34. Mercury load-reduction simulation scenarios.

[THG_F, aqueous filterable mercury; ng/L, nanograms per liter]

Type	Scenario	Changes to mercury loading	
Existing conditions	1	All current mercury loads included.	
Future conditions	2	Point sources increased to maximum permitted discharge, outfall 011 added, precipitation and interflow concentrations reduced.	Precipitation, interflow, and spring flow THG_F concentrations reduced.
Single source reductions	3A	Point sources reduced to target stream concentrations.	
	3B	Channel margin inputs eliminated, point sources at maximum permitted.	
	3C	Runoff cleaned up to background conditions, point sources at maximum permitted.	
Multiple source reductions	4A	Channel margin loads eliminated and runoff cleaned to background conditions, point sources at max permitted.	
	4B	Additionally reduce point sources to 3.8 ng/L.	

Table 35. Changes in median simulated total mercury concentrations, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia.

[%, percent]

Model scenario	Waynesboro (01626000)	Hopeman Parkway (01626850)	Dooms (01626920)	Harriston (01627500)	Port Republic
1	Existing conditions				
2	7%	43%	13%	4%	2%
3A	7%	–14%	–11%	–9%	–10%
3B	7%	–51%	–77%	–85%	–86%
3C	7%	43%	9%	1%	0%
4A	7%	–52%	–78%	–87%	–88%
4B	34%	–94%	–97%	–97%	–98%

Waynesboro monitoring station and increase slightly at Hopeman Parkway (table 36). Mercury loads can decrease even though median mercury concentrations increase because loads are dominated by high flow periods whereas median concentrations are dominated by low flow periods. The violation of target concentrations in reaches 2–5 does not change under "future conditions." Simulated THG concentrations under future conditions at the Harriston monitoring station are shown in figure 51.

Table 36. Percentage change to in-stream total mercury loads, relative to existing conditions, April 1, 2005, through March 31, 2007, South River, Virginia.

[%, percent]

Model scenario	Waynesboro (01626000)	Hopeman Parkway (01626850)	Dooms (01626920)	Harriston (01627500)	Port Republic
1	---------------------- Existing conditions ----------------------				
2	–5.7%	0.1%	0.0%	0.0%	0.0%
3A	–5.9%	–0.9%	–0.4%	–0.3%	–0.3%
3B	–5.7%	–96.9%	–96.0%	–85.1%	–83.8%
3C	–7.2%	–0.1%	–2.7%	–13.5%	–14.8%
4A	–7.2%	–97.0%	–98.7%	–98.7%	–98.6%
4B	–5.6%	–99.6%	–99.9%	–99.7%	–99.9%

Single Source Reductions

Sources of mercury to the South River were reduced one at a time to determine the resulting changes in river mercury concentrations. Under Scenario 3A, point-source loads are lowered by setting point-source THG concentrations to the target THG concentration of 3.8 ng/L, while keeping flow rates at the maximum permitted rates used in the "future conditions" of Scenario 2. All point-source mercury concentrations are set to 3.8 ng/L in Scenario 3A. The only other change to mercury source loads under Scenario 3A, as compared to the existing conditions of Scenario 1, is the reduction of atmospheric mercury deposition and interflow THG_F concentrations as previously described. A comparison of the simulated THG values at the Harriston station (01627500) from Scenario 3A with those of Scenario 2 shows that reducing point source inputs lowers THG concentrations during low-flow periods (figs. 51–52). The results in table 36 indicate that point sources make a relatively small contribution to total loads. THG loads decrease by 6 percent at Waynesboro and decrease by less than 1 percent at reaches 2–5 downstream from the plant site. Point sources make a relatively larger contribution to median THG concentrations because median concentrations are more sensitive than loads to low THG concentrations (tables 35–36). Upstream from the plant site at Waynesboro, median concentrations increase by 7 percent, as they do under Scenario 2, and downstream from the plant site in reaches 2–5, median concentrations decrease

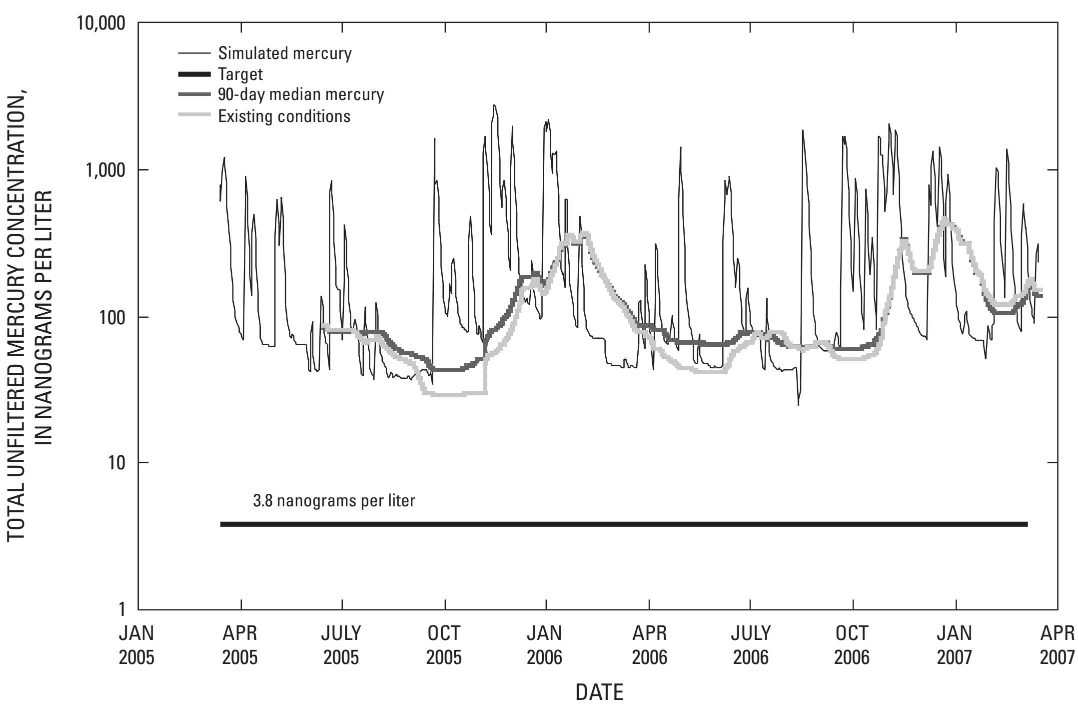


Figure 51. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions, Scenario 2. (Existing 90-day median simulated mercury concentrations shown for comparison.)

from 9–14 percent. Simulated THG concentrations for Scenario 3A at Harriston are shown in figure 52.

Under Scenario 3B, channel margin mercury loads are eliminated, simulating the potential future effects of remediation strategies focused on streambanks. Reduction of atmospheric mercury deposition and interflow THG_F concentrations to reflect expected future changes are also included. Point sources are restored to future conditions. The results of Scenario 3B show large declines in both mercury loads and concentrations downstream from the plant site (fig. 53 and tables 35–37). THG loads decline by 84 percent to 97 percent, and median THG concentrations decline from 51 percent to 86 percent in reaches 2–5 downstream from the plant site. Despite the large THG concentration declines, all downstream monitoring stations are still in violation of target concentrations 100 percent of the time. Simulated THG concentrations for Scenario 3B at Harriston are shown in figure 53.

Under Scenario 3C, mercury contaminated sediment runoff is cleaned to background conditions to simulate a hypothetical future remediation of South River flood plains. THG_{Sed} concentrations on sediment from contaminated flood-plain areas are reduced to THG_{Sed} concentrations of uncontaminated land areas. Reductions of atmospheric mercury deposition and interflow THG_F concentrations are again included. Point sources and channel margin inputs are restored to future conditions. Simulated THG concentrations from Scenario 3C at the Harriston monitoring station are shown in figure 54. With mercury contaminated runoff cleaned up, THG loads decrease from 0.1 percent to 14.8 percent at monitoring stations downstream from the plant site. Median THG concentrations under this scenario increase relative to existing conditions because point sources are assumed to have maximum permitted flows, which particularly increases mercury loads to the river during base-flow periods. Median THG concentrations increase by 43 percent at Hopeman Parkway, 9 percent at Dooms, and 1 percent at Harriston. All monitoring stations downstream from the plant site remain in violation of target THG values under this scenario.

Table 37. Percentage of time that simulated 90-day median total mercury concentrations exceed the 3.8 nanogram per liter target concentration, April 1, 2005, through March 31, 2007, South River, Virginia.

[%, percent]

Model scenario	Waynesboro (01626000)	Hopeman Parkway (01626850)	Dooms (01626920)	Harriston (01627500)	Port Republic
1	0%	100%	100%	100%	100%
2	0%	100%	100%	100%	100%
3A	0%	100%	100%	100%	100%
3B	0%	100%	100%	100%	100%
3C	0%	100%	100%	100%	100%
4A	0%	100%	100%	100%	100%
4B	0%	0%	0%	0%	0%

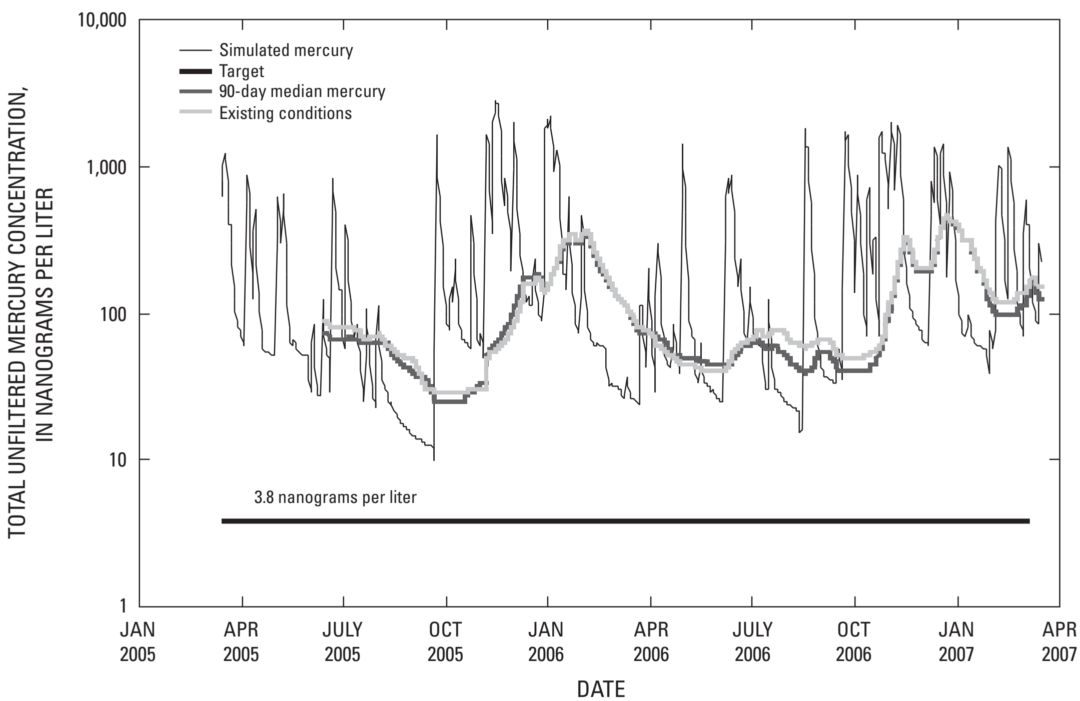


Figure 52. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with point sources cleaned up, Scenario 3A. (Existing 90-day median simulated mercury concentrations shown for comparison.)

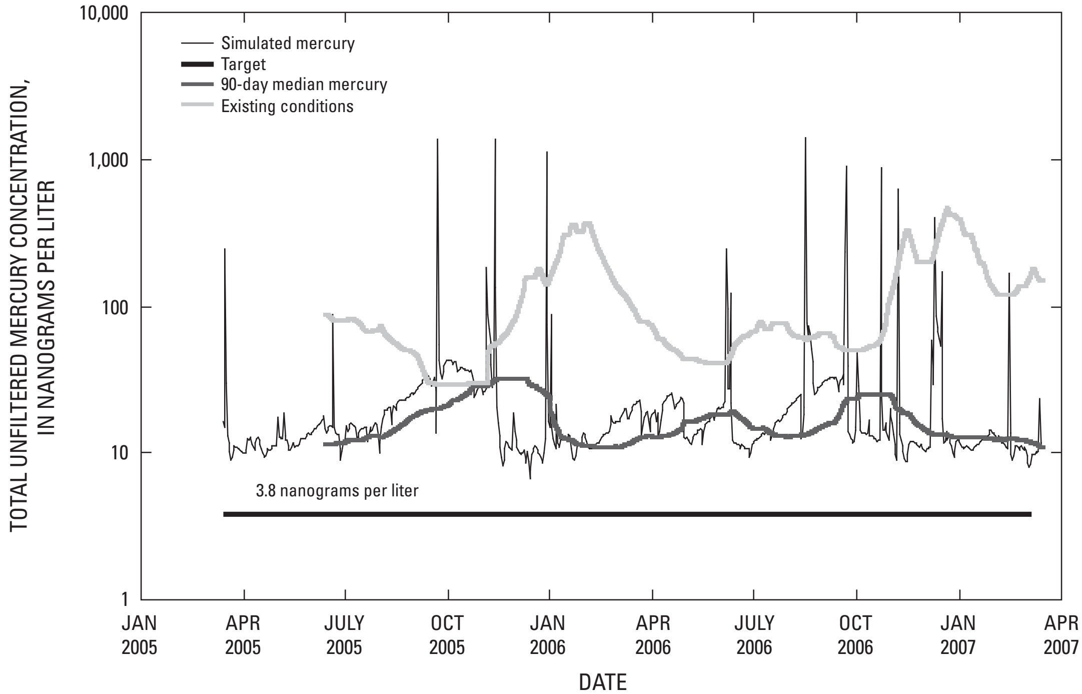


Figure 53. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with channel margin mercury sources cleaned up, Scenario 3B. (Existing 90-day median simulated mercury concentrations shown for comparison.)

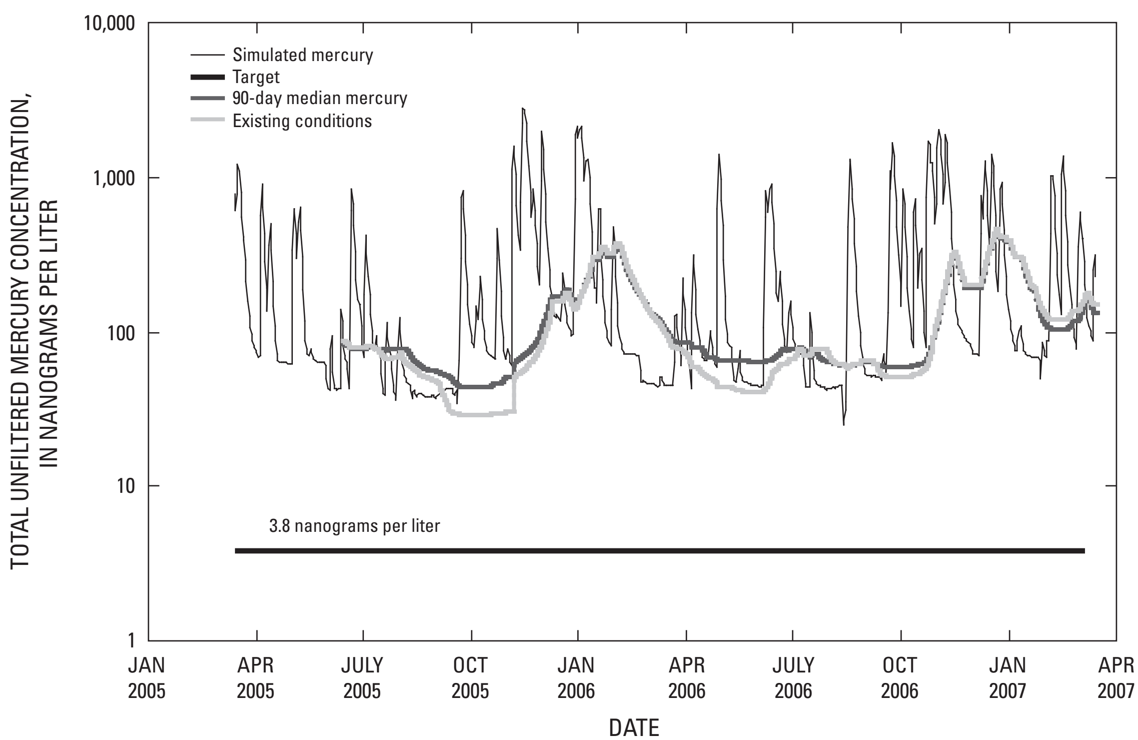


Figure 54. Simulated total unfiltered mercury values for the South River at Harriston, Virginia (USGS station number 01627500), under future conditions with runoff cleaned up, Scenario 3C. (Existing 90-day median simulated mercury concentrations shown for comparison.)

Multiple Source Reductions and Total Maximum Daily Load (TMDL) Scenario

The results of Scenarios 3A–3C demonstrate that THG concentrations cannot be brought below target concentrations unless channel margin mercury loads are drastically reduced and other loads are also reduced. Under Scenario 4A, multiple loads are reduced; channel margin loads are totally eliminated and sediment runoff concentrations, THG_{Sed}, are reduced to background levels. Together, these two sources account for 99.2 percent of total mercury loads to the river (table 29). Precipitation and interflow are again reduced to reflect future reductions in atmospheric mercury deposition. The remaining mercury loads are from point sources, groundwater, and background mercury levels in precipitation, interflow, runoff, and precipitation. Results from Scenario 4A indicate that in spite of greatly reduced mercury loads, violations of THG target concentrations still occur at all of the monitoring stations downstream from the plant site, as shown in figure 55 for the Harriston monitoring station.

Under Scenario 4B, mercury loads to the river are further reduced, resulting in mercury concentrations that meet TMDL requirements. Mercury loads from channel margin inputs and surface runoff are again reduced and a further load reduction is made by lowering all point sources to the target THG concentration of 3.8 ng/L. Because this scenario will be used for load allocation under TMDL regulations by the VDEQ, all point sources are assigned a fixed concentration of 3.8 ng/L, including the Stuart's Draft wastewater plant and Genicom, which under existing conditions have THG concentrations below 3.8 ng/L. Results show that 90-day median THG concentrations stay below 3.8 ng/L in all river reaches, as shown in figure 56 for the Harriston monitoring station.

TMDL requirements are satisfied under Scenario 4B, and the TMDL for mercury to the South River above its confluence with the South Fork Shenandoah at Port Republic is 2.0 kg/yr (table 38). This value is reasonable from a mass balance point of view, considering the low target concentrations. As an example, if the target concentration of 3.8 ng/L is multiplied by the simulated annual volume of water passing Port Republic, 2.7×10^{11} L, the result is 1.0 kg of mercury, which is less than the TMDL value of 2.0 kg/yr. The TMDL value of 2.0 kg/yr is higher because the 90-day median statistic reduces the importance of stormflows, which carry most of the mercury load.

There are several reasons for the large percentage reduction in mercury loads required to achieve target in-stream THG concentrations. The first is that THG concentrations of inputs to the river are very high relative to the target concentration of 3.8 ng/L. Precipitation THG_F is about 5 times higher than target THG concentrations, interflow THG_F from uncontaminated land occupying most of the watershed is about 3 times higher than target THG concentrations, and some point-source THG concentrations are two to three

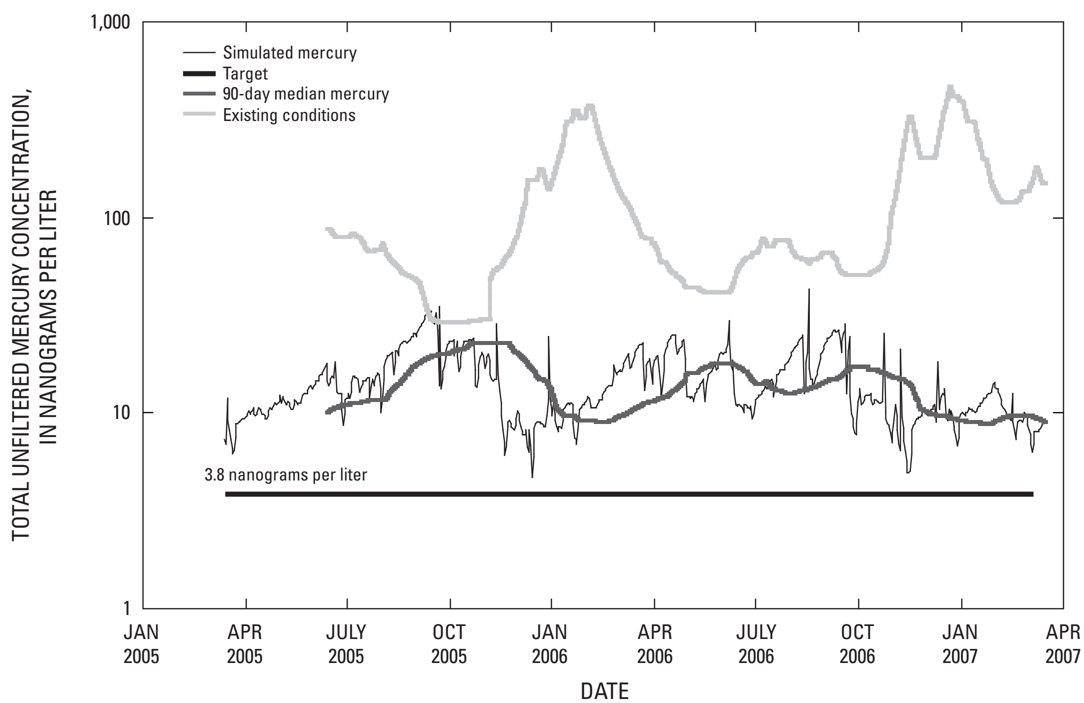


Figure 55. Simulated total unfiltered mercury concentrations for Scenario 4A, reduced channel margin and runoff mercury loads, South River at Harriston, Virginia (USGS station number 01627500). (Existing 90-day median simulated mercury concentrations shown for comparison.)

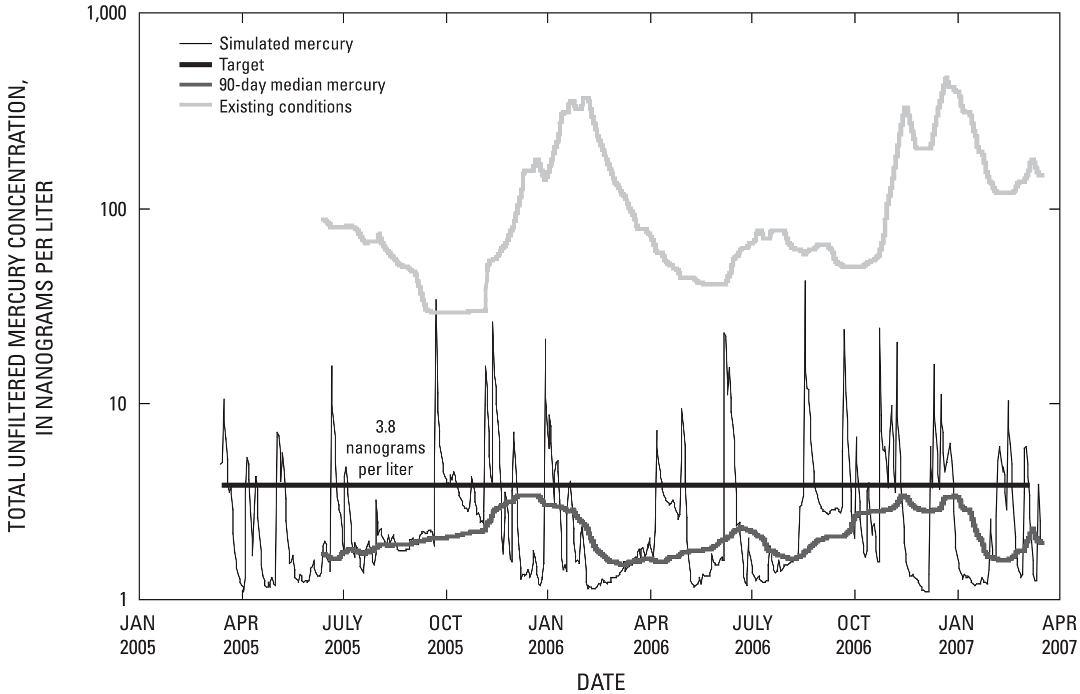


Figure 56. Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South River at Harriston, Virginia (USGS station number 01627500). (Existing 90-day median simulated mercury concentrations shown for comparison.)

Table 38. Annual mercury loads under Total Maximum Daily Load (TMDL) conditions (Scenario 4B), South River, Virginia.

	Total mercury load (grams)					
	1	2	3	4	5	Total all reaches
Point sources	21.0	72.9	1.1	0.0	16.8	112
Direct precipitation to river	22.6	5.7	1.3	8.9	6.4	45
Interflow discharge	309.2	50.6	39.2	124.8	33.8	558
Groundwater discharge	53.9	7.8	7.5	23.9	5.7	99
Runoff	572.8	96.7	87.0	354.1	105.0	1,216
Channel margin inputs	0.0	0.0	0.0	0.0	0.0	0
Reach loads	980	234	136	512	168	2,029
Watershed loads	980	1,213	1,349	1,861	2,029	2,029

orders of magnitude higher than target THG concentrations. A smallmouth bass at the background reference station upstream from the plant site had average mercury concentrations of 0.24 mg/kg from 1999–2007, which indicates that the mercury concentrations must be reduced to near background levels to achieve the fish tissue mercury concentration goal of 0.3 mg/kg.

Results of the simulations indicate that large percentage reductions in multiple mercury loads to the river would be required to lower fish tissue methylmercury concentrations to below the 0.3 mg/kg criterion. Although the largest contributing load in the simulations is from channel margin inputs, other loads that would need to be addressed include runoff from contaminated flood plains and point-source discharges. Due to the large reductions needed (over 99 percent of the total mercury load), achieving the goal of maintaining fish tissue methylmercury concentrations below 0.3 mg/kg in the South River will be challenging.

Sensitivity of Total Maximum Daily Load (TMDL) Results to Model Parameter Values

The sensitivity of model results to input parameter values was assessed by altering parameter values and measuring the resulting changes to simulated mercury concentrations. Model sensitivity was assessed both under existing conditions and TMDL conditions (Scenarios 1 and 4B). Input parameters selected for the sensitivity analysis were those expected to have the greatest control over simulated THG concentrations (table 39). Most of the parameters analyzed have multiple values in the calibrated model because of variation by HRU or by time period. For the sensitivity analysis, changes were made to all values of a parameter on a percentage basis of ±50 percent. When precipitation was decreased by 50 percent, for example, all daily precipitation values for all HRUs were decreased by 50 percent. Instream mercury loads are reported to the tenth of a kilogram. Because thousands of input values go into the simulation of annual mercury loads, the appropriate number of significant figures for reporting model results cannot be formally computed. For the purposes of this report, the numbers have been rounded as much as possible, while still showing the differences among locations and runs.

Under the existing conditions scenario (Scenario 1), sensitivity was measured as the change in simulated median THG concentration at the Harriston monitoring station for the period April 1, 2005, through March 31, 2007. Results of the sensitivity analysis under existing conditions are shown in table 40. Under the TMDL Scenario, sensitivity was measured as the change in the percent of time that 90-day rolling median THG concentrations at Harriston exceeded the 3.8 ng/L target concentration (table 41).

Results of the sensitivity analysis under existing conditions (table 41) show that median THG concentrations are most sensitive to parameters affecting suspension and deposition of sediment in the river during low-flow periods (TAUCD, TAUCS, and W). Under the TMDL Scenario, violation of the 3.8 ng/L target THG concentration is affected most by KRER, the sediment detachment rate, and TAUCD, the critical shear stress for deposition of suspended sediment. THG concentrations are most sensitive, under both existing conditions and TMDL conditions, to parameters controlling suspended sediment in the river because most mercury in the river is attached to suspended sediment. Sensitivities do not appear particularly high in this analysis, as ±50 percent changes to parameter values cause at most a ±24 percent change in THG concentrations and ±4 percent change in time that 90-day median concentrations exceed 3.8 ng/L. However, because the model treats channel margin loads very simply, this sensitivity analysis does not express the full uncertainty associated with the channel margin mercury loads. Future investigations that improve conceptual understanding and computer simulation of processes controlling the channel margin inputs have the potential to provide that needed aspect of the sensitivity analysis.

Table 39. Model input parameters changed during sensitivity analysis.

[HSPF, Hydrological Simulation Program–FORTRAN]

Type	HSPF module	Name	Description	Original values
Hydrology	EXT SOURCES	Precipitation	Precipitation rates (inches per year)	39–43
Sediment	PERLND>SEDMNT>DETACH	KRER	Sediment detachment rate coefficient	0.02–4.0
	PERLND>SEDMNT>SOSED1	KSER	Sediment runoff transport coefficient	0.1–20.0
	RCHRES>SEDTRN (Silt and clay only)	W	Settling velocity	0.0035–0.03
		TAUCD	Critical shear stress—Deposition	0.6
		TAUCS	Critical shear stress—Suspension	0.02–0.15
		M	Erodibility of bed sediment	0.03–0.07
Mercury sorption in river	RCHRES>GQUAL>ADSEDS	KD	Adsorption coefficient	1
		ADRATE	Mercury phase transfer rate coefficient	25

Table 40. Results of sensitivity analysis for existing conditions, changes to median concentrations for the period April 1, 2005, through March 31, 2007, resulting from + or –50 percent in model parameter values, South River at Harriston, Virginia (U.S. Geological Survey station number 01627500).

[HSPF, Hydrological Simulation Program–FORTRAN; THG, total unfiltered mercury; ng/L, nanograms per liter; %, percent; in/yr, inches per year]

Parameter					Expected range	Median THG (ng/L)		
Type	HSPF module	Name	Description	Original values		–50%	Existing conditions	+50%
Hydrology	EXT SOURCES	Precipitation	Precipitation rates (in/yr)	39–43	Observed[a] 27.1–66.5	92.3	91.4	91.1
Sediment	PERLND>SEDMNT> DETACH	KRER	Sediment detachment rate coefficient	0.02–4.0	0.05–0.75[b]	79.0	91.4	96.1
	PERLND>SEDMNT> SOSED1	KSER	Sediment runoff transport coefficient	0.1–20.0	0.1–10.0[b]	80.5	91.4	96.9
	RCHRES>SEDTRN (Silt and Clay only)	W	Settling velocity (in/yr)	0.0035–0.03	0–0.10[c]	78.8	91.4	108.7
		TAUCD	Critical shear stress—Deposition	0.6	0.001–1.0[b]	76.0	91.4	98.3
		TAUCS	Critical shear stress—Suspension	0.02–0.15	0.01–3.0[b]	95.6	91.4	71.1
		M	Erodibility of bed sediment	0.03–0.07	0.001–5.0[b]	101.1	91.4	79.7
Mercury sorption in river	RCHRES>GQUAL> ADSEDS	KD	Adsorption coefficient	1	0.003–10.0[d]	89.7	91.4	92.1
		ADRATE	Mercury phase transfer rate coefficient	25	10^{-5}–any[c]	89.5	91.4	92.3

[a] See report section Meteorological and Climatic Data

[b] U.S. Environmental Protection Agency (2006)

[c] Bicknell and others (2001);

[d] Horvat and others (2004), Lyons and others (1997), Gbondo-Tugbawa and Driscoll (1998)

Table 41. Results of sensitivity analysis under the Total Maximum Daily Load (TMDL) Scenario, changes to percent of time that 90-day median concentrations exceed the 3.8 ng/L target concentration, resulting from + or –50 percent in model parameter values, South River at Harriston, Virginia (U.S. Geological Survey station number 01627500), April 1, 2005, through March 31, 2005.

[%, percent]

Parameter			Time in violation, in percent		
Type	Name	Description	–50%	Scenario 4B	+50%
Hydrology	Precipitation	Precipitation rates (inches per year)	0	0	0
Sediment	KRER	Sediment detachment rate coefficient	0	0	3.9
	KSER	Sediment runoff transport coefficient	0	0	0
	W	Settling velocity (inches per year)	0	0	0
	TAUCD	Critical shear stress—Deposition	0	0	2.5
	TAUCS	Critical shear stress—Suspension	0	0	0
	M	Erodibility of bed sediment	0	0	0
Mercury sorption in river	KD	Adsorption coefficient	0	0	0
	ADRATE	Hg phase transfer rate coefficient	0	0	0

Implications for the Downstream South Fork Shenandoah River and Shenandoah River

The South Fork Shenandoah River and Shenandoah River are also part of the mercury TMDL, and are discussed here in light of the South River modeling results. Monitoring data were not collected in the South Fork Shenandoah and Shenandoah Rivers specifically for this study, but the VDEQ regularly collects surface-water samples for THG analysis at sites along the South Fork Shenandoah River. The most downstream site with sufficient mercury data for comparison to the South River is the South Fork Shenandoah River near Luray, Virginia (01629500) (fig. 57).

Twenty-seven data pairs of THG concentration values from the VDEQ were used to compare THG concentrations in the South Fork Shenandoah River to those in the South River. The analysis compared THG concentrations from the South River at Harriston (01627500) to those from the South Fork Shenandoah near Luray, Virginia (01629500), which were collected within 6 hours of each other between August 2001 and January 2007. A linear fit to the plot of South Fork Shenadaoah River vs. South River THG concentrations (fig. 57) has an r^2 value of 0.81, indicating a strong positive correlation. Instantaneous THG loads at sample times were estimated by multiplying THG concentrations by streamflow. THG loads were usually smaller at Luray than upstream in the South River at Harriston, with 22 of 27 sampling events showing a downstream decrease in load and an average decrease of 25 percent. This is in spite of the fact that the South Fork Shenandoah River near Luray receives drainage from the South River and from other tributary streams, most notably the Middle and North Rivers.

A possible explanation for the decrease in mercury load at the Luray monitoring station is that mercury from the South River may be sorbing to suspended solids in the South Fork Shenandoah and being deposited on the channel bed. Although sediment-deposition characteristics of the South Fork Shenandoah are not well known, long-term accumulation of large volumes of sediment seems unlikely for that reach.

For this TMDL, mercury concentrations in the South Fork Shenandoah near Luray were estimated from a mixing model of South River water and water at background THG concentrations from other tributaries to the South Fork Shenandoah. It is assumed that all mercury exiting the South River remains in the water column and moves downstream to the South Fork Shenandoah. Based on the ratio of annual streamflow for the South Fork Shenandoah River near Luray to annual streamflow for the South River at Port Republic from the HSPF model (4.96), it is estimated that 79.9 percent of the flow at Luray originates from outside the South River

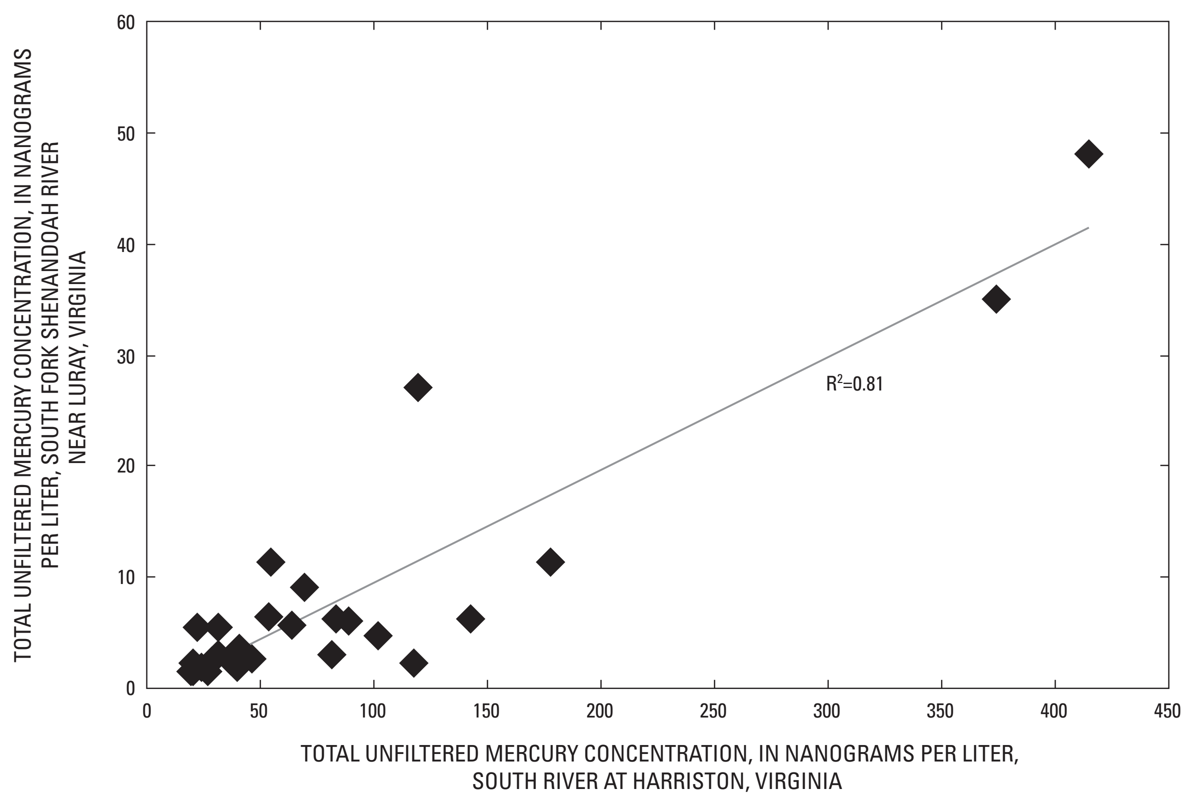


Figure 57. Comparison of total unfiltered mercury concentrations (Virginia Department of Environmental Quality samples only) from the South River at Harriston, Virginia (USGS station number 01627500) to same-day total unfiltered mercury concentrations from the South Fork Shenandoah River near Luray, Virginia (USGS station number 01629500).

watershed. All water entering the South Fork Shenandoah River above Luray from uncontaminated subwatersheds is assumed to have background THG concentrations equal to 1.81 ng/L, the mean for observed THG concentrations (VDEQ samples only) in the North River. THG concentrations for the South Fork Shenandoah near Luray were then estimated as a mix of South River mercury and background aqueous mercury. This estimation was made for existing conditions (Scenario 1) and for the TMDL Scenario (Scenario 4B). Resulting time series are shown in figure 58 relative to the 3.2 ng/L target concentration for the South Fork Shenandoah River.

The results shown in figure 58 indicate that 90-day median THG concentrations in the South Fork Shenandoah River under existing conditions exceed the 3.2 ng/L target concentration. Under the TMDL Scenario (4B), in which runoff, channel margin inputs, and point sources are cleaned up, 90-day median concentrations stay below the target concentration of 3.2 ng/L; therefore, no violations occur. The mercury load originating from areas other than the South River is estimated at 1.8 kg/yr, based on Luray flow volume minus South River Flow volume times the background mean THG concentration of 1.8 ng/L in the North River. The mercury TMDL for the South Fork Shenandoah River near Luray is therefore 3.8 kg/yr, obtained by adding 1.8 kg/yr to the South River mercury TMDL. By use of the same methods, a mercury TMDL of 4.1 kg/yr is estimated for the South Fork Shenandoah at Front Royal, Virginia (01631000), just upstream from the confluence with the North Fork Shenandoah River.

The Shenandoah River, formed at the confluence of the North Fork and South Fork Shenandoah Rivers in Front Royal, Virginia, also requires a mercury TMDL. Therefore, a TMDL was estimated using the same methods as those used for the South Fork Shenandoah River. However, there are few mercury data available for the Shenandoah River and there is no streamflow-gaging station in the affected part of the river, from Front Royal downstream to the Craig Run confluence. Annual average flow for the Shenandoah River at Craig Run is 2,791 ft^3/s, based on the USGS EDNA calculator (http://edna.usgs.gov/), which calculates drainage areas from digital elevation models and flow accumulation regression methods (Vogel and others, 1999; http://edna.usgs.gov/). The South River occupies 9.8 percent of the drainage area and is assumed to provide 9.8 percent of flow in the Shenandoah River at the confluence with Craig Run. The remaining 90.2 percent of flow is assumed to originate from uncontaminated parts of the watershed that contribute water at background mercury concentrations. By again assuming that water from uncontaminated subwatersheds has a background THG concentration of 1.81 ng/L, THG concentrations were estimated on a daily basis for the Shenandoah River at the confluence with Craig Run (fig. 59). The TMDL for mercury in the Shenandoah River at the Craig Run confluence, calculated as the sum of mercury from the South River plus mercury from uncontaminated subwatersheds, is 6.1 kg/yr (table 42).

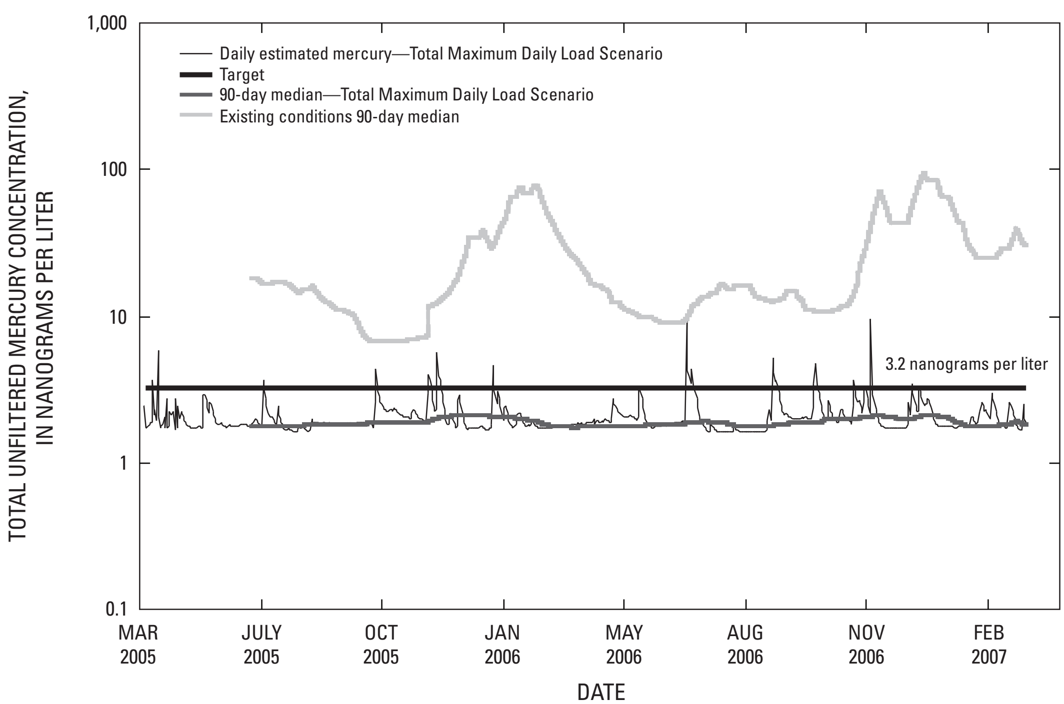


Figure 58. Simulated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, South Fork Shenandoah River near Luray, Virginia (USGS station number 01629500). (Existing 90-day median simulated mercury concentrations shown for comparison.)

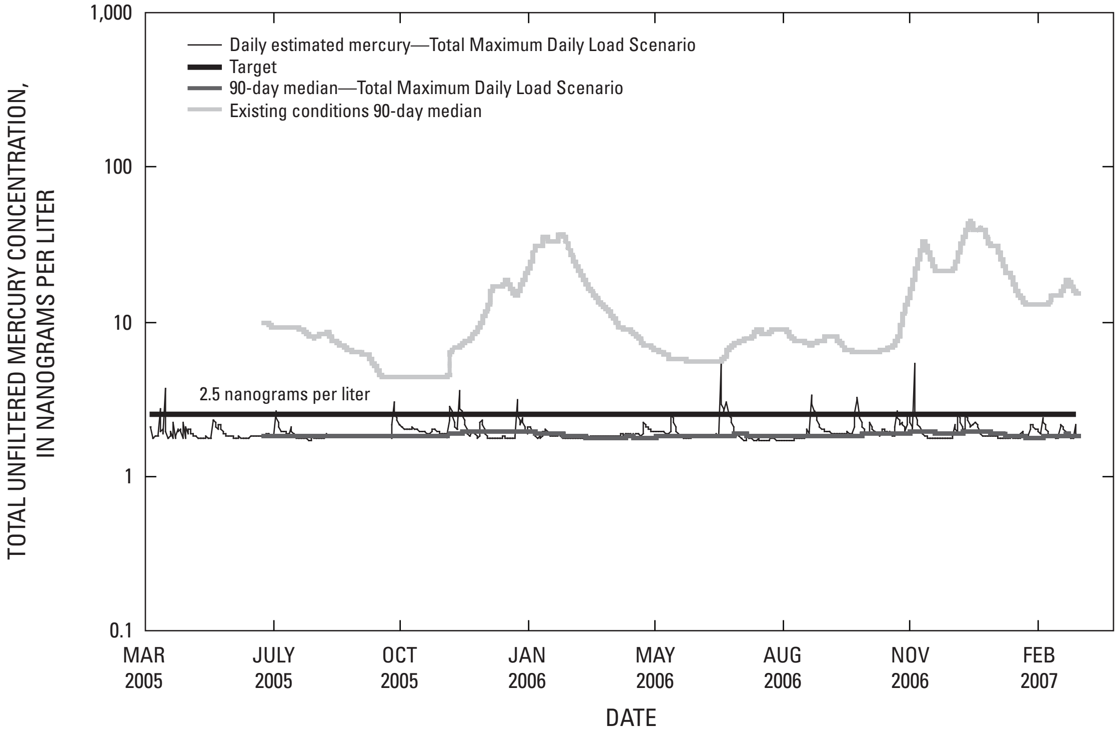


Figure 59. Estimated total unfiltered mercury concentrations for the Total Maximum Daily Load Scenario (Scenario 4B), reduced channel margin, runoff, and point-source mercury loads, Shenandoah River at the confluence with Craig Run, Clarke County, Virginia. (Existing 90-day median simulated mercury concentrations shown for comparison.)

Table 42. Estimated total maximum daily loads (TMDLs) for mercury for listed waters in the Shenandoah Valley, Virginia.

[THG, total unfiltered mercury; ng/L, nanograms per liter; kg/yr, kilograms per year]

River	Target THG concentration (ng/L)	Total mercury TMDL (kg/yr)
South River at Port Republic, Virginia	3.8	2.0
South Fork Shenandoah River near Luray, Virginia	3.2	3.8
South Fork Shenandoah River at Front Royal, Virginia	3.2	4.1
Shenandoah River at Craig Run, Virginia	2.5	6.1

Summary

The U.S. Geological Survey (USGS), in cooperation with the Virginia Department of Environmental Quality and the U.S. Environmental Protection Agency, conducted a study to develop a total maximum daily load (TMDL) for methylmercury in fish tissue in the South, South Fork Shenandoah, and Shenandoah Rivers of Virginia. These rivers have fish with methylmercury concentrations above the U.S. Environmental Protection Agency criterion of 0.3 mg/kg (milligrams methylmercury per kilogram of fish tissue). A numerical watershed model based on Hydrological Simulation Program–FORTRAN (HSPF) software was developed to simulate water, sediment, and mercury transport in the South River watershed. This model was calibrated with field data collected in this study. Data were also compiled from other studies to describe other media including fish tissue and to expand coverage of downstream rivers and time periods prior to 2005. On the basis of results from the calibrated watershed model, the mercury load to the South River under existing conditions for the period April 2005 through March 2007 is estimated at 189 kilograms per year. Using a site-specific empirical bioaccumulation model, the Virginia Department of Environmental Quality calculated concentrations of methylmercury in fish tissue from water column concentrations of total mercury. On the basis of the bioaccumulation model, to reduce fish tissue methylmercury concentrations below the U.S. Environmental Protection Agency criterion of 0.3 mg/kg, water column concentrations of total mercury need to be below target concentrations of 3.8 ng/L (nanograms per liter) in the South River, 3.2 ng/L in the South Fork Shenandoah River, and 2.5 ng/L in the Shenandoah River. Reductions in mercury loads to the South River were simulated using the calibrated HSPF model to determine the source-load reductions required to meet these conditions. Simulation results indicate that the TMDL for mercury in the South River that would be protective of methylmercury in fish tissue is 2.0 kilograms of total mercury per year. A mixing model and conservative mercury transport based on the South River modeling results were used to calculate mercury TMDLs for the South Fork Shenandoah and Shenandoah Rivers, which were 4.1 and 6.1 kilograms of mercury per year, respectively. Under the assumptions used in this study, if mercury loads to the South River are reduced to TMDL levels, fish tissue methylmercury concentrations in the South Fork Shenandoah River and Shenandoah River will also be reduced to less than 0.3 mg/kg.

Major findings and conclusions of this study are:

- The calibrated South River watershed model simulates observed characteristics of streamflow, sediment load, and mercury transport.
- Analysis of mercury loads to the South River indicates that nonpoint-source loads account for over 99 percent of total loads under existing conditions.
- Channel margin mercury load, a nonpoint-source load, makes up an estimated 84 percent of total mercury load to the South River. The channel margin mercury loads originate from contaminated sediment in close proximity to the river, but the pathways and mechanism(s) responsible for moving the channel margin mercury to the river are not well understood.
- A 99 percent or greater reduction in the current mercury load delivered to the South River is required to meet target water-column mercury concentrations that are protective of the U.S. Environmental Protection Agency 0.3 mg/kg criterion for methylmercury in fish tissue.
- The mercury TMDL is estimated to be 2.0 kg/yr for the South River at Port Republic, 4.1 kg/yr for the South Fork Shenandoah River at Front Royal, and 6.1 kg/yr for the Shenandoah River at the Craig Run confluence.

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Appendix 1. Data Sources Used to Define Point-Source Loading in the Model

Appendix 1. Data sources used to define point-source loading.

[ft³/s, cubic feet per second; mg, milligrams; VAPDES, Virginia Pollution Discharge Elimination System; %, percent; FPBS, Frew Pond Baker Spring; TSS, total suspended solids; SSC, suspended sediment concentration; Hg, mercury; ng/L, nanograms per liter; THG, total unfiltered mercury; mg/L, milligrams per liter; DEQ, Department of Environmental Quality; conc., concentration; GW, groundwater; K, hydraulic conductivity; Disch., discharge]

Point sources		Discharge (ft³/s)			Suspended solids concentration (TSS or SSC), mg/L			Total unfiltered Hg concentration (THG), ng/L		
Name	Model ID	Data source and type	Model value assignment: Periods with data	Model value assignment: Periods of no data	Data source and type	Model value assignment: Periods with data	Model value assignment: Periods of no data	Data source and type	Model value assignment: Periods with data	Model value assignment: Periods of no data
Stu Draft STP	101-103	VAPDES monthly 2001–2007	Monthly observed values	Average monthly	VAPDES monthly 2001–2007	Monthly observed values	Average monthly	Periodic samples, n=1	—	THG = 0.7 ng/L
Loth Spring	201-203	None	—	Estimate = 25% of FPBS	None	—	Use FPBS average TSS = 9 mg/L	None	—	Use FPBS avg. THG = 4.1 ng/L
Invista Outfalls		Data from Invista, DuPont, and VAPDES			Data from Invista, DuPont, and VAPDES			Data from DuPont and DEQ		
001	211-213	Daily 1998–2007	Daily observed values	Average monthly	Periodic samples, n=45	—	Base flow TSS average = 2.6 mg/L Stormflow TSS average = 3.4 mg/L	Periodic samples, n=41	—	Regression on Flow
003	231-233	Periodic measurements	—	Regression on daily river flow	Periodic samples, n=31	—	Base flow TSS average = 4.5 mg/L Stormflow TSS average = 8.9 mg/L	Periodic samples, n=40	—	Base flow THG avg. = 41.2 ng/L Stormflow THG avg. = 61.6 ng/L
004	241-243	Periodic measurements	—	Regression on daily river flow	Periodic samples, n=13	—	Base flow TSS average = 1.1 mg/L Stormflow TSS average = 25.7 mg/L	Periodic samples, n=8	—	Base flow THG avg = 15.5 ng/L Stormflow THG avg = 42.1 ng/L
006		Ignored based on insignificant contribution			Ignored based on insignificant contribution			Ignored based on insignificant contribution		
008	281-283	Periodic measurements	—	Regression on daily river flow	Periodic samples, n=26	—	Base flow TSS average = 6.3 mg/L Stormflow TSS average = 32 mg/L	Periodic samples, n=31	—	Base flow THG avg. = 298.4 ng/L Stormflow THG avg. = 134.9 ng/L
009	291-293	Periodic measurements	—	Base flow = 0 Stormflow simulated by HSPF	Periodic samples, n=4	—	No base flow Stormflow average TSS = 7.2 mg/L	Periodic samples, n=4	—	No base flow Stormflow THG avg. = 81.9 ng/L
010	221-223	Periodic measurements	—	Base flow = 0 Stormflow simulated by HSPF	Periodic samples, n=3	—	No base flow Stormflow average TSS = 46.8 mg/L	Periodic samples, n=4	—	No base flow Stormflow THG avg. = 228.4 ng/L
011	271-273	Daily 1998–2002 and overflow event monitoring 2005–2006	Daily observed values	Average monthly	Periodic samples, n=28	—	Base flow TSS average = 24.5 mg/L Stormflow TSS average = 20.3 mg/L	Periodic samples, n=37	—	Base flow THG avg. = 2,278 ng/L Stormflow THG avg. = 393 ng/L
012	274-276	None	—	Base flow = 0 Stormflow simulated by HSPF	None	—	Set = 010 conc. at given time and flow	None	—	Set = 010 conc. at given time and flow
013	277-279	Overflow event monitoring	Individual overflow events	Average annual volume	None	—	Set = 001 conc. for stormflow events	None	—	Set = 001 conc. for stormflow events

Appendix 1. Data sources used to define point-source loading.—Continued

[ft³/s, cubic feet per second; mg, milligrams; VAPDES, Virginia Pollution Discharge Elimination System; %, percent; FPBS, Frew Pond Baker Spring; TSS, total suspended solids; SSC, suspended sediment concentration; Hg, mercury; ng/L, nanograms per liter; THG, total unfiltered mercury; mg/L, milligrams per liter; DEQ, Department of Environmental Quality; conc., concentration; GW, groundwater; K, hydraulic conductivity; Disch., discharge]

Point sources		Discharge (ft³/s)			Suspended solids concentration (TSS or SSC), mg/L			Total unfiltered Hg concentration (THG), ng/L		
Name	Model ID	Data source and type	Model value assignment		Data source and type	Model value assignment		Data source and type	Model value assignment	
			Periods with data	Periods of no data		Periods with data	Periods of no data		Periods with data	Periods of no data
014	224-226	Overflow event monitoring	Individual overflow events	Average annual volume	None	—	Set = 001 conc. for stormflow events	None	—	Set = 001 conc. for storm-flow events
FPBS	204-206	Periodic monitoring	—	Average plus seasonal variation of ± 29%	Periodic samples, n=3	—	Average TSS = 9 mg/L	Periodic samples, n=3	—	Average THG = 4.1 ng/L
GW Disch.	207-209	Darcian flux GW levels (7 wells), slug test K (5 wells)	—	Average flux	None	—	Assume TSS = 0	Periodic samples, n=32	—	Average THG = 6.9 ng/L
Wboro STP	261-263	VAPDES monthly 2001–2007	Monthly observed values	Average monthly	VAPDES monthly 2001–2007	Monthly observed values	Average monthly values	Periodic samples, n=1	—	THG = 7.6 ng/L
Genicom	301-303	VAPDES monthly 2001–2007	Monthly observed values	Average monthly	None	—	Assume TSS = 0	Periodic samples, n=1	—	THG = 0.2 ng/L
Alcoa	501-503	VAPDES monthly 2001–2007	Monthly observed values	Average monthly	VAPDES monthly 2001–2007	Monthly observed values	Average monthly values	Periodic samples, n=1	—	THG = 18.3 ng/L

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