Calibration and Verification
of Upper Potomac River Model
Volume I

Prepared by:

Interstate Commission on Potomac River Basin
6110 Executive Boulevard
Rockville, Maryland 20852-3903

Prepared for:

Maryland Department of Environment
Baltimore, Maryland

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Summary and Conclusions

The key water quality issue in the Potomac basin, as well as the Chesapeake Bay basin, is nutrient enrichment and eutrophication. Within Chesapeake Bay, a 40% reduction of nitrogen and phosphorus inputs from point and non-point sources to the Bay has been established as a long term planning goal for the basin. Water quality management plans developed for the Upper Potomac River basin must conform to these overall nutrient reduction goals specified by the 1987 Governor's Agreement.

The relative effectiveness of point and non-point source control measures for nutrient enrichment and eutrophication of the Upper Potomac River and the Potomac estuary are central issues for the development of water quality management plans for the Upper Potomac basin. This study has developed a steady state water quality model for characterizing the spatial distributions of dissolved oxygen, phytoplankton, CBOD and nutrients within the freshwater Upper Potomac River under summer conditions of low-flow and high temperature. The purpose of the model is to provide a framework to: (1) allow credible evaluations of various nutrient management scenarios; and (2) obtain scientific insight into the key processes controlling phytoplankton, nutrient and oxygen distributions in the Upper Potomac River.

Four time periods were selected for calibration and verification of the steady state model. Streamflow, effluent and water quality data were used to compute monthly averages to represent approximate steady state summer conditions during relatively high flow periods (October 1984; July 1987) and low flow periods (September 1985; September 1986). Streamflow, effluent and water quality data were compiled from available State and EPA databases. Where data were not available to describe various processes, the literature was used to estimate the required information. No new data was collected by field surveys for this study.

In general, the results of the model are in reasonable agreement with the observed data for all four cases. The major trends influencing water quality from the North Branch of the Potomac to Chain Bridge appear to be adequately represented in the model. In particular, reflecting the earlier conclusions of Hydroscience (1976), the incorporation of a non-point source of nutrients from forest and agricultural land uses is a key factor in reproducing the observed data.

The model confirms that nutrient enrichment and excessive eutrophication is a potential problem downstream of the Monocacy River in the vicinity of Seneca Pool because of the combination of nutrient loading from the Monocacy drainage basin and a reduction in hydraulic flushing rate as the river broadens, deepens and becomes sluggish. Further upstream, however, the flushing rate of the river is sufficiently rapid to prevent the accumulation of excessive algal biomass.

The major new finding of this study is the evaluation of the potential significance of benthic processes on oxygen and nutrient distributions in the shallow waters of the Upper

Potomac. Model parameterization of: benthic algae production; benthic nitrification and denitrification; sediment oxygen demand and benthic nutrient regeneration were found to be key processes in reproducing the observed nutrient and oxygen trends.

Recommendations

Based on the technical credibility achieved with this steady state water quality analysis of the Upper Potomac River, the Potomac River Model can be used to evaluate the effectiveness of nutrient control plans on dissolved oxygen and nutrient enrichment. The Potomac River Model (PRM) can be used to develop waste load allocations for point source NPDES permit alternatives under low-flow and high temperature conditions. The steady state model can be used for preliminary evaluations of the relative effectiveness of point and non-point source control measures on: (1) water quality of the mainstem Upper Potomac River; and (2) nutrient loading delivered to the tidal portion of the Potomac River downstream of Chain Bridge during summer and early fall flow conditions. A fully time variable, seasonal model is required, however, to adequately integrate seasonal variability in nutrient loading across the fall line reported for the OWML continuous monitoring station at Chain Bridge.

Development of the Potomac River Model should be continued to address: (1) seasonal variability of flow and nutrient loading; (2) expansion of the benthic sub-model to explicitly account for nutrient uptake and growth of benthic algae; and (3) incorporate a coupled sediment-water column sub-model for the deeper reaches downstream of the Monocacy River to explicitly link changes in nutrient loading.

Field data collection programs should be undertaken to provide data for processes identified in the model as potentially significant factors of the nutrient and oxygen balance of the Upper Potomac River. In addition to ongoing routine monitoring of the Upper Potomac River, additional special data collection efforts for characteristic hydrologic regimes of the Upper Potomac (e.g. North Branch, Seneca Pool etc.) should focus on the following measurements and processes:

- water transparency/secchi depth/light extinction
- phytoplankton primary productivity
- phytoplankton nutrient uptake
- sediment oxygen demand
- benthic nutrient regeneration
- benthic nitrification/denitrification
- water column nitrification
- benthic algae biomass/gross productivity/respiration
- benthic algae nutrient uptake
- benthic community metabolism/production
- diurnal oxygen measurements

1.0 Introduction

1.1 Background

The State of Maryland and the ICPRB has identified the need for a state of the art modeling tool for water quality management planning studies related to waste load allocations and assessments of critical conditions for the Upper Potomac River from Cumberland, Maryland to Chain Bridge. An EPA supported model, WASP4 and EUTRO4, has been selected as a flexible framework to conduct steady state water quality analyses. The flexible design of the input data files used to develop the model will enable future refinements for a seasonal time variable analysis. The purpose of the present project is to develop scientifically credible calibration and verification analyses based on four steady state time periods selected by the ICPRB.

The steady state Potomac River water quality model describes the transport and fate of non-point and point source inputs of nutrients, oxygen and CBOD over a 200 mile domain of the Upper Potomac River from Luke, Maryland to the fall line at Chain Bridge, Virginia. The EPA supported models, WASP4 and EUTRO4, have been used to develop a mass balance analysis of nutrients, phytoplankton, CBOD and oxygen for two calibration periods (October 1984 and September 1986) and two verification periods (September 1985 and July 1987). Water quality data, hydrologic streamflow data for the mainstem Upper Potomac River and tributaries to the Upper Potomac River, wastewater discharge data and tributary water quality data has been identified, compiled and synthesized for the steady state analysis.

1.2 Water Quality Issues

The key water quality issue in the Potomac basin, as well as the Chesapeake Bay basin, is nutrient enrichment and eutrophication. Based on a preliminary 2-D steady state water quality model of Chesapeake Bay (HydroQual, 1987), a 40% reduction of nitrogen and phosphorus inputs from point and non-point sources to the Bay has been established as a long term goal (EPA, 1987 Governors Agreement). Water quality management plans developed for the Upper Potomac River basin must conform to these overall nutrient reduction goals specified by the 1987 Governor's Agreement.

The Potomac River Model (PRM) can be used to develop waste load allocations for point source NPDES permit alternatives under extreme low-flow and high temperature conditions. The model can also address the relative effectiveness of point and non-point nutrient control plans on water quality of the mainstem Upper Potomac River.

A key concern for long term water quality management planning for the Potomac estuary and Chesapeake Bay is the assessment of nutrient loading over the fall line at Chain Bridge. The steady state version of the model can be used to evaluate the effectiveness of point and non-point source control measures on nutrient loading delivered to the tidal portion of the Potomac River downstream of Chain Bridge during summer and early fall flow conditions. A seasonal model is required, however, to adequately integrate the seasonal variability in nutrient loading across the fall line reported for the OWML continuous monitoring station at Chain Bridge (MWCOG, 1989).

1.3 Purpose and Scope of Study

The relative effectiveness of point and non-point source control measures for nutrient enrichment and eutrophication of the Upper Potomac River and the Potomac estuary are central issues for the development of water quality management plans for the Upper Potomac basin. This study has emphasized the development of a steady state modeling framework for characterizing the spatial distributions of oxygen, phytoplankton, CBOD and nutrients within the freshwater Upper Potomac River. The purpose of the model is to provide a framework to: (1) allow credible evaluations of various nutrient management scenarios; and (2) obtain scientific insight into the key processes controlling phytoplankton, nutrient and oxygen distributions in the Upper Potomac River.

The scope of the study included the analysis of four time periods selected for calibration and verification of the steady state model. Streamflow, effluent and water quality data were used to compute monthly averages to represent approximate steady state summer conditions during relatively higher flow periods (October 1984; July 1987) and lower flow periods (September 1985; September 1986). Streamflow, effluent and water quality data were compiled from available State and EPA databases. Where data were not available to describe various processes, the literature was used to estimate the required information. No new data was collected by field surveys for this study.

2.0 Study Area Description

2.1 Geology

The Potomac River drainage basin covers the eastern slopes of the Appalachian Mountains in the Mid Atlantic region of the eastern United States over a drainage area of 11,560 square miles (Figure 1). The Potomac River basin is characterized by the distinctive southwest-northeast alignment of the Appalachian Mountains and the sedimentary margin of the Coastal Plain east of the Appalachian Mountains. The region consists of six major physiographic regions: Allegheny Plateau; Ridge and Valley Province; Great Valley; Blue Ridge; Piedmont Plateau; and the Coastal Plain. The river flows from the Allegheny Mountains in the west through a series of ridges and valleys until it discharges into the coastal plain near Washington, D.C. (McHarg, 1969).

2.2 Hydrology

Within the Allegheny Plateau, the North Branch of the Potomac is characterized by high precipitation, steep topographic gradients and swift flowing waters. Wills Creek is a major tributary to the North Branch of the Potomac in the Allegheny Plateau. In the Valley and Ridge Provinces, precipitation is low but the stream gradient and current velocity remains high. Major tributaries within the Valley and Ridge Provinces are: the South Branch of the Potomac; and the Cacapon River. Within the Great Valley, stream gradients and current velocity are relatively low with Conococheague and Antietam Creeks and the Shenandoah River the major tributaries. The Piedmont region is characterized by gently rolling terrain and tributary streams with broad, shallow valleys. The Monocacy River is the major tributary to the Potomac River in the Piedmont. The downstream region of the Upper Potomac River,the Coastal Plain, is characterized by the fall line at Great Falls and tidal influence of the freshwater Potomac estuary (McHarg, 1969; Trainer and Watkins, 1975).

The 11,560 square miles drainage area of the Upper Potomac Basin included in this study is over 200 miles in length from Luke, Maryland on the North Branch of the Potomac to Little Falls near Washington, D.C. The mainstem of the Potomac is formed 21 miles downstream of Cumberland, Maryland at the confluence of the North and South Branches of the Potomac. The major tributaries, drainage areas and river mile coordinates are summarized in Table 1 and Figure 1a.

Table 1
Drainage Areas of the Major Tributaries
to the Upper Potomac River

Sub-Basin	River Mile	Drainage Area (sq miles)
Major Tributaries		
North Branch	340.1	1328
Wills Creek	307.3	247
South Branch	285.1	1493
Cacapon River	247.7	683
Conococheague Creek	210.8	563
Opequon Creek	201.9	345
Antietam Creek	179.3	292
Shenandoah River	171.5	3054
Monocacy River	153.1	970

2.3 Land Uses of the Upper Potomac River Basin

Land use characteristics of the basin are a major factor in assessing non-point source nutrient loading estimates for the Upper Potomac River (e.g. Palmer, 1975). The Upper Potomac Basin is primarily forested (54% of total basin) with agricultural uses (cropland; pasture) accounting for about 38% of the total basin. Urban and recreational uses account for the remaining 8% (Hydroscience, 1976). General land use patterns are shown in Figure 2. Land use of the Upper Potomac basin can be characterized as follows (after Hydroscience, 1976):

o western portion upstream of Conococheague Creek
(70% forested; 25% cropland and pasture)

o portion from Conococheague Creek to Monocacy River
(over 50% cropland and pasture)

o area from Monocacy River to Great Falls
(primarily agricultural; increasing urban component)

o area from Great Falls to Washington, D.C.
(primarily urban)

Figure 1- Location Map of Upper Potomac River Basin (after Hydroscience 1976)

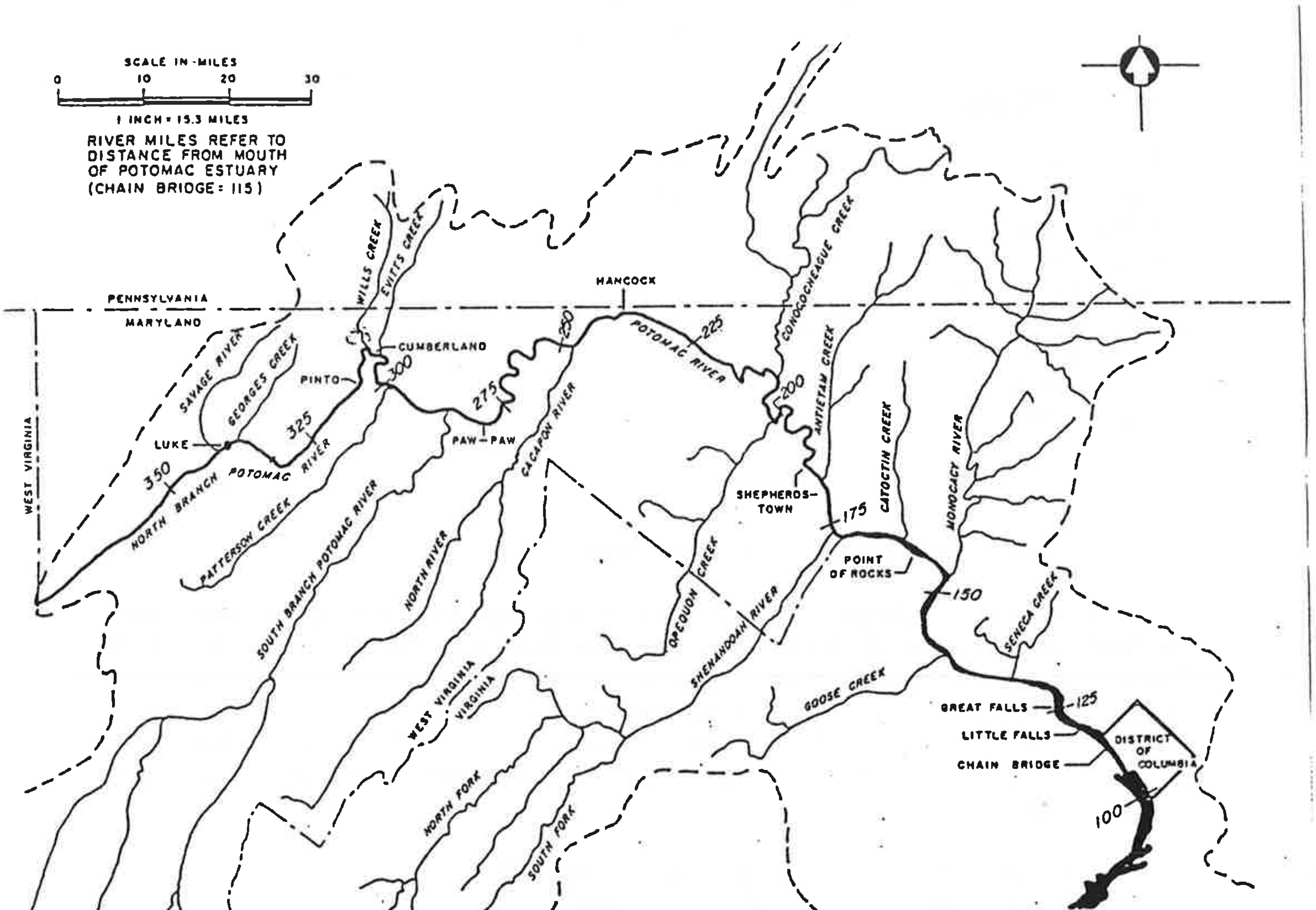


Figure 1a- Upper Potomac River Drainage Area (after Hydroscience, 1976)

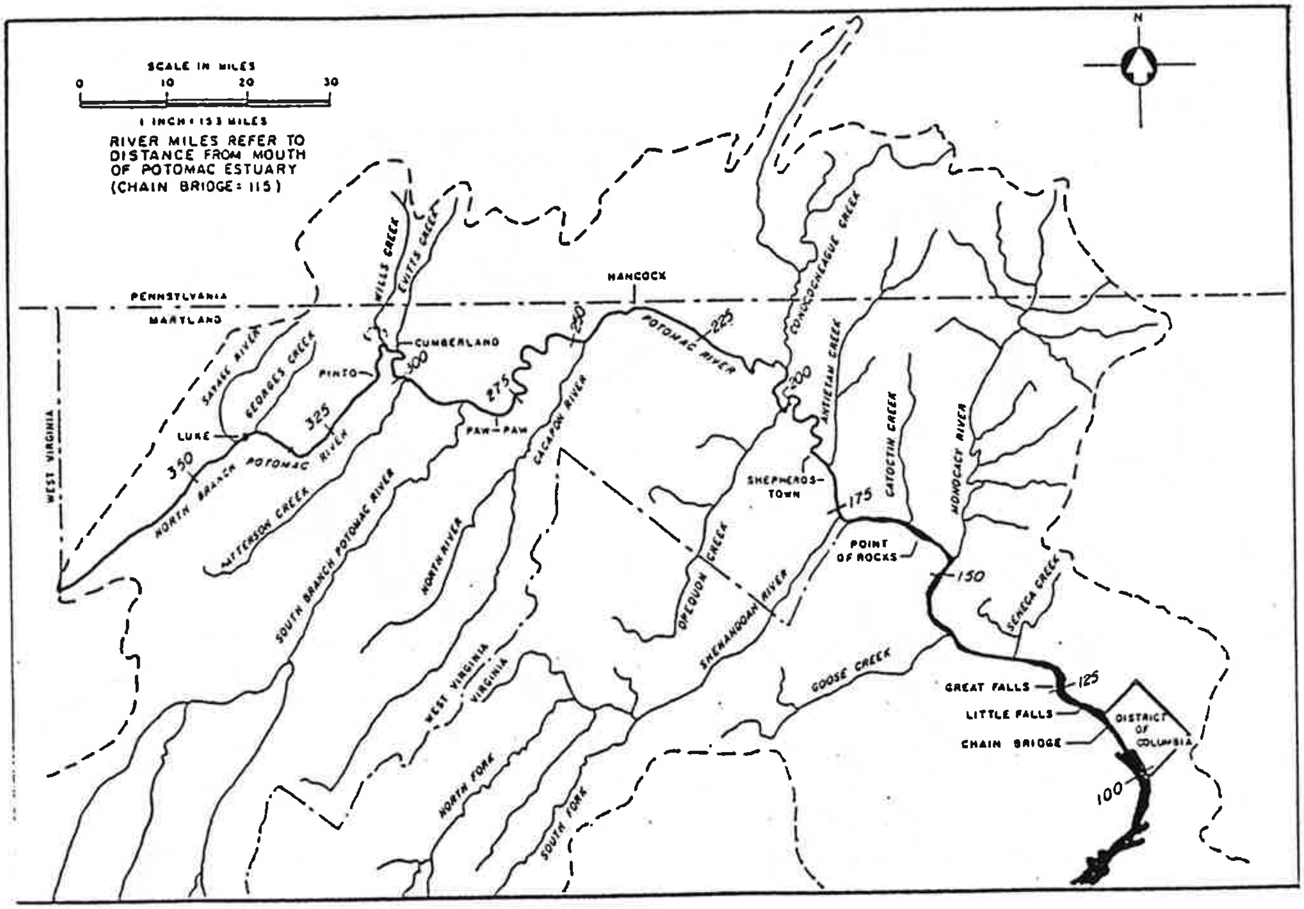
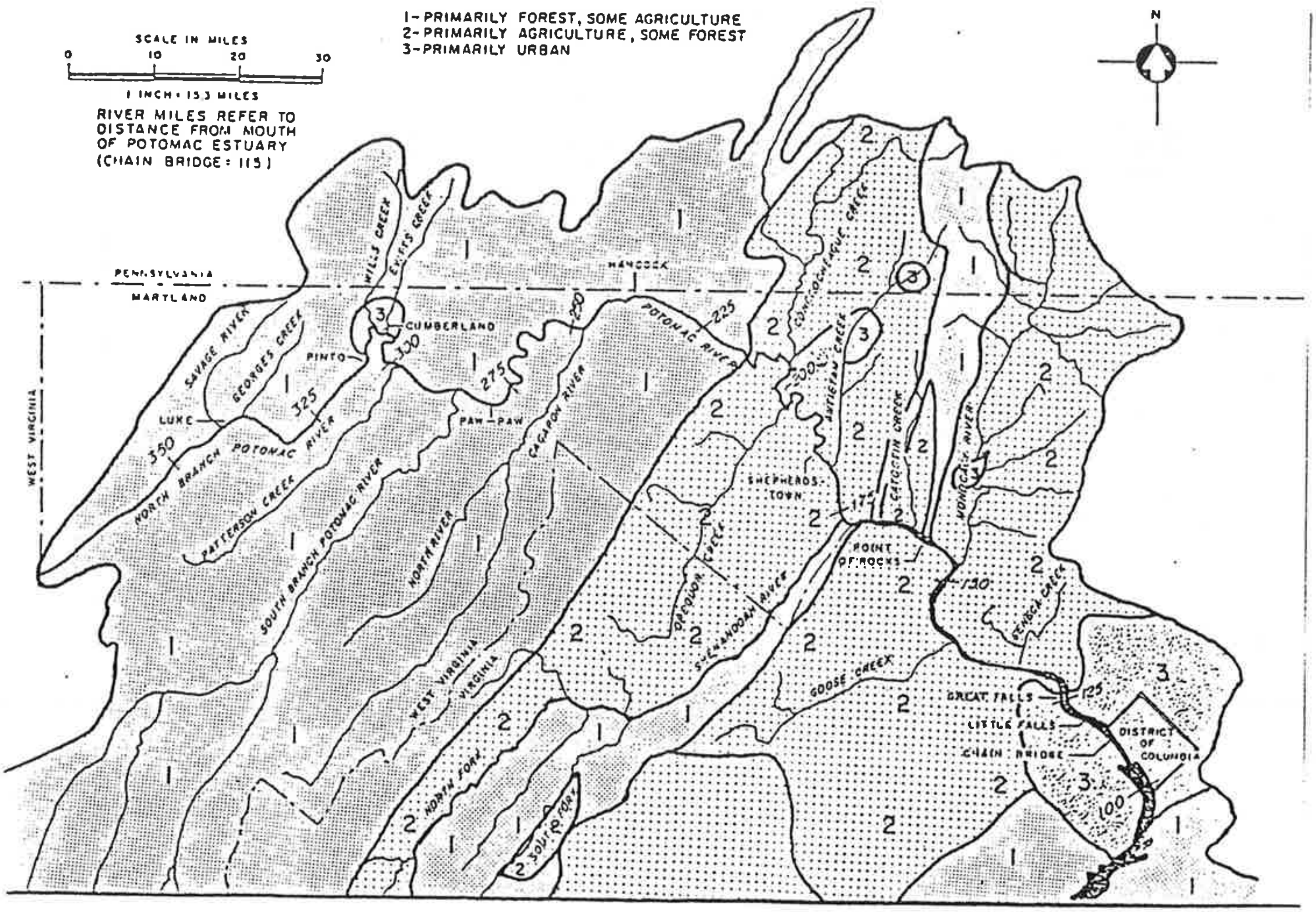


Figure 2- General land use patterns of the Upper Potomac Basin (after Hydroscience 1976)



3.0 Upper Potomac River and Tributary Flows

3.1 Mainstem Upper Potomac River

The overall pattern of streamflow for the Upper Potomac reflects regional meteorology and the varying geologic and physiographic domains of the basin (see Trainer and Watkins, 1975). The USGS maintains seven streamflow gauges along the mainstem of the Upper Potomac River (Table 2). Runoff of the Allegheny Plateau, recorded at the USGS gauge station at Cumberland, Maryland, dominates the North Branch of the Potomac. With a drainage area of over 1500 square miles, the South Branch of the Potomac is the largest tributary of the upper basin. Runoff from the Allegheny Plateau and the South Branch is recorded at Hancock, Maryland. Drainage from the Great Valley in the Shenandoah River accounts for the largest tributary to the Potomac River. At the Blue Ridge demarcation of the Piedmont from the Great Valley, the USGS gauge at Point of Rocks, Maryland provides a continuous long term data set. Low flow summary statistics (7Q10) for the mainstem Potomac River gauges are summarized in ICPRB (1991) (see p124).

Regional climatological patterns result in a fairly consistent interannual and seasonal variation of streamflow with high spring runoff following snowmelt and low evapotranspiration and low flow during August and September. Typical annual minimum flow occurs in September. Figure 3 illustrates the interannual and seasonal patterns of streamflow for the Point of Rocks gauge station.

Table 2- USGS streamflow gauges along the mainstem of the Upper Potomac River

Seg#	Description	RM	USGS# Gauge
0	No.Br.Potomac @Luke	340.8	1598500
16	No.Br.Potomac @Cumberland	304.6	1603000
22	Potomac River @Paw Paw	277.0	1610000
26	Potomac River @Hancock	238.6	1613000
32	Potomac River @Sheperdstown	183.6	1618000
39	Potomac River @Point Rocks	159.5	1638500
47	Potomac River near Wash DC	117.4	1646500

3.2 Gauged Tributaries

As with the mainstem of the Upper Potomac, the pattern of streamflow for the tributaries also reflect regional meteorology and the varying geologic and physiographic domains of the basin (see Trainer and Watkins, 1975). The USGS maintains streamflow gauges at the tributaries summarized in Table 3. Low flow summary statistics (7Q10) for the tributary gauges are summarized in ICPRB (1991)(see pp 124).

3.3 Ungauged Tributaries

Within the Upper Potomac basin, numerous tributaries discharge directly to the Potomac that are not gauged by USGS monitoring stations. Ungauged tributaries (see Table 4) were accounted for the model framework by assigning streamflow required to balance upstream and downstream mainstem observed flow with observed (or estimated) diversions, point source and tributary inflows.

Figure 3 -Interannual and seasonal patterns of streamflow for the Point of Rocks USGS gauge station, 1983-1989.

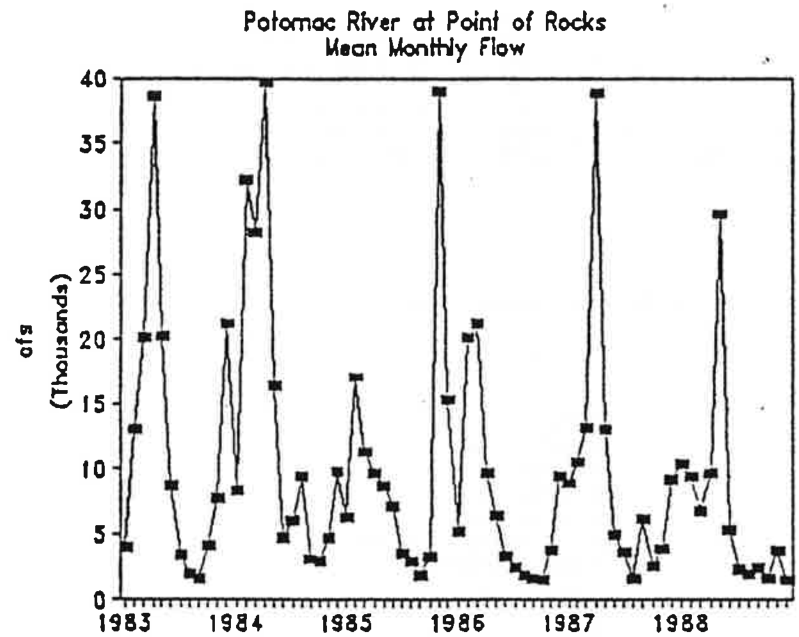


Table 3- USGS streamflow gauges for Tributaries to the Upper Potomac River

Seg#	Description	RM	USGS#	Tributary
2	Georges Ck @ Franklin	338.7	1599000	GEORGES CREEK
14	Wills Ck nr Cumberland	307.2	1601500	WILLS CREEK
19	S.Br.Potomac nr Spring	285.1	1608500	S. BR. POTOMAC RIVER
20	Town Ck nr Oldtown MD	282.6	1609000	TOWN CREEK
30	Conococheague Ck @Fair	210.8	1614500	CONOCOCHEAGUE CREEK
31	Opequon Ck @Martinsburg	201.9	1616500	OPEQUON CREEK,WV
34	Antietam Ck nr Sharpsburg	179.3	1619500	ANTIETAM CREEK
36	Shenandoah R @Millville	171.5	1636500	SHENANDOAH RIVER
38	Catoctin Ck MD	163.4	1637500	CATOCTIN CREEK,MD
39	Catoctin Ck VA		1638480	CATOCTIN CREEK,VA
40	Monacacy R @Jug Br	153.1	1643000	MONACACY RIVER
42	Goose Ck nr Leesburg VA	142.2	1644000	GOOSE CREEK,VA
43	Seneca Ck @Dawsonville MD	133.9	1645000	SENECA CREEK

Table 4- Ungauged Tributaries to the Upper Potomac River

Seg#	Tributary	Seg#	Tributary
1	Montgomery Run	27	Big Run
3	Powder House Run	27	Cherry Run
3	Slaughterhouse Run	28	Back Creek
4	Thunderbill Run	28	Green Spring Run
5	Limestone Run	28	Harlan Run
5	New Creek	28	Jordan Run
8	Ashcabin Run	29	Little Conococheague
9	Mill Run	31	Downey Branch
12	Warrior Run	32	Marsh Run
16	Evitts Creek	32	Rockymarsh Run
17	Collier Run	33	Rattlesnake Run
18	Brice Hollow Run	33	Town Run
18	Broad Hollow Run	34	Elk Branch
18	Green Spring Run	36	Dutchman Creek
18	Mill Run	36	Israel Creek
18	Round Bottom Hollow	36	Piney Run
18	Spring Run	37	Little Catoctin Ck
19	Seven Spring Run	37	Quarter Branch
19	Stony Run	39	Tuscarora Creek
21	Purslane Run	40	Limestone Branch
22	Big Run	40	Little Monocacy
22	Dawson Run	42	Broad Run
22	Little Steer Run	42	Cabin Branch
22	Steer Run	42	Chriel Branch
24	Rockwell Run	42	Horsepen Branch
24	Willett Run	42	Sugarland Run
25	Little Tonoloway Ck	43	Muddy Branch
25	Sir Johns Run	43	Nichols Run
26	Ditch Run	45	Bullneck Run
26	Dry Run	45	Dean Run
26	Sleepy Creek	45	Difficult Run
26	Stoney Run	45	Rock Run
26	Tonoloway Creek	45	Scott Run
26	Warm Spring Run	45	Turkey Run

4.0 Water Quality, Streamflow and Effluent Data

4.1 Water Quality and Streamflow

Water quality monitoring data provides information for developing initial conditions, boundary conditions and forcing functions for the calibration and verification of the model. Data were obtained from a number of sources, evaluated and edited into a single composite database for use in the development of the model. Data sources included: EPA/STORET; USGS; Virginia State Water Control Board (VWCB); West Virginia Department of Natural Resources (WVDNR); the Maryland Department of the Environment (MDE); and the Occoquan Watershed Monitoring Laboratory (OWML). ICPRB (1991) presents a summary documentation of: (1) data sources; and (2) temporal and spatial trends in water quality and streamflow data from 1983-1989 for the Upper Potomac River and its major tributaries.

4.2 Point Source Effluent and Tributary Data

A substantial effort was required to compile a point source load inventory for the characterization of effluent flow and concentration for the major direct municipal and industrial dischargers to the Potomac River (see ICPRB, 1991). Effluent data sources included: NPDES discharge monitoring reports (DMR's); NPDES permit limits; and operating data from waste treatment plants. Where actual data were not available to characterize a specific effluent parameter (e.g. ammonia), estimates of pre- and post-phosphorus ban effluent concentrations for secondary waste treatment plants were based on default estimates prepared for the EPA Chesapeake Bay watershed model (Lewis Linker, EPA/CBP Annapolis, Maryland, personal communication, February, 1991). Gauged tributary water quality data has been compiled to characterize non-point source flow and pollutant loading for both gauged and ungauged tributaries discharging to the Upper Potomac basin.

5.0 Model Framework for the Potomac River Model

5.1 Model Selection

The EPA supported model, WASP4 and EUTRO4 (Ambrose et al. 1988), has been selected as the modeling framework to conduct the steady state analysis of the Upper Potomac River. WASP4 has been used in a number of water quality modeling studies, including the Potomac estuary (PEM, Thomann and Fitzpatrick, 1982). The existing version of WASP4 and EUTRO4 has been modified to include additional nutrient loading from atmospheric deposition and sediment nitrate flux to the water column. The flexible design of WASP4 and the data management approach used for pre-processing input data files will enable future refinements to the model based on a seasonal time variable analysis. The model simulates the basic eight state variables of WASP4: dissolved oxygen, CBOD5, phytoplankton, inorganic and organic nitrogen and phosphorus.

5.2 Model Formulation

The structure of the Potomac River Model (PRM) consists of four sub-models: (1) transport; (2) biological; (3) chemical; and (4) benthos. The transport sub-model, based on earlier work by Hydroscience (1976), provides the advection and dispersion coefficients for steady state flow balances. The biological and chemical sub-models describe the linear and non-linear interactions of nutrients, oxygen and phytoplankton. The benthos sub-model represents the net mass flux of oxygen and nutrients as external boundary forcing functions to the chemical sub-model. A major effort in developing the model has been the formulation of a technically credible benthos sub-model to account for the observed spatial gradients of oxygen and nutrients.

5.3 Model Segmentation

PRM has been developed as a one-dimensional (longitudinal), steady state model with depth and lateral gradients assumed to be averaged over the network of model segments (N=48). An active sediment, or benthos, layer that is directly coupled to the water column is not incorporated in this steady state model. A dummy benthos layer (Seg #48) is included, however, in the segmentation scheme to account for particulate deposition from the water column. The net mass flux of nutrients and oxygen across the sediment-water interface is accounted for by empirical bottom forcing functions.

Segmentation data and model geometry coefficients for velocity, depth and cross sectional area are based on an earlier study of the Upper Potomac River (Hydroscience,1976). Model segments are defined on the basis of: (1) location of flow inputs from tributaries or wastewater discharges; and (2) significant changes in river geometry, or physical and chemical characteristics. Table 5 presents a summary of model segments and river mile coordinates. Model geometry data for the calibration and verification cases is presented in Appendix L through Appendix O of this report.

5.4 Model Kinetics

The state variables of PRM include: (1) ammonia-N; (2) nitrite + nitrate-N; (3) phosphate; (4) phytoplankton; (5) CBOD5; (6) dissolved oxygen; (7) organic N; and (8) organic P. Particulate and dissolved fractions are specified for inorganic phosphate, CBOD5, organic N and organic P to account for settling loss of these constituents through the water column. Recycle fractions are also specified for the partitioning of organic and inorganic nitrogen and phosphorus from phytoplankton death terms.

Nutrients, CBOD, phytoplankton and oxygen are input as boundary condition point source loads from the upstream boundary of the North Branch of the Potomac, tributaries and waste treatment plant discharges. Nutrients are also input as non-point sources from atmospheric deposition and overland runoff as a function of the major land use characteristics.

Kinetic processes for nitrogen include: phytoplankton and attached periphyton uptake of ammonia and nitrate with preferential uptake of ammonia; recycle of inorganic and organic nitrogen through phytoplankton respiration and mortality; mineralization of organic nitrogen; water column nitrification; oxygen dependent water column denitrification; sediment regeneration of ammonia; and zero-order benthic nitrification and denitrification (Williams and Lewis 1986). Benthic nitrification, denitrification, and inorganic nitrogen uptake of attached periphyton are accounted for as external forcing functions via the sediment ammonia and nitrate flux terms.

Kinetic processes for phosphorus include: phytoplankton and periphyton uptake of inorganic phosphorus; recycle of inorganic and organic phosphorus through phytoplankton respiration and mortality; mineralization of organic phosphorus; sediment regeneration of phosphate; and deposition of particulate inorganic phosphorus via sorption-desorption. Phosphate uptake of attached periphyton is accounted for as an external forcing function via the sediment phosphate regeneration term.

Kinetic processes for dissolved oxygen include: (1) source terms for atmospheric reaeration; photosynthetic oxygen production of the phytoplankton and attached periphyton; oxygen production through water column denitrification; and (2) sink terms for phytoplankton respiration; oxidation of organic carbon (CBOD5); water column nitrification; benthic nitrification; sediment oxygen demand; and benthic respiration of attached periphyton. Net oxygen production of attached periphyton is accounted for as an external forcing function via the sediment oxygen demand term.

Kinetic processes for phytoplankton include: temperature, light and nutrient dependent growth; temperature dependent respiration; non-predatory mortality; and settling loss through the water column. Zooplankton grazing is not included in the Potomac River Model since planktonic processes are not considered a major component of nutrient and carbon pathways in the Upper Potomac River (see MWCOG, 1984).

Detailed discussions of the kinetic processes, interactions, assumptions and theory of the eutrophication model is presented in Ambrose et al. (1988); Thomann and Fitzpatrick (1982) and Thomann and Mueller (1987). The state equations and model parameters used in the Potomac River Model are detailed in the WASP4 User's Manual (Ambrose et al., 1988). The assumptions and data sources used to specify model parameter values are presented in Section 6 of this report.

5.5 Computational Methods

The computational framework of WASP4 is designed to represent the seasonal variation of nutrients and oxygen within the theory of eutrophication processes. High frequency diurnal variability of oxygen and phytoplankton is not explicitly addressed in WASP4. The appropriate time scale for the model is coupled to the availability of data used to construct the forcing functions for the model. Since the frequency of water quality and pollutant loading observations is usually available only on a time scale of weeks to months, the model is best suited for use as a long term projection tool for the evaluation of nutrient control measures where the time scale of concern is typically seasonal in nature (see Thomann and Fitzpatrick, 1982). The use of the model as a steady state tool is thus appropriate since the time interval for the simulations (25 days) is sufficiently long to allow spin up of the model to an approximate equilibrium condition based on the total travel time of 20-25 days from Luke, Maryland to Chain Bridge.

The coupled differential equations describing the transport, point and non-point source loading and kinetics are solved using a finite difference approximation technique (Thomann and Mueller, 1987) with a general water quality model (WASP4, Ambrose et al. 1988). With eight state variables and 48 segments, 384 simultaneous differential equations are solved at every time step (dt = 0.02 days). Model results, written at 5 day intervals of the 25 day simulation period, are compared with the observed data for the final time interval of the simulation. Using a 386SX 20 mHz PC, the computations require approximately 15 minutes clock time for a 25 day simulation. Pre- and post-processing steps for model output extraction and graphics require an additional 15-20 minutes clock time. Details of the computational techniques of WASP4 are presented in Ambrose et al. (1988) ; Thomann and Fitzpatrick (1982) and Thomann and Mueller (1987).

Table 5- Potomac River Model Segments and River Mile Coordinates

	Upstr	Dwnstr	Seg Cntr
SG001 Westvaco	340.0	338.7	339.35
SG002 Georges Ck	338.7	338.2	338.45
SG003 UPRC STP	338.2	336.3	337.25
SG004 Stony Run	336.3	332.7	334.50
SG005 Keyser	332.7	331.4	332.05
SG006 21st Br	331.4	328.5	329.95
SG007 Dawson	328.5	326.0	327.25
SG008 Black Oak	326.0	322.0	324.00
SG009 Rawlings	322.0	318.3	320.15
SG010 Pinto	318.3	314.1	316.20
SG011 Cresaptown	314.1	313.4	313.75
SG012 Celanese	313.4	309.6	311.50
SG013 Md.Jnctn.	309.6	307.3	308.45
SG014 Wills Ck	307.3	305.2	306.25
SG015 Wiley Ford	305.2	304.0	304.60
SG016 Cumbrlnd STP	304.0	298.5	301.25
SG017 Mexico Field	298.5	294.1	296.30
SG018 Pattersn Ck	294.1	285.1	289.60
SG019 So. Branch	285.1	282.6	283.85
SG020 Town Ck	282.6	279.8	281.20
SG021 L Cacapon R	279.8	276.5	278.15
SG022 Paw Paw	276.5	255.2	265.85
SG023 15 Mile Ck	255.2	251.3	253.25
SG024 SidelingH.Ck	251.3	247.7	249.50
SG025 Cacapon R	247.7	238.6	243.15
SG026 Hancock	238.6	231.2	234.90
SG027 Licking Ck	231.2	227.1	229.15
SG028 Ft Frederick	227.1	217.4	222.25
SG029 Dam #5	217.4	210.8	214.10
SG030 Conocochg Ck	210.8	201.9	206.35
SG031 Opequon Ck	201.9	195.3	198.60
SG032 Dam #4	195.3	183.6	189.45
SG033 Sheperdstown	183.6	179.3	181.45
SG034 Antietam Ck	179.3	173.1	176.20
SG035 Pleasntv.Dam	173.1	171.5	172.30
SG036 Shenandoah R	171.5	165.8	168.65
SG037 Brunswick	165.8	163.4	164.60
SG038 CatoctinCkMD	163.4	159.5	161.45
SG039 Pt of Rocks	159.5	153.1	156.30
SG040 Monacacy R	153.1	147.1	150.10
SG041 Whites Ferry	147.1	142.2	144.65
SG042 Goose Ck	142.2	133.9	138.05
SG043 Seneca Ck	133.9	129.1	131.50
SG044 Watts Branch	129.1	126.3	127.70
SG045 Gr Falls Dam	126.3	118.4	122.35
SG046 Ruppert Isl.	118.4	117.4	117.90
SG047 L. Falls Dam	117.4	115.9	116.65
SG048 Dummy Sed.Layer	340.0	115.9	227.95

6.0 Documentation of WASP4 Model Input Data

The purpose of this section is to provide an overview of the data sources and key assumptions used to develop the model. The documentation is organized according to the input file structure of WASP4 and EUTRO4 (Ambrose et al. 1988).

Data Group A- Simulation Control Data
Data Group B- Exchange Coefficients
Data Group C- Segment Volumes
Data Group D- Flows and Transport
Data Group E- Boundary Conditions
Data Group F- Point Sources
Data Group G- Spatial Forcing Functions
Data Group H- Chemical and Kinetic Constants
Data Group I- Time Varying Forcing Functions
Data Group J- Initial Conditions

6.1 Data Group A- Simulation Control Data

The starting and ending time period for each steady state analysis is based on the travel time from Luke, Maryland to Chain Bridge. For each case, travel time ranged from 20-25 days (Figure 4) . Using a time step of 0.02 days based on the minimum travel time within the model segments, the simulation interval of 25 days allowed for spin up to approximate steady-state equilibrium conditions. Model output was transformed to calendar date (as mm/dd/19yy and Julian date) and 24 hr clock time for post-processing. Segment coordinates, depth, surface area and volume are presented in Appendix L through Appendix M.

6.2 Data Group B- Exchange Coefficients

Longitudinal dispersion coefficients, based on 1964 and 1981 USGS dye studies in the Potomac, were documented by ICPRB (1991) in a preliminary report. Model segmentation (N=48) is based on Hydroscience (1976) (see Table 5). Dispersion coefficients, characteristic lengths and cross sectional areas for each case are presented in Appendix L through Appendix O.

6.3 Data Group C- Segment Volumes

Segment geometry (cross sectional and surface area, length, depth and volume) is based on flow dependent data compiled for an earlier study of the Upper Potomac River by Hydroscience (1976). Velocity, depth, cross-sectional area and width for each segment are computed as power functions of streamflow (Hydroscience, 1976; Ambrose et al., 1988).

The effect of turbulent reaeration over the numerous dams and rapids areas on the oxygen balance of the Upper Potomac River under relatively low flow conditions (<6,000 cfs at Little Falls) have been incorporated in the determination of the flow dependent coefficients for velocity, depth, cross sectional area and segment width (Hydroscience, 1976). Explicit incorporation of an additional term to account for the reaeration effect of dams and rapids on the oxygen balance (see Thomann and Mueller, 1987) is thus not needed for this model. Physical characteristics of velocity, depth, width and cross sectional area are computed for each model segment as follows:

Velocity: $U = a\,Q^{b}$

Depth : $H = c\,Q^{d}$

Width : $W = e\,Q^{f}$

Cross Section Area: $A = g\,Q^{h}$

Segment geometry and the velocity and depth hydraulic coefficients for each case are presented in Appendix L through Appendix O.

6.4 Data Group D- Transport

Transport data consists of advective flow coefficients based on a steady state flow balance of: USGS gauged streamflow in the mainstem Potomac and tributaries; observed (or assumed) effluent discharge rates for point sources; and reported water supply diversion withdrawals. Flow balances were developed for each case to allocate "missing" flow to the numerous ungauged tributaries that discharge directly to the Upper Potomac River Flows were developed to characterize individual waste treatment discharges, gauged and ungauged tributary inflows and water supply diversion. Summary flows were computed to characterize total inflow and outflow for each segment for model input. Cumulative mainstem flow and for each case is presented in Figure 5. Velocity and depth distributions computed for each case are presented in Figure 6a and Figure 6b. Individual point source and aggregate flows for the four cases are presented in Appendix L.

Spatially varying vertical settling velocities were specified for WASP4 solids fields for organic nutrients; phytoplankton and particulate inorganic phosphorus. The settling velocities for the phytoplankton and phosphorus were primarily used as "tuning" parameters to properly characterize the observed spatial distributions (Table 6).

Figure 4- Travel time for the Potomac River Model: October 1984, September 1985, September 1986 and July 1987

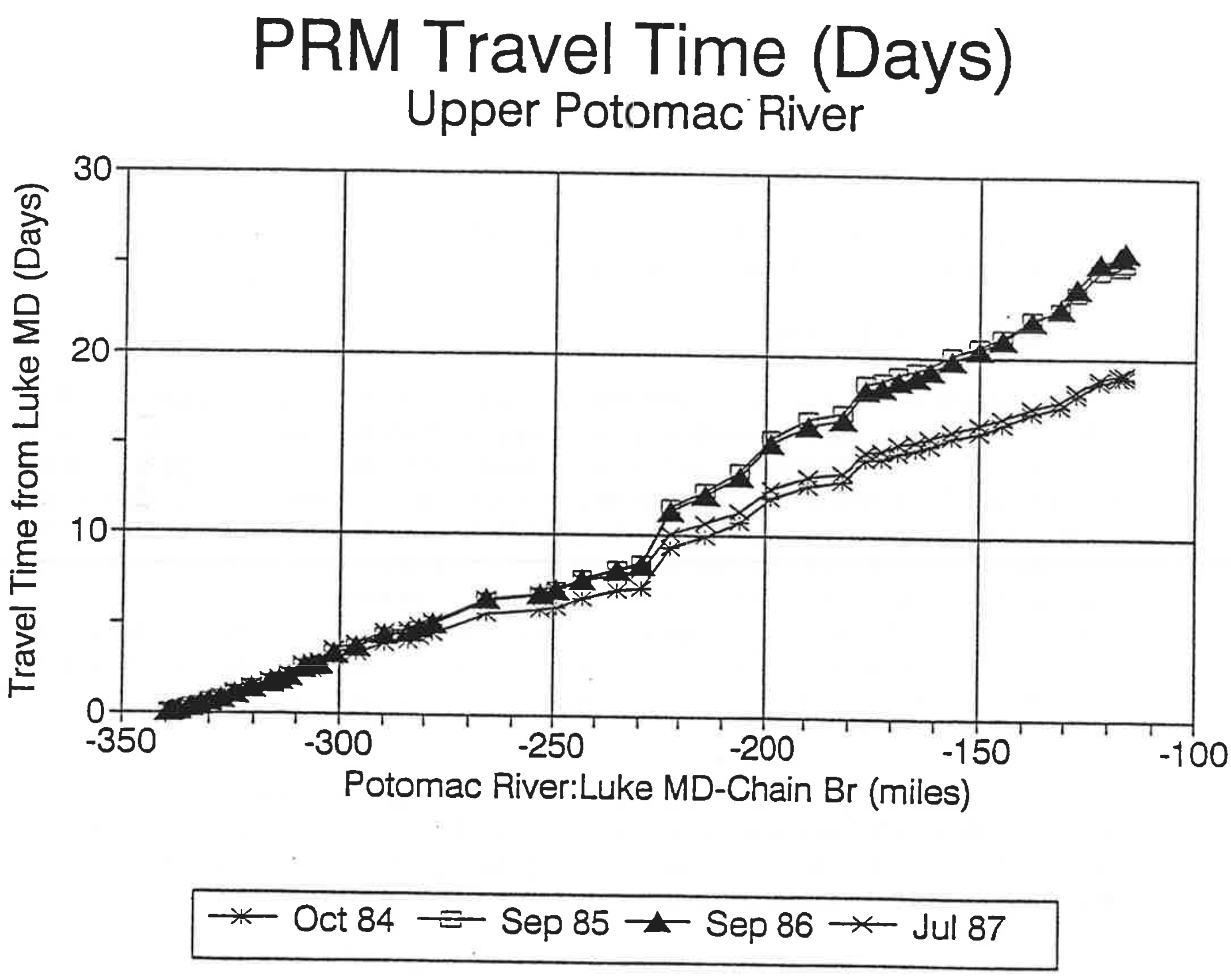


Figure 5- Cumulative Mainstem Flow for the Potomac River Model: October 1984, September 1985, September 1986 and July 1987

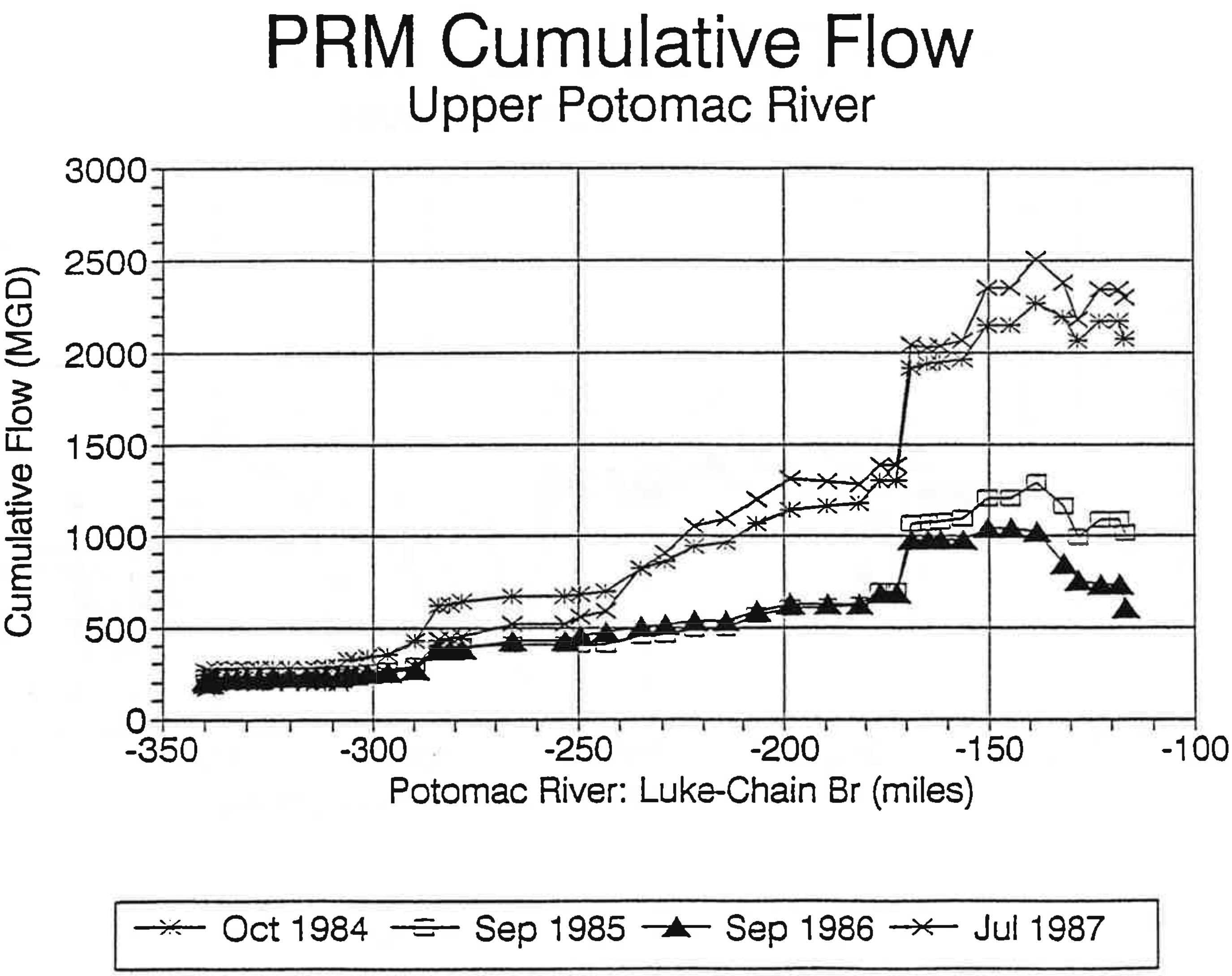


Figure 6a- Velocity distributions for the Potomac River Model: October 1984, September 1985, September 1986 and July 1987

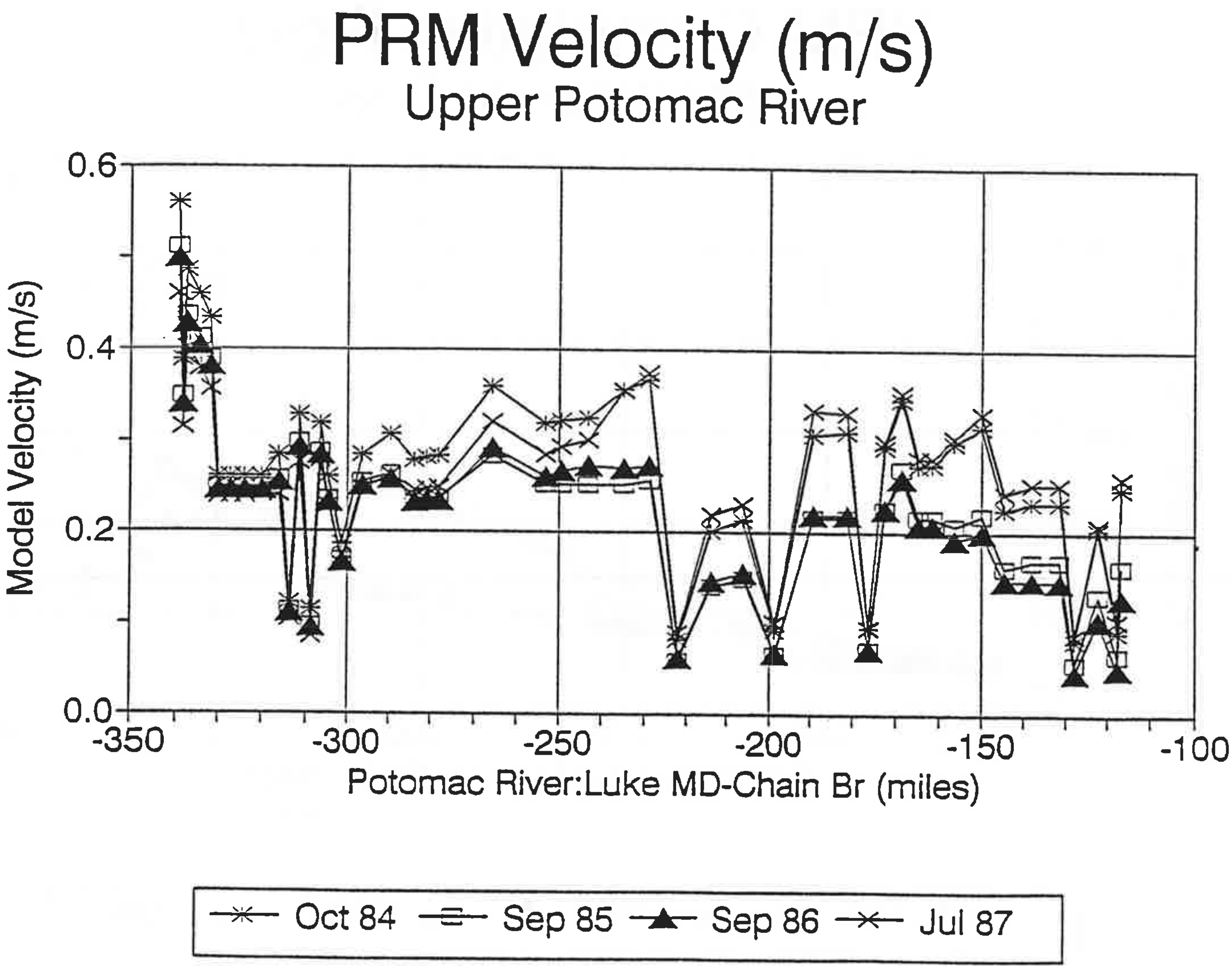


Figure 6b- Depth distributions for the Potomac River Model: October 1984, September 1985, September 1986 and July 1987

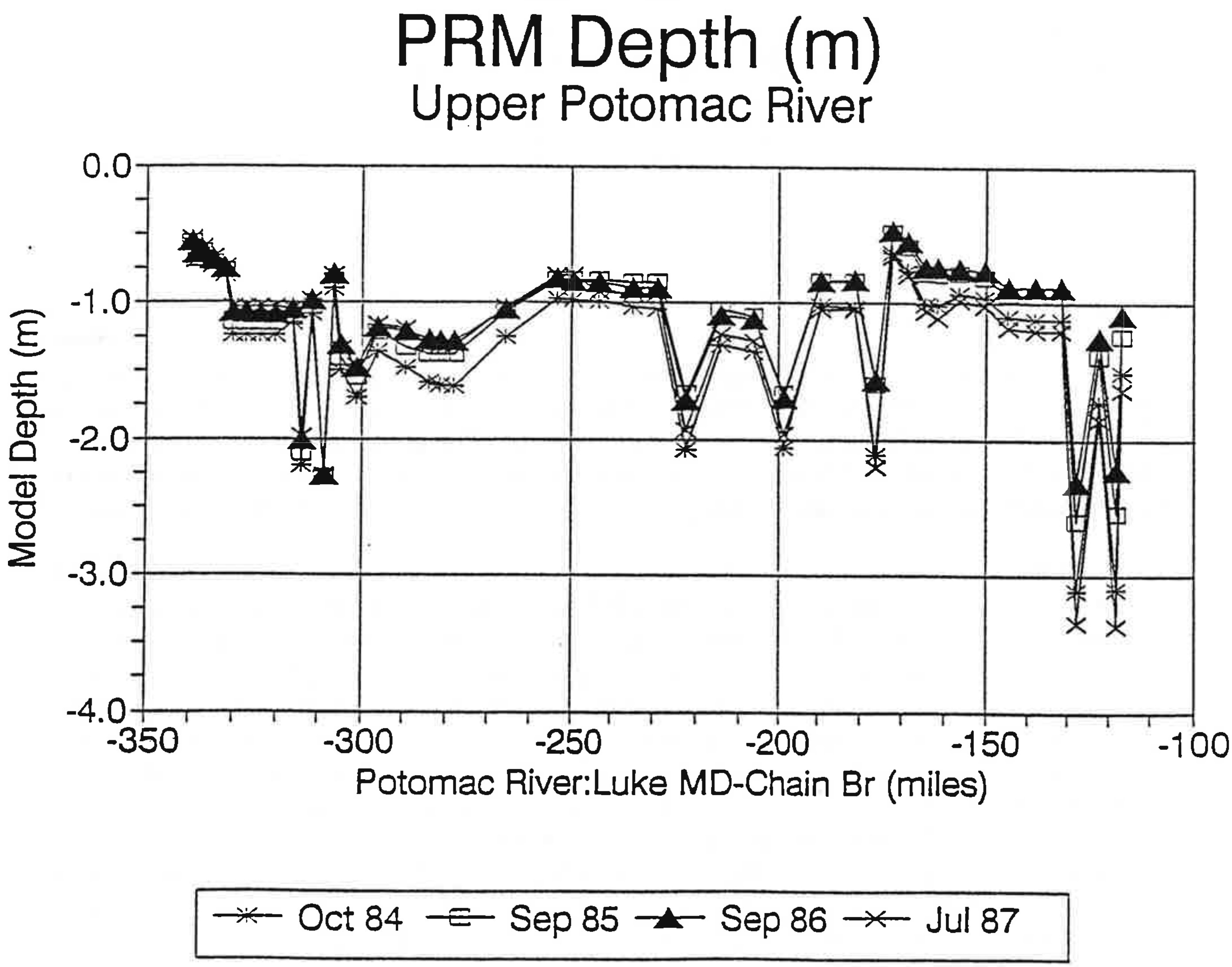


Table 6- Settling velocity for particulate organics (F#3); phytoplankton (F#4); and particulate inorganic phosphorus (F#5)

Seg#	F#3 Oct 1984	F#3 Sep 1985	F#3 Sep 1986	F#3 Jul 1987
01-47	0.05	0.05	0.05	0.05

Seg#	F#4 Oct 1984	F#4 Sep 1985	F#4 Sep 1986	F#4 Jul 1987
01-39	0.05	0.05	0.05	0.05
40-47	0.25	0.75	0.05	0.75

Seg#	F#5 Oct 1984	F#5 Sep 1985	F#5 Sep 1986	F#5 Jul 1987
01-04	25.00	25.00	25.00	25.00
05-15	5.00	5.00	5.00	5.00
16-21	3.00	3.00	3.00	3.00
22-33	3.00	3.00	3.00	3.00
34-47	4.00	1.50	4.00	4.00

6.5 Data Group E - Boundary Conditions

Boundary conditions are specified for each of the eight state variables for the upstream (Luke, Maryland: RM 340) and downstream (Chain Bridge: RM 115) regions of the Upper Potomac River as well as all tributary and point source discharges of municipal and industrial effluent. All flow and mass inputs are thus accounted for in both the transport flow balance and the boundary loading of nutrients, phytoplankton, CBOD and oxygen.

Where observed effluent data were not available, default parameter values of nutrients and CBOD developed by the EPA Chesapeake Bay Program for secondary treatment plants were used to estimate mass loading (Table 7). Different default data were used to account for the pre- and post- 1986 phosphate detergent ban for Maryland municipal dischargers. Water quality data for ungauged tributary discharges was estimated by assigning the nearest available gauged tributary water quality data as a default concentration (e.g. observed Goose Creek data assigned to Difficult Run etc.). Gauged water quality data compiled for the major tributaries to the Potomac River is summarized in Appendix L through Appendix O. Missing water quality data for a specific tributary or effluent input was estimated according to the following hierarchy: nutrient ratios based on available data paired for the time increment (e.g. TN missing; TP available then TN = TP * TN/TP); constant value nearest (in time); linear interpolation in time; or default value.

Appendix L through Appendix O presents individual point source and segment summaries for boundary condition concentration and loads used to characterize loading for each simulation case.

Table 7- Default parameter values of nutrients, oxygen and CBOD for municipal secondary waste treatment plants (after EPA Chesapeake Bay Program)

	STPDEF04 .F84 (a)	STPDEF09 .F86 (b)	STPDEFVA .F84 (c)
NH3_N mg N/L	9.000	9.000	13.7
NO2+NO3 mg N/L	6.300	6.300	2.1
O_PO4_P mg P/L	2.600	2.600	5.2
Phytopl ug Chl/L	0.000	0.000	0
CBOD5 mg/L	27.500	27.500	27.5
Oxygen mg/L	6.250	6.250	6.25
Org_N mg N/L	2.700	2.700	2.9
Org_P mg P/L	0.400	0.400	1.2
TKN mg N/L	16.000	16.000	16.6
TN mg N/L	18.000	18.000	18.7
TP mg P/L	6.000	3.000	6.4

Nutrient []'s in mg/l for Point Sources with Secondary Treatment
(a) Maryland, W Va 1984-1985 effluent characterization
(b) Maryland, W Va 1986-1987 effluent characterization
(c) Va 1984-1987 effluent characterization

6.6 Data Group F- Point Sources

Since all tributaries, municipal and industrial discharges were accounted for as boundary conditions, no "point source" loading data were required for the model. The model input file consisted of a dummy data set of zero loads for one segment for each state variable.

6.7 Data Group G- Spatial Forcing Functions

Time invariant spatial forcing functions were defined on the basis of actual field data and best estimates from the literature. Spatial forcing functions for the Potomac River Model included: water temperature; background extinction coefficients; sediment oxygen demand; benthic ammonia and phosphate regeneration and benthic nitrification and denitrification. In addition, WASP required input for velocity functions and salinity distributions that were not used in this analysis.

A major component of effort in calibrating the model consisted of developing a benthos sub-model as an empirical external boundary forcing function for nutrients and oxygen. WASP4 allows for the specification of sediment fluxes of ammonia, phosphate and oxygen. An additional sediment source flux of nitrate was added to the model to account for sediment nitrate production and losses. The benthos sub-model consisted of the following components: sediment oxygen demand; benthic ammonia and phosphorus regeneration as stoichiometric equivalents of SOD; benthic nitrate loss (denitrification) or production (nitrification); benthic nitrification; gross primary production by benthic algae (periphyton); and nutrient uptake by benthic algae. In addition, non-point source loading of nitrate and phosphate from agricultural and forest land use areas were incorporated in the net nitrate and phosphate source term.

Data tables used to develop model input files for the spatial forcing functions are presented in Appendix L through Appendix O for each of the four simulation case.

Water temperature. The spatial distribution of ambient water temperature was based on monthly grab sample mainstem monitoring station data and daily temperature records from the following raw water intakes: Rockville, WSSC, Washington County, and Williamsport raw water intakes, and the gauge at Pinto. Figure 7a through 7d shows the spatial distributions of water temperature used for each of the four simulation cases.

Background extinction coefficient. Background extinction coefficients were initially estimated using assumptions of water clarity and a chlorophyll-secchi depth relationship reported by Lorenzen (1980). Since actual field measurements of light extinction in the water column was not available, the preliminary calibration results were unsatisfactory for the 1985 and 1987 cases. Preliminary assumptions of non-chlorophyll related water clarity coupled with assumed chlorophyll levels resulted in apparently unrealistic estimates of secchi depth and total extinction coefficient. Final calibration and verification for the four cases is based on a constant background extinction coefficient for clear water (0.04 m^{-1}) (Parsons and Takahashi, 1973) for all segments. Total water column light extinction in the model is the sum of the background extinction coefficient and the chlorophyll dependent extinction coefficient (Ambrose et al. 1988; Riley, 1956).

Sediment oxygen demand. The significance of sediment oxygen demand (SOD) on the oxygen balance of lakes, rivers, coastal and estuarine systems has been well documented (e.g. Butts and Evans, 1978; Butts, 1974; Hatcher, 1986). In the absence of field data, parameterization of SOD for use in a water quality model is somewhat complicated since observed rates of sediment oxygen demand reflect the net oxygen balance of a number of simultaneously occurring biochemical and biological processes.

Biochemical oxidation of organic carbon is obviously a major component of observed SOD. The overall community metabolism of benthic macroinvertebrates, macrophytes and epiphytic primary producers, however, can be significant components of observed SOD (see Terry and Morris, 1986; Jeppesen and Thyssen, 1984). In particular, attached benthic algae can represent a significant component of the net oxygen balance resulting in substantial diurnal variability of dissolved oxygen, as reported for the South Fork of the Shenandoah River (Deb and Bowers, 1983).

Since field data are not available to characterize SOD over the 200 mile reach of the Upper Potomac River, an external spatial forcing function for SOD was parameterized for the model. SOD was estimated on the basis of river velocity, typical ranges of SOD values for various substrates (Thomann and Mueller, 1987; Bowie et al. 1985; Murphy and Hicks, 1986), oxygen demand of assumed benthic nitrification rates and assumed rates of net primary productivity of periphyton. SOD was empirically parameterized for each segment as the product of: (1) maximum SOD specified for each segment [SOD_{max} (x)]; (2) temperature dependence for SOD [$f_{sod}(T)$]; and (3) normalized function of current velocity, [$f_{sod}(U)$] as follows:

$$SOD\ (x) = SOD_{max}\ (x) * f_{sod}(T) * f_{sod}(U)$$

Consistent with a recent SOD model (DiToro,1986; 1990), SOD and velocity dependence data reported by Whittemore (1986) was used to develop a normalized Gaussian function wherein SOD increases as a function of velocity. Figure 8 presents the normalized velocity function used to parameterize SOD for the Potomac River Model. The function is based on a Gaussian distribution with a mean value of 100 cm/s and a standard deviation of 42.5 cm/s. Figure 8 also presents the observed data of Whittemore (1986) that is in fair agreement with the model formulation.

The oxygen demand resulting from zero-order benthic nitrification and net photosynthesis and respiration of attached periphyton was accounted for in estimating the total SOD distribution. Figures 9 through 12 present the empirical SOD distributions used for the four model cases with the components indicated for biochemical SOD, benthic nitrification and net oxygen production of periphyton.

Benthic algae production. In shallow streams and rivers, attached epiphytic algae and benthic macrophytes can account for significant components of observed oxygen and nutrient distributions (Jeppesen and Thyssen, 1984). In particular, steep gradient reaches of rivers with high current velocity (ca. 50 cm/s) and sufficient nutrient supply are typically characterized by maximum rates of benthic primary productivity from periphyton (Hynes, 1970; Horner and Welch, 1981; Welch et al. 1989). Consistent with other studies reported in the literature, stream velocity increases of up to ~50 cm/s have been observed to result in enhanced biomass accumulation and productivity of attached periphyton (Horner and Welch, 1981). Velocities higher than ~50 cm/s tend to result in reduced biomass accumulation because of physical scouring and removal of attached biomass.

Since the North Branch of the Potomac is characterized by steep elevation gradients, pools and riffles and high velocity conditions, it is probable that attached periphyton can exert a significant influence on oxygen and nutrient distributions. Other reaches of the Upper Potomac River are also characterized by physical conditions conducive to the development of attached periphyton (e.g. Harpers Ferry to Point of Rocks) that could also account for significant components of the observed oxygen and nutrient distributions.

Based on the physical characteristics of the Upper Potomac River, and observations reported in the literature, gross primary production of attached periphyton was parameterized in the model using a normalized velocity dependent function similar to that used for SOD. Figure 13 presents the normalized velocity function used to parameterize gross periphyton production for the Potomac River Model. The function is based on a Gaussian distribution with a mean value of 50 cm/s and a standard deviation of 17 cm/s. Figure 13 also presents observed data sets summarized by Horner and Welch (1981) that are in very good agreement with the model formulation.

Since no data were available to describe benthic biomass or benthic primary productivity for the Upper Potomac River, literature values were used to estimate parameter values for gross benthic algae production and production/respiration ratios (P/R) (e.g. Bott et al. 1985). From these literature values, gross benthic algae productivity appears to be on the order of ~0.5 to 5.0 g C m^{-2} d^{-1}. Based on photosynthetic efficiency and assuming that 1 mole O_2 = 112 kcal), gross benthic production (as mg O_2 m^{-2} day^{-1}) is on the order of 0.5 to 5.0 % of total incoming solar radiation (see Thomann and Mueller, 1987).

In a comparative long term seasonal study of four rivers across the USA (Oregon,Michigan, Pennsylvania, and Idaho), Botts et al. (1985) reported summer benthic algae productivity rates of ~0.25 to 2.5 g C m^{-2} d^{-1}. Botts et al. (1985) also reported a range of values of P/R ratios consistent with the "River Continuum Concept" where transitions in community metabolism (i.e. P/R) tend to occur over the domain of a river as small streams develop into larger rivers over a drainage basin (Williams, 1981) (see Figure 14). In general, the data of Botts et al. (1985) tend to support the hypothesis as summarized below:

Upper reach of river : predominant heterotrophy (P/R <1) Middle reach of river: predominant autotrophy (P/R >1)

Lower reach of river : predominant heterotrophy (P/R <1)

Gross periphyton production was parameterized as the product of segment dependent maximum gross production [Pb_{max} (x)] , temperature dependence [$f_{pb}(T)$] and the velocity dependent normalized productivity function [$f_{pb}(U)$] as follows:

$$Pb(x) = Pb_{max}(x) * f_{pb}(T) * f_{pb}(U)$$

Temperature dependence was accounted for by assuming a typical biological Q_{10} of 2.0. Based on the "River Continuum Concept", the P/R data of Botts et al. (1985) (summer P/R ranged from 0.14 to 1.97) and calibration to the observed oxygen data of the Upper Potomac River, a spatial distribution of P/R ratios was specified for the model (Figure 15a through 15d). Figures 15a through 15d also presents the empirical gross periphyton productivity distributions used for the four model cases.

Benthic nutrient regeneration. Since data are not available to characterize these processes for the Upper Potomac River, sediment flux rates of ammonia and phosphate are estimated as the stoichiometric equivalent of the biochemical component of SOD using the "Redfield" ratios (by weight) for O:C:N:P (109: 41: 7.2: 1) (Redfield et al. 1963). Using the O:N ratio of 109 mg O_2: 7.2 mg N benthic regeneration of ammonia is estimated as:

$$jNH3 = SOD * [1000 \text{ mg } O_2 / \text{g } O_2] * [1 \text{ mg N}/15.14 \text{ mg } O_2]$$

where SOD is in units of g O_2/sq m-day and jNH3 has units of mg N/sq m-day. DiToro (1986) has summarized paired measurements of SOD and JNH3 flux to substantiate the assumption of an approximate stoichiometric equivalence of SOD and jNH3 (see Figure 16).

Although the sediment-water interactions for phosphorus recycling are complex, Redfield stoichiometry is appropriate for a preliminary estimate of phosphate flux from the sediments under aerobic conditions. Using the N:P ratio of 7.2 mg N/1.0 mg P, benthic regeneration of phosphate is estimated as:

$$jPO4 = jNH3 * (1 \text{ mg P}/7.2 \text{ mg N})$$

where jPO4 is in units of mg P/sq m-day and jNH3 has units of mg N/sq m-day.

Benthic nitrification and denitrification. A number of studies have demonstrated that nitrification and denitrification may be dominated by benthic processes, particularly in fast moving shallow streams and rivers. Enumerations of nitrifier organisms have demonstrated that benthic populations can be two to three orders of magnitude greater than water column populations (Williams and Lewis, 1986), including a study in the tidal freshwater portion of the Potomac estuary (Shultz, 1989). Several studies have shown that up to 80 to 95% of total nitrification can be accounted for by benthic processes. Studies have included the James River, Virginia (Cerco, 1981), shallow streams in North Carolina (Kreutzberger and Francisco, 1977; Lewis, 1983), the Trent River, England (Curtis et al. 1975; Garland 1978) and the Passaic River (Matulewich and Finstein, 1978).

The sequential forward reactions of mineralization of organic nitrogen and nitrification suggest that nitrate should accumulate as an end product of the reactions. Several data sets, however, suggest instead removal of nitrate from the water column along with the conversion of ammonia to nitrite and nitrate (see Seitzinger, 1988). Simultaneous benthic nitrification and denitrification has been observed in the James River (Cerco, 1981); shallow streams in North Carolina (Williams and Lewis, 1986) and incorporated into water quality models of oxygen and nitrogen distributions (Cerco, 1981; Williams and Lewis, 1986).

Seitzinger (1988) has observed that measured rates of denitrification in most river, lake, estuarine and coastal sediments (i.e. production of N_2O gas) are higher than the corresponding nitrate loss rates to the sediments. The major source of nitrate for sediment denitrification underlying an aerobic water column is nitrate produced in the sediments during nitrification rather than nitrate diffusing from the overlying water column into the sediments.

Observed nitrate distributions in the Upper Potomac River consistently demonstrate a decrease from the confluence of the South Branch of the Potomac (RM 285) to the confluence of the Cacapon River (RM 248). A reduction in nitrate is also observed in the lower portion of the river downstream of the Monacacy River that could be attributed to either phytoplankton uptake or benthic denitrification (see Figure 17).

Based on the literature and observed nitrate distributions in the Upper Potomac River, benthic nitrification and denitrification was incorporated in the Potomac River Model as zero-order external spatial forcing functions for the sediment flux terms for ammonia and nitrate (see Williams and Lewis, 1986). Consistent with bacterial uptake studies reported in Horner and Welch (1981), benthic nitrification is also assumed to be described by the velocity dependence relationship developed for benthic algae production. Reported observations of sediment nitrification and sediment nitrate loss rates are summarized in Table 8. The calibration values used to describe benthic nitrification and benthic nitrate loss rates (at 20C) for the Potomac River Model are shown in Figure 18a and Figure 18b. Temperature dependence is accounted for with temperature coefficients described in Ambrose et al. (1988) for nitrification (1.08) and denitrification (1.045).

Non-Point Input of Nutrients. Although nutrient loading from gauged and ungauged tributaries is strongly influenced by overland runoff from forested and agricultural components of the drainage basin, preliminary calibration runs suggested that additional non-point loading of nutrients was required to match the observed nutrient distributions for all cases. These results are consistent with an earlier nutrient balance model of the Upper Potomac River (Hydroscience, 1976) where an additional non-point nutrient load (29.1 mg N/sq m-day; 7.4 mg P/sq m-day averaged over 20.2 x 10^6 sq m surface area of Segment 40-47) downstream of the Monocacy River (RM 153) was needed to match nitrogen and phosphorus data for July and August 1966. Hydroscience (1976) also observed that Conococheague Creek (~RM 220) was a demarcation between dominance by forest based non-point inputs and agriculturally based loads.

Based on an assessment by ICPRB (1975) of the non-point source input of nutrients from different land uses of the Upper Potomac Basin (see Table 9), spatial distributions of non-point input of nitrate and phosphate (Figure 19) were developed for the Potomac River Model. Aggregation of the ICPRB (1975) non-point loading data over the model segment surface areas resulted in segment flux estimates of agricultural loading rates for nitrate (~268 mg N/sq m-day); phosphate (~56 mg P/sq m-day) and TKN (~29 mg N/sq m-day) (see Table 9). Assuming that ammonia is ~10% of TKN, the agricultural non-point organic nitrogen load is ~26 mg N/sq m-day and the forested non-point contribution is ~ 69 mg N/sq m-day.

The ratio of nitrate to phosphate non-point land yields was estimated by ICPRB (1975) as 4.8 for forest land uses and 4.0 for agricultural land uses. Based on ICPRB (1975), the ratio of agricultural:forest inputs ranged from 2.5 for phosphate to 3.0 for nitrate. In developing the non-point loading functions for phosphate, it was assumed that a ratio of 4.0 described the relative input of nitrate to phosphate over the entire domain of the Upper Potomac, i.e. both forested and agricultural land uses.

The data reported by Hydroscience (1976) and ICPRB (1975) was used as the basis for estimating the appropriate order of magnitude for non-point loading functions for nitrate, phosphate and organic nitrogen and phosphorus for the Potomac River Model.

Table 8- Reported rates of benthic nitrification and benthic nitrate loss (as mg N/sq m-d) (negative values indicate water column loss to the sediments; positive values indicate sediment source to the water column)

Study Site	Range	Reference
Benthic Nitrification		
Lake Mendota	-540 to -900	Kaushik et al. (1981)
Sewage enriched stream	0 to -150	Kaushik et al. (1981)
Laboratory stream	-29[a] to -69[b]	Kaushik et al. (1981)
Benthic Nitrate Loss		
Sewage effluent/canals	-913[c]	Kaushik et al. (1981)
Swifts Brook/Ontario	-480	Kaushik et al. (1981)
Duffin Creek/Ontario	- 40 to -300	Kaushik et al. (1981)
Laboratory columns	- 61 to -166	Kaushik et al. (1981)
Silt enriched columns	-100 to -251	Kaushik et al. (1981)
Sand/Gravel columns	- 20 to - 60	Kaushik et al. (1981)
Streams	-50[a] to -90[b]	Kaushik et al. (1981)
Upper Potomac estuary	-266 to + 23	MWCOG (1987)
Gunston Cove,Potomac	- 36	Seitzinger (1988)

Notes:

[a] absence of tubificid worms

[b] presence of tubificid worms enhances nitrification and denitrification/nitrate loss rates

[c] reported units are mg NO3-N/sq m-d

Table 9- Estimated nutrient loading in the Upper Potomac Basin above Great Falls (after ICPRB, 1975 Table 12)

Land Use	DA (sq mi)	PO4	NO3+NO2	TKN	TN
		(lb/day)			
Forest	6800	3400	13600	2720	16320
Agriculture	4100	5100	24500	2660	27160
Urban	100	110	300	65	365

Upper Potomac Drainage Area Land Yield Coefficients

Land Use	DA (sq mi)	PO4	NO3+NO2	TKN	TN
		(lb/sq mi-day)			
Forest	6800	0.50	2.00	0.40	2.40
Agriculture	4100	1.24	5.98	0.65	6.62
Urban	100	1.10	3.00	0.65	3.65

Land Yield Aggregated Over Potomac River Model Segments

Land Use	PRM Sfc Area (10^6 sq m)	PO4	NO3+NO2	TKN	TN
		(mg/sq m-day)			
Forest (Seg 1-29)	16.15	96.0	384.0	76.8	460.8
Agric. (Seg 30-47)	41.65	55.8	268.2	29.1	297.4

Figure 7a Spatial distribution of water temperature: October 1984

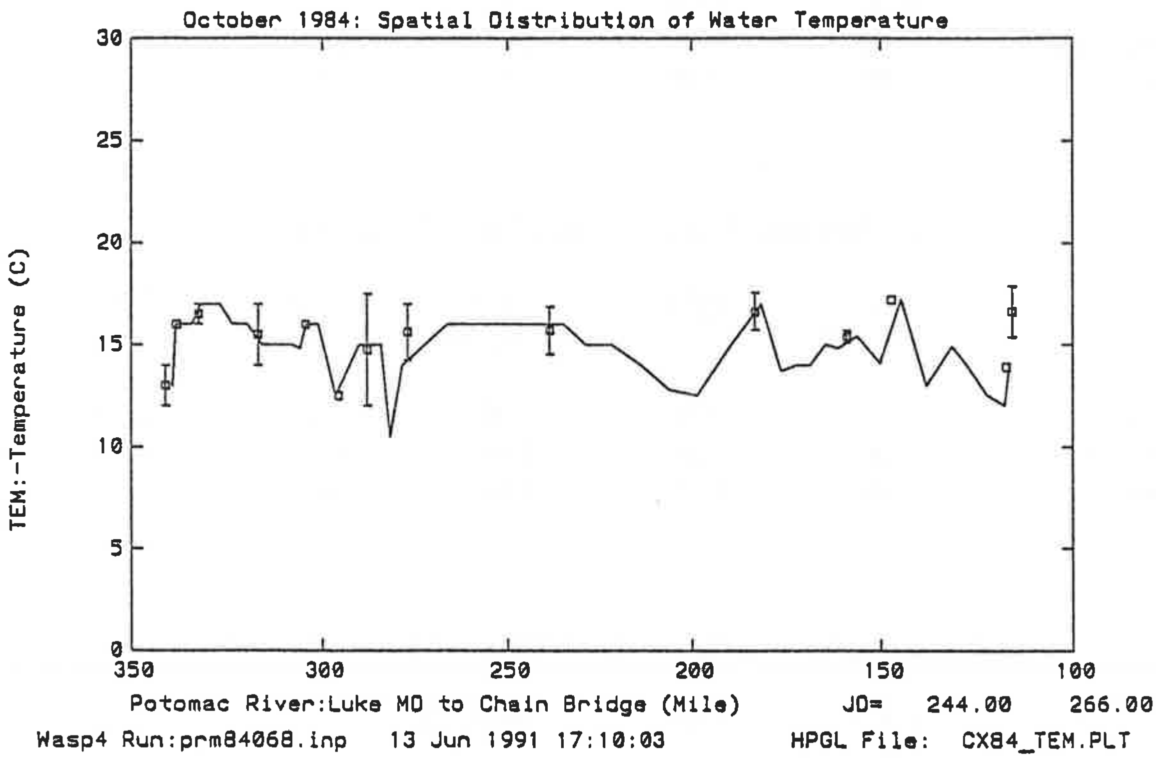


Figure 7b Spatial distribution of water temperature: September 1985

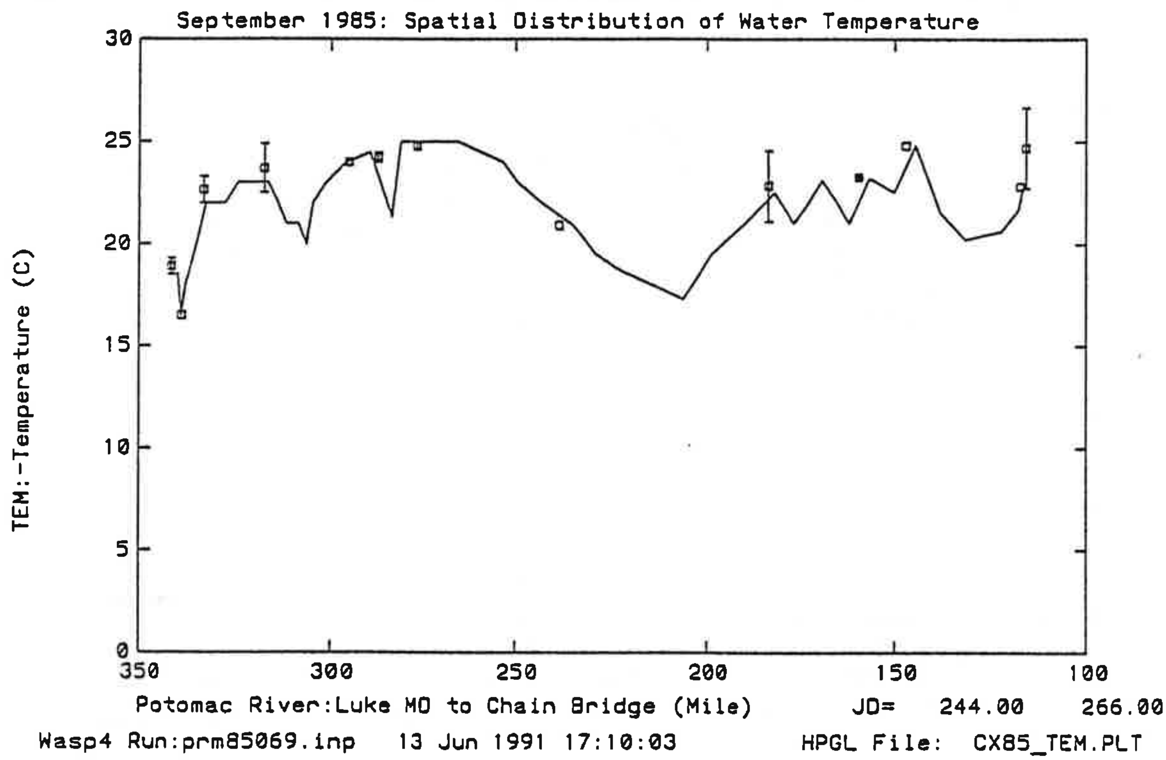


Figure 7c Spatial distribution of water temperature: September 1986

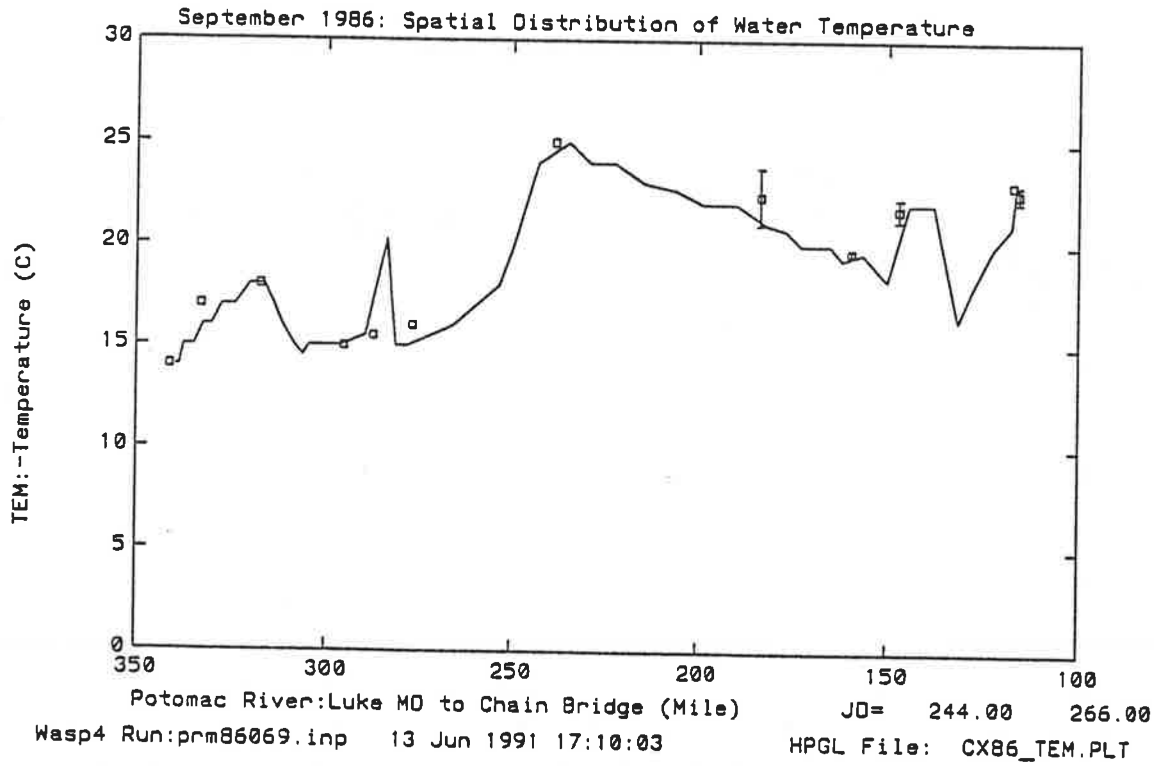


Figure 7d Spatial distribution of water temperature: July 1987

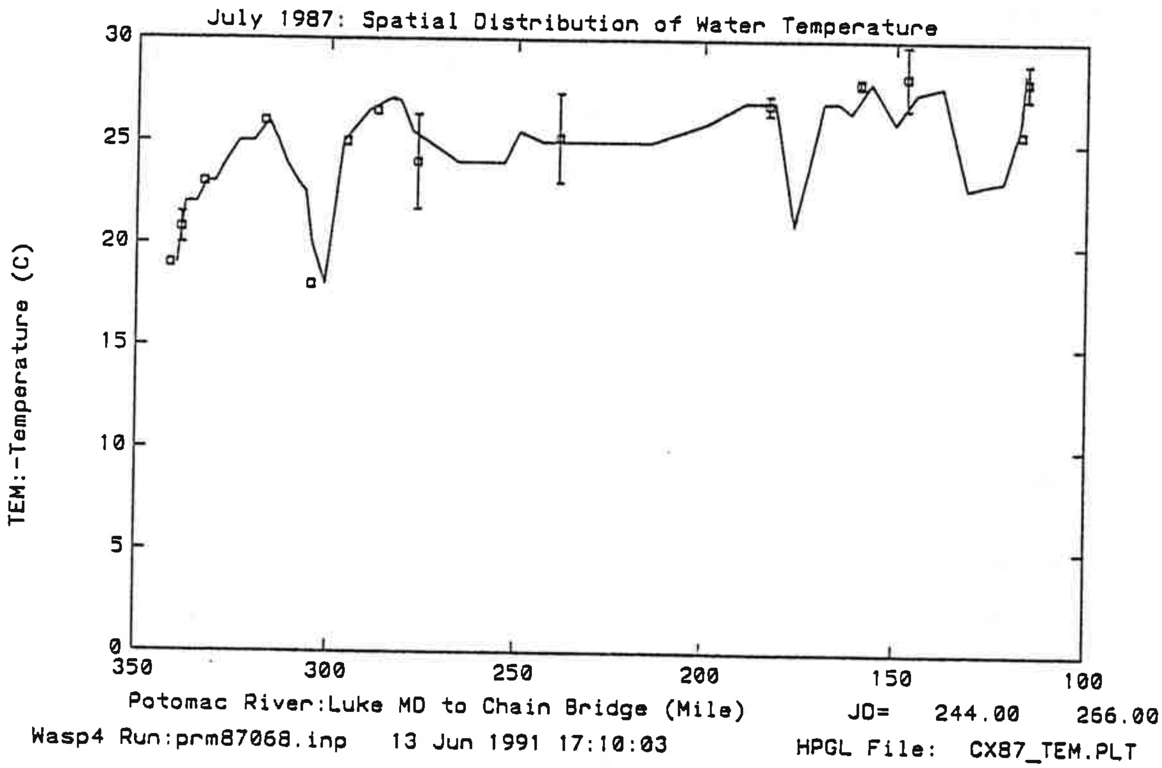


Figure 8 -Normalized velocity function used to parameterize SOD for the Potomac River Model: mean = 100 cm/s ; standard deviation = 42.5 cm/s. Experimental data are from Whittemore (1986).

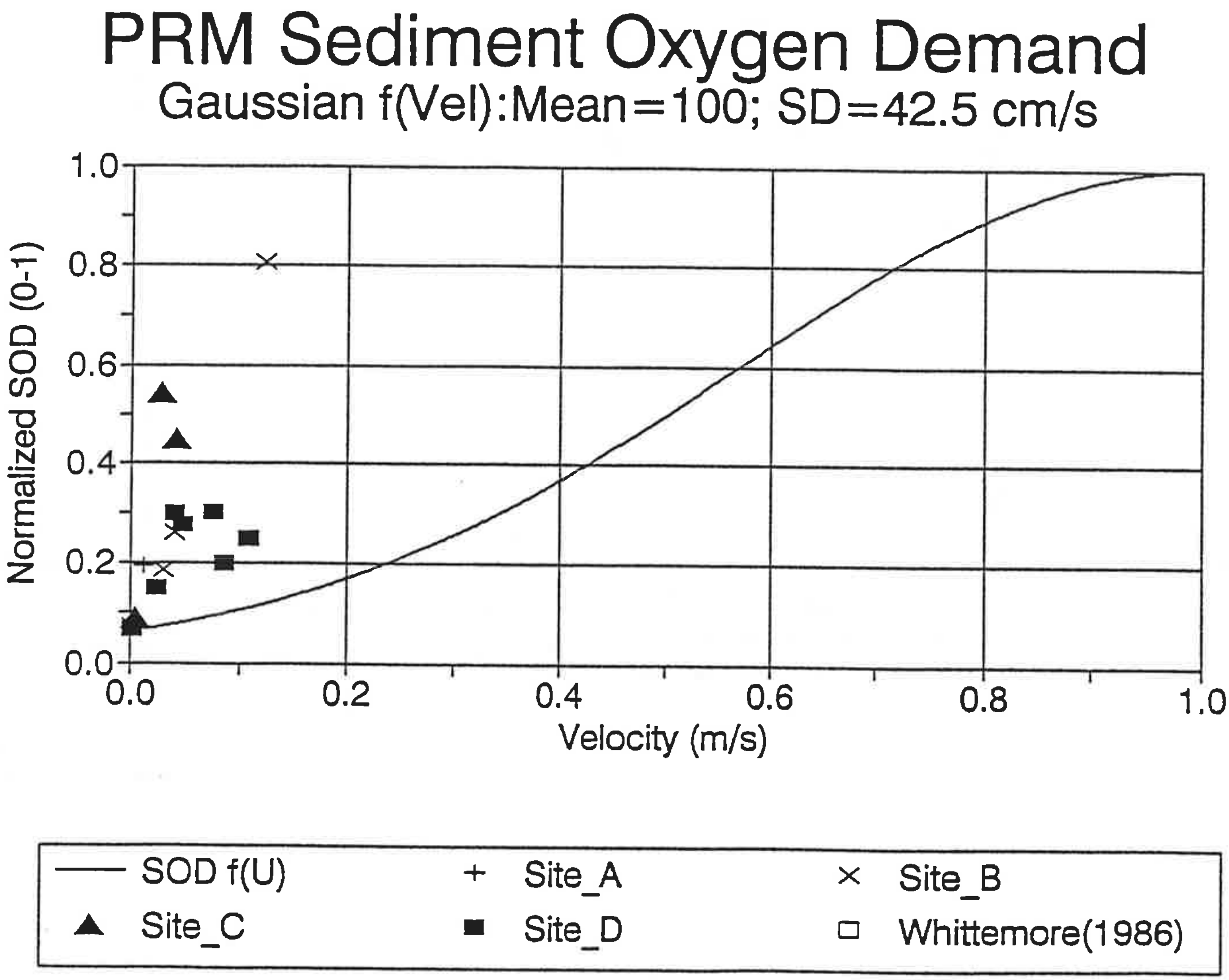


Figure 9- Parameterized SOD distribution used for the Potomac River Model: October 1984

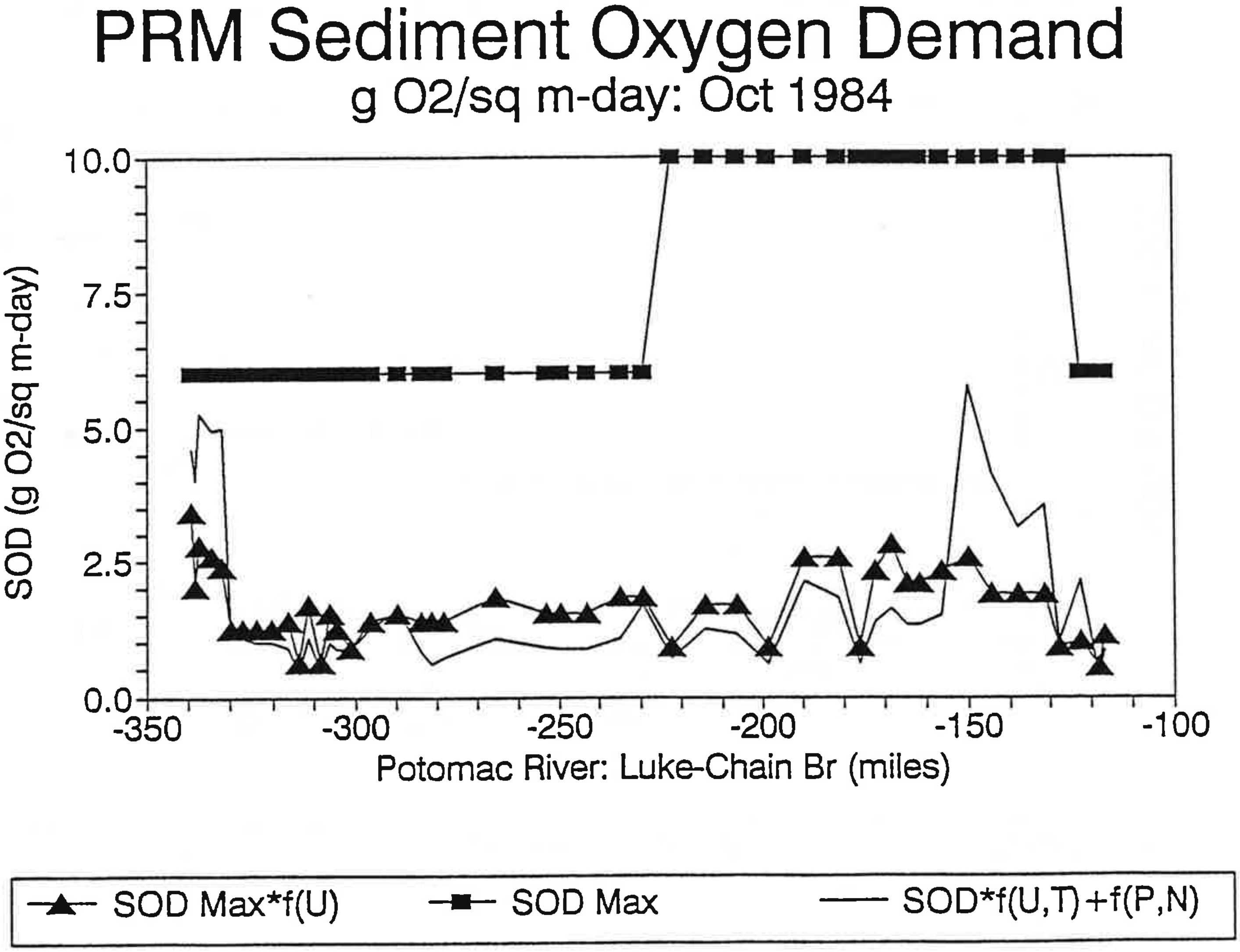


Figure 10- Parameterized SOD distribution used for the Potomac River Model: September 1985

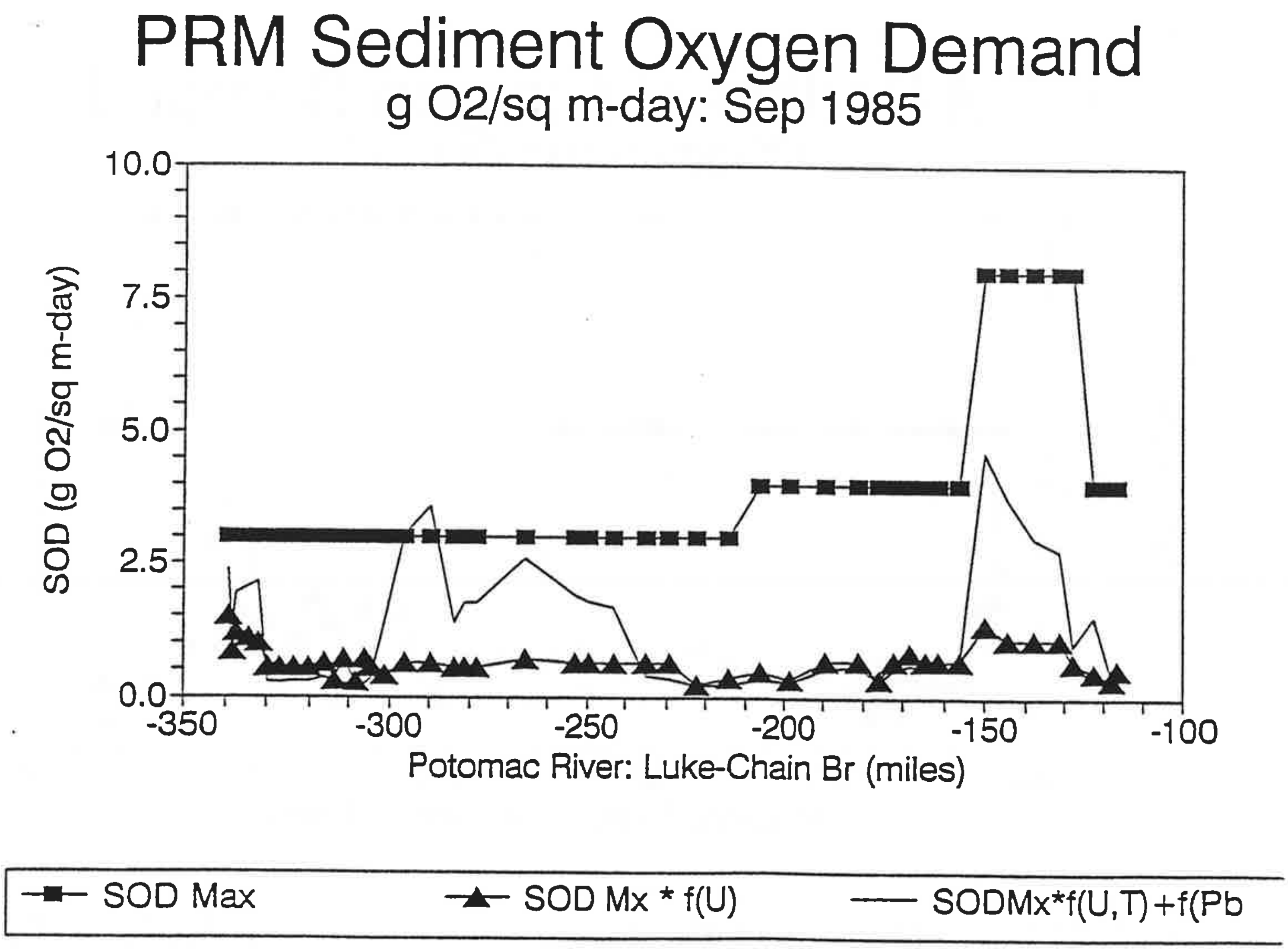


Figure 11- Parameterized SOD distribution used for the Potomac River Model: September 1986

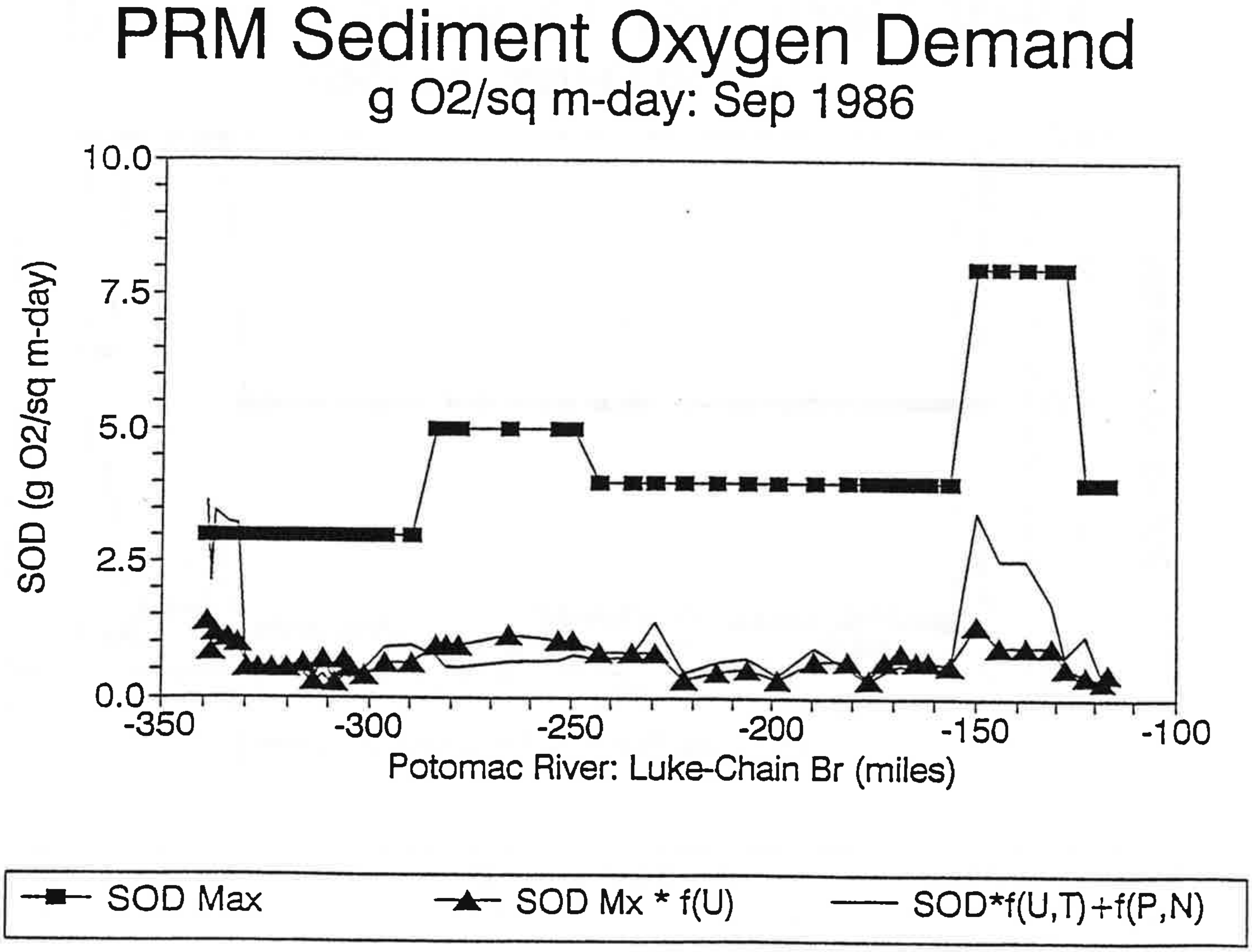


Figure 12- Parameterized SOD distribution used for the Potomac River Model: July 1987

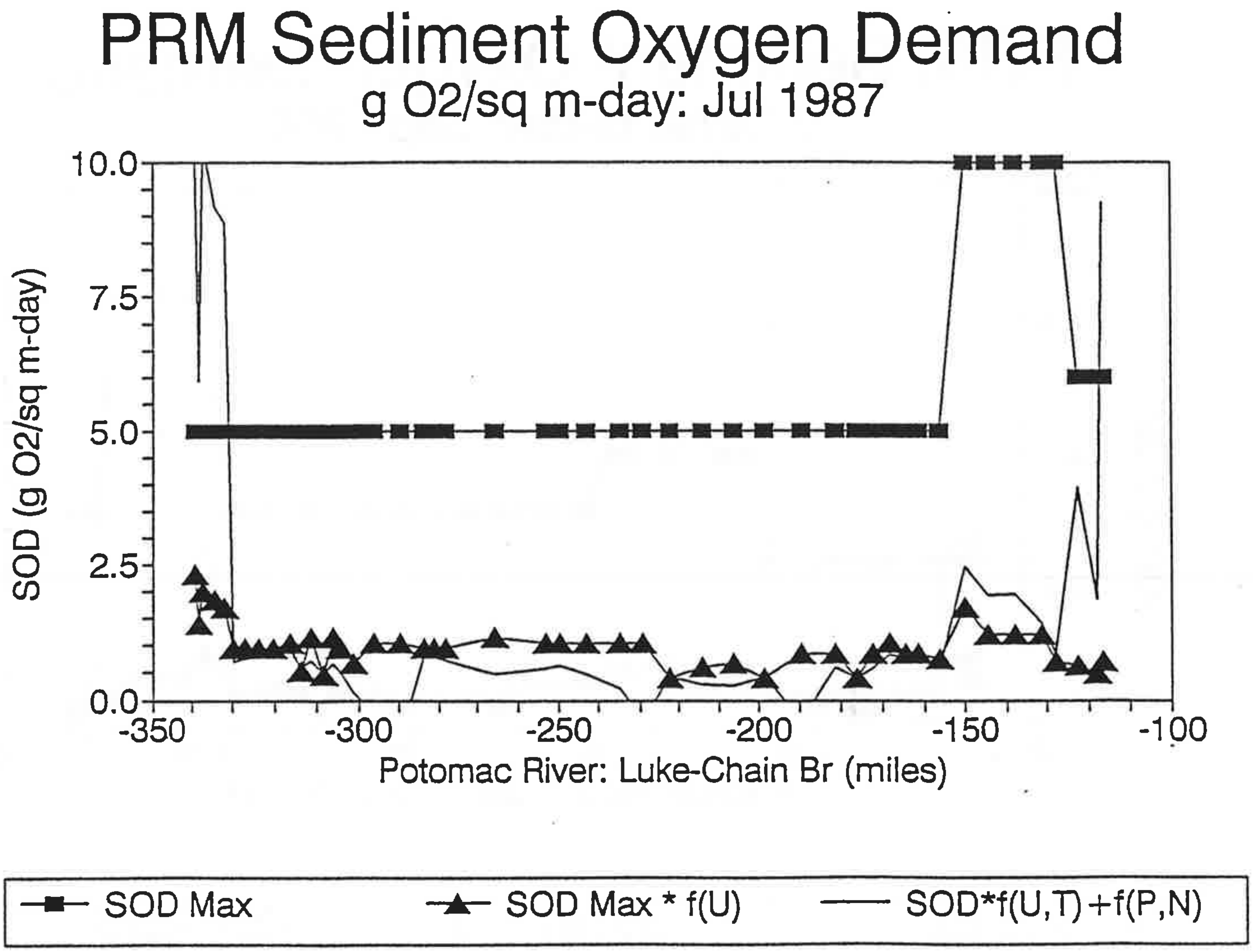


Figure 13 -Normalized velocity function used to parameterize gross periphyton productivity for the Potomac River Model:
mean = 50 cm/s ; standard deviation = 17 cm/s. Observed data are taken from Horner and Welch (1981).

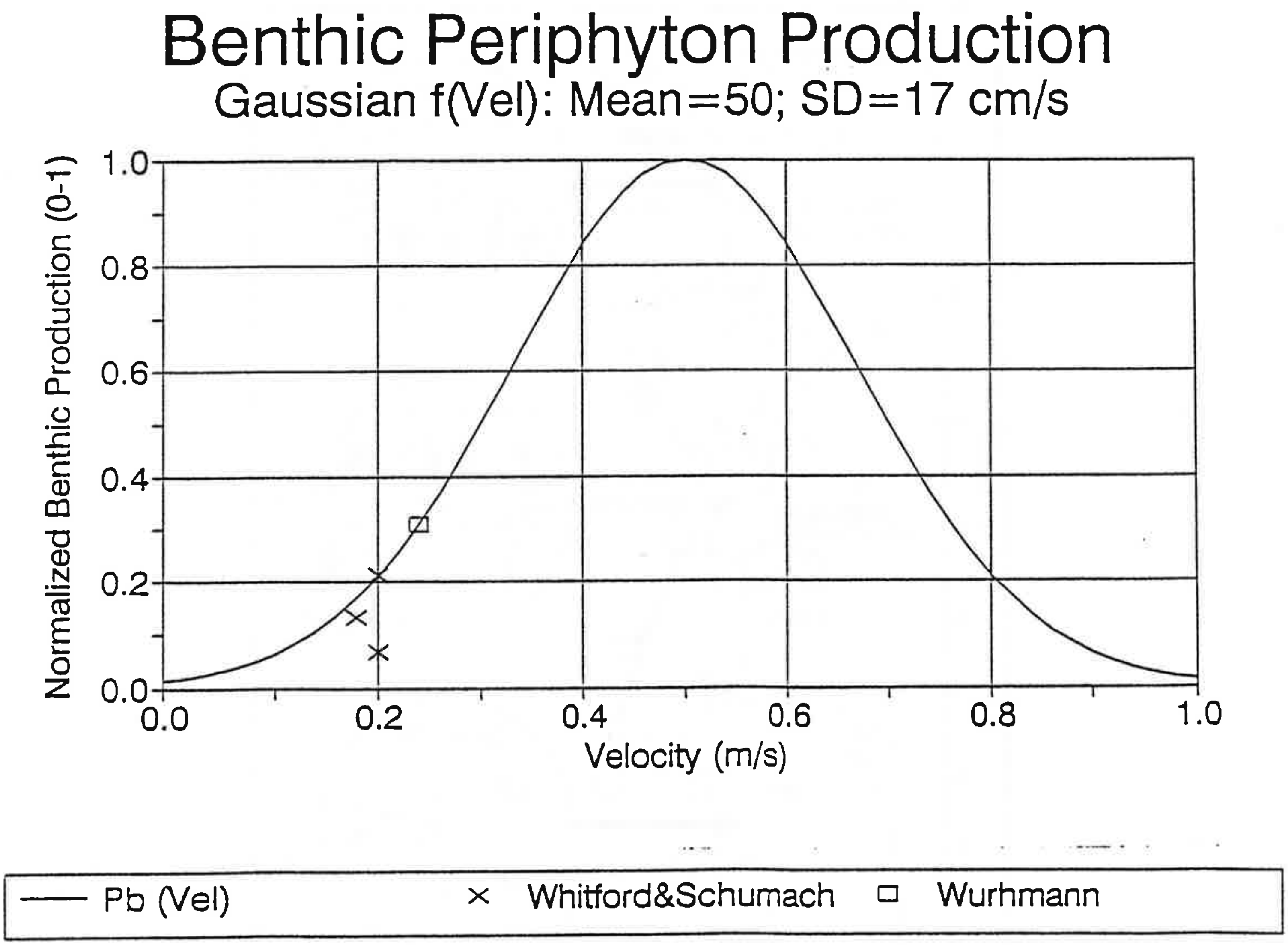


Figure 14- General summary of the longitudinal changes seen in the benthic community of a watercourse (after Williams, 1981 and Cummins 1977).

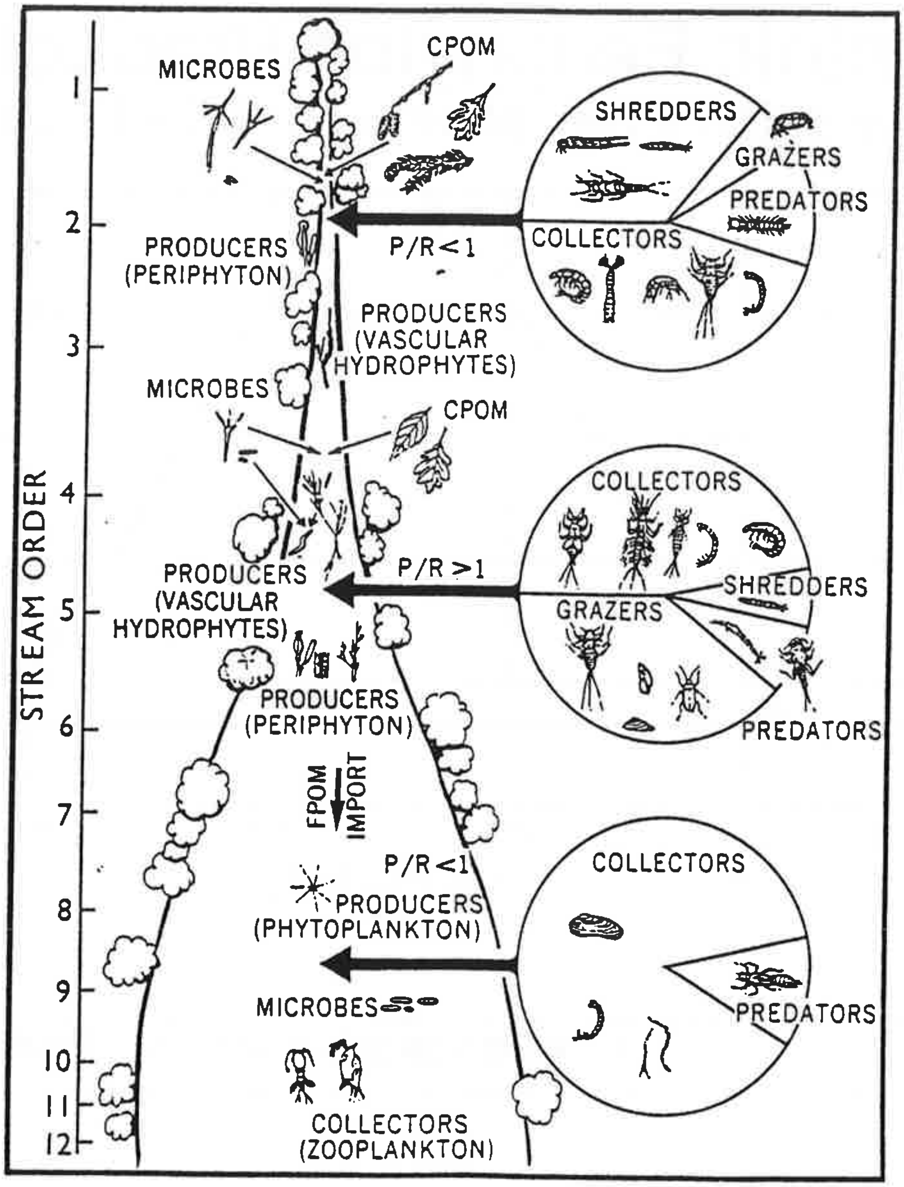


Figure 15a- Spatial distribution of gross periphyton productivity and P/R ratios for the Potomac River Model: October 1984

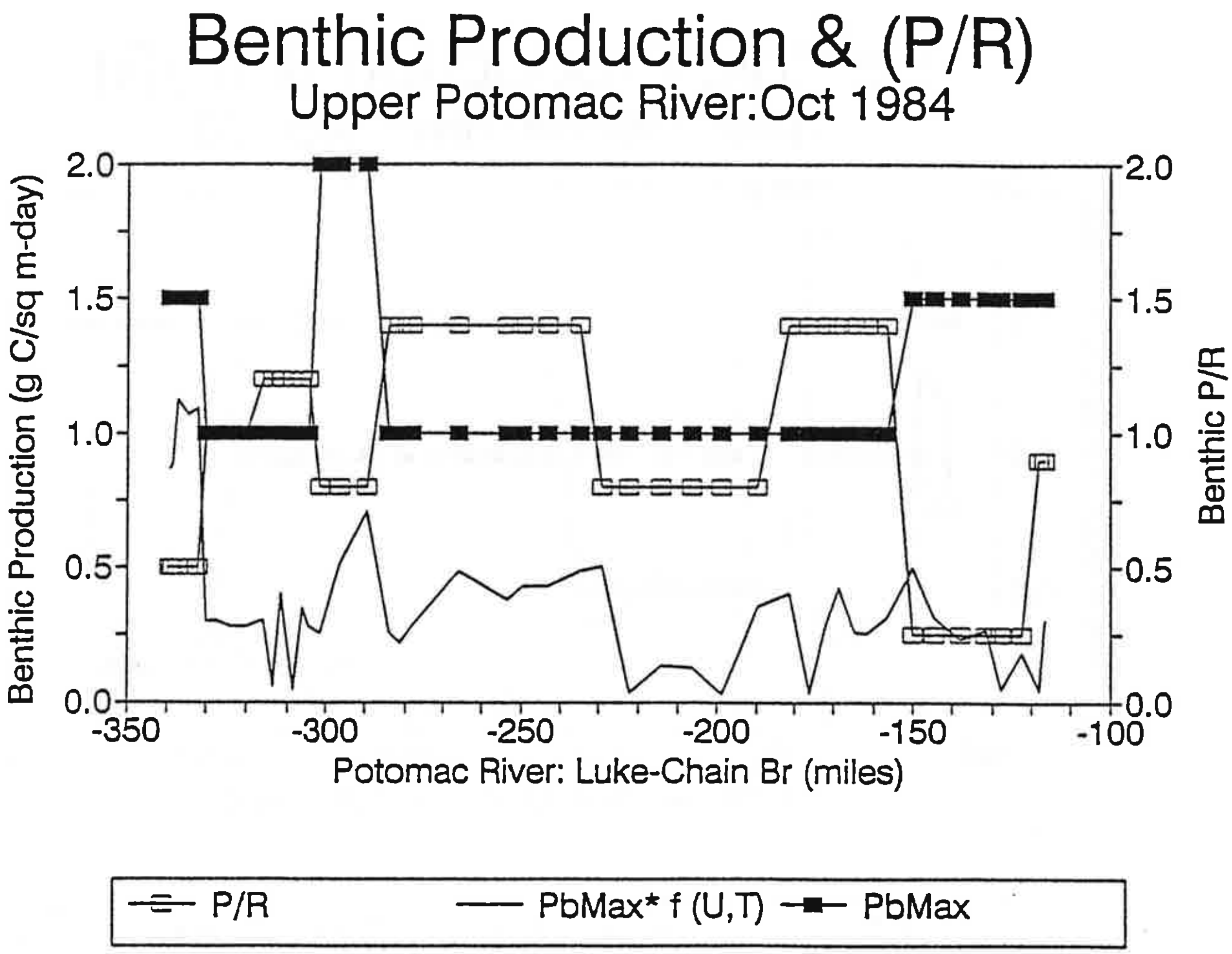


Figure 15b- Spatial distribution of gross periphyton productivity and P/R ratios for the Potomac River Model: September 1985

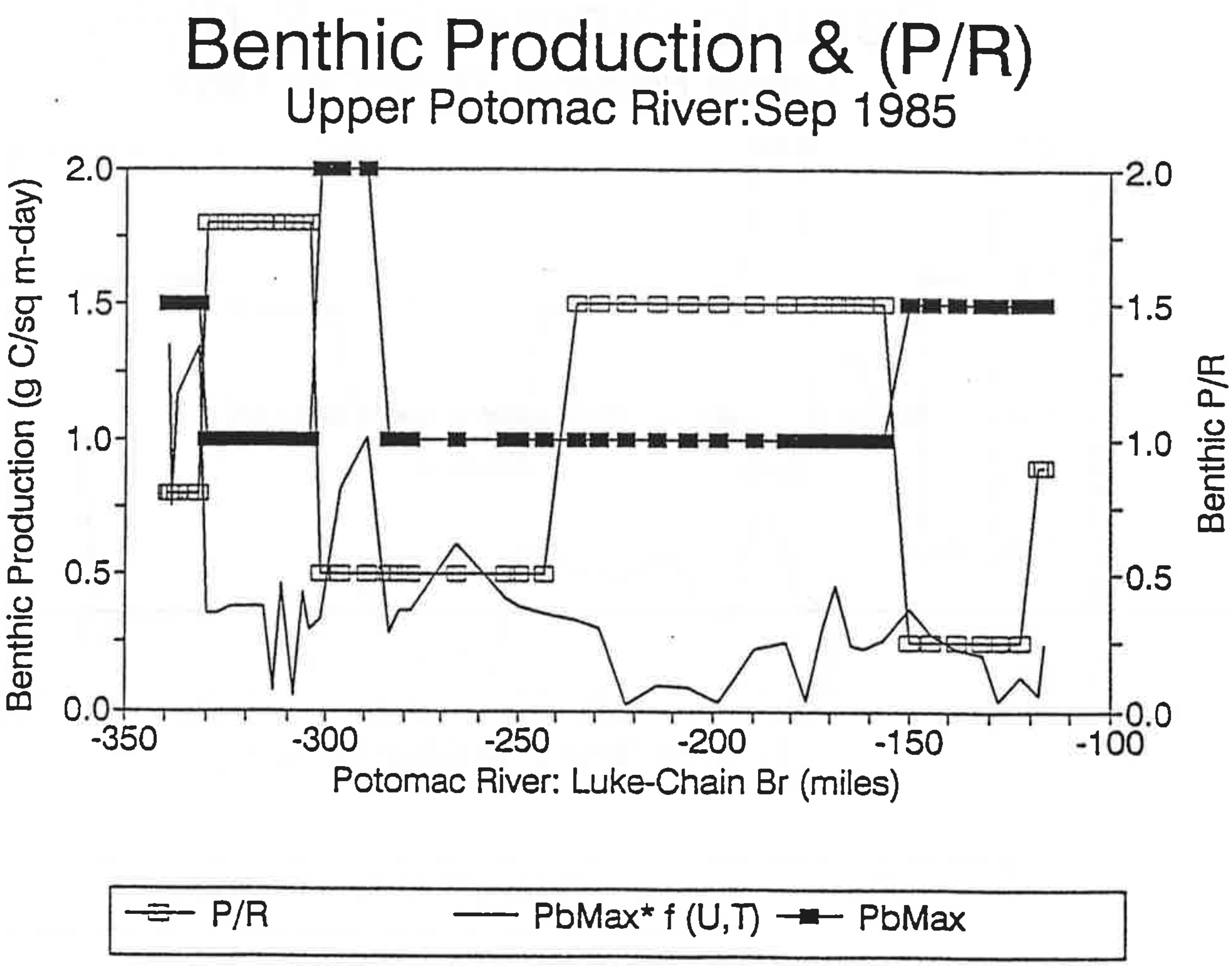


Figure 15c- Spatial distribution of gross periphyton productivity and P/R ratios for the Potomac River Model: September 1986

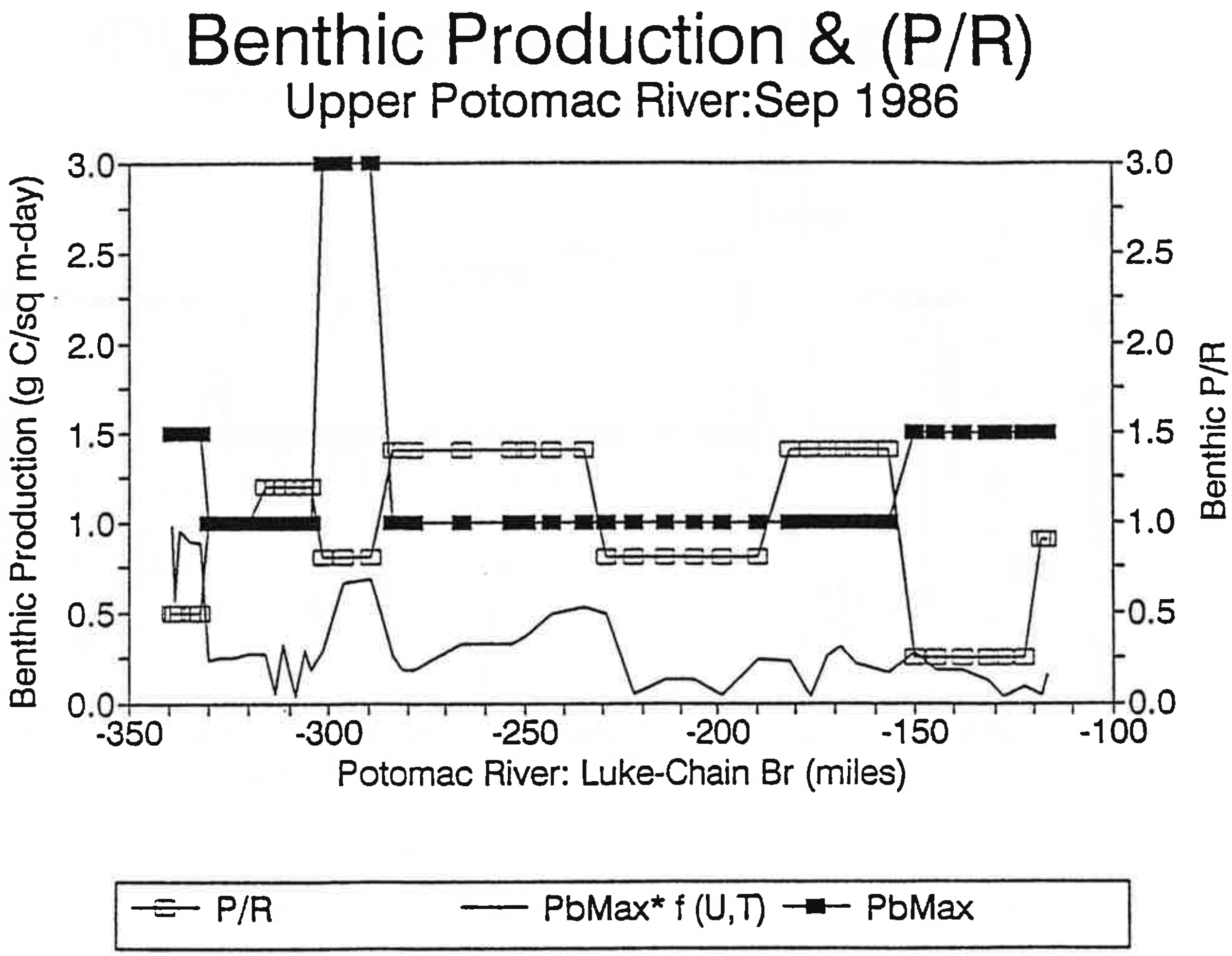


Figure 15d- Spatial distribution of gross periphyton productivity and P/R ratios for the Potomac River Model: July 1987

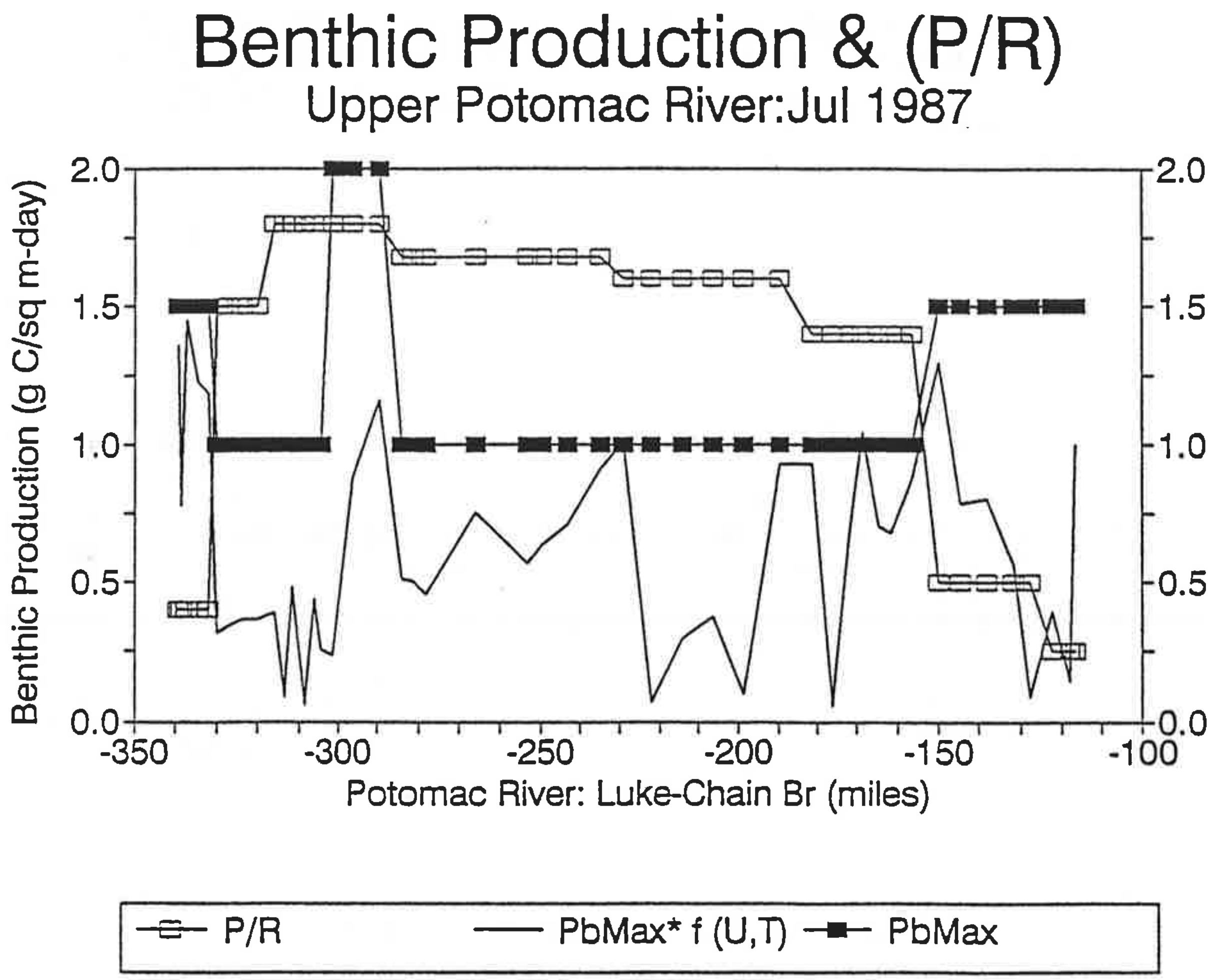


Figure 16- Stoichiometric relationship of paired measurements of SOD and ammonia flux (after DiToro, 1986).

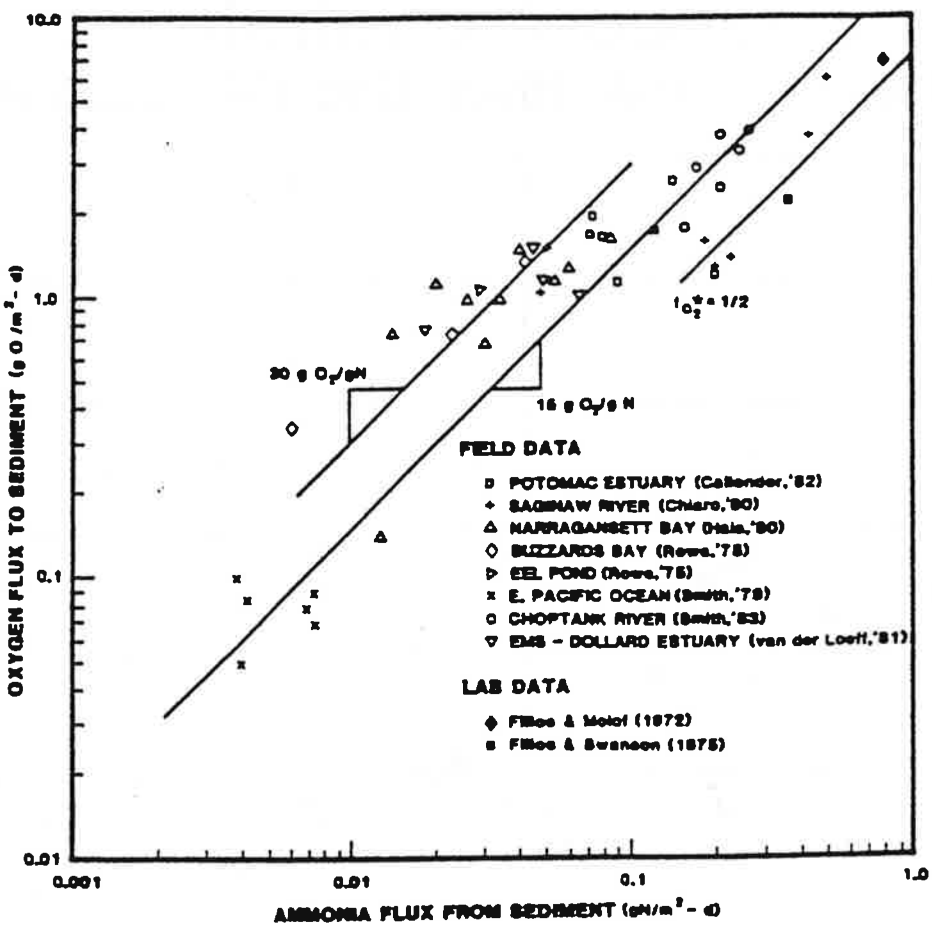


Figure 17- Observed nitrate distribution for the Upper Potomac River: September 1985 and July 1987

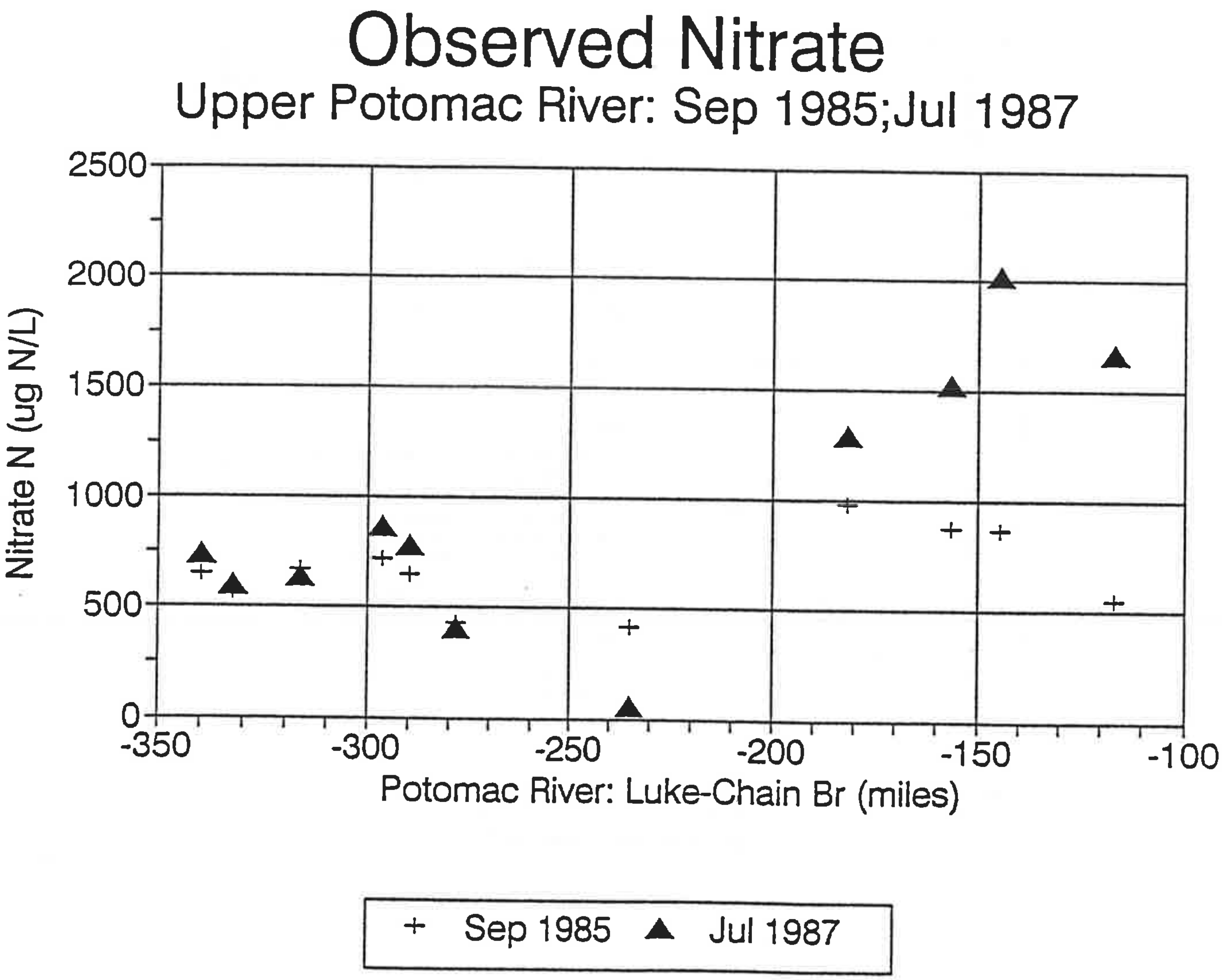


Figure 18a- Model parameterization of benthic nitrification (as mg N/sq m-day): October 1984, September 1985, September 1986 and July 1987

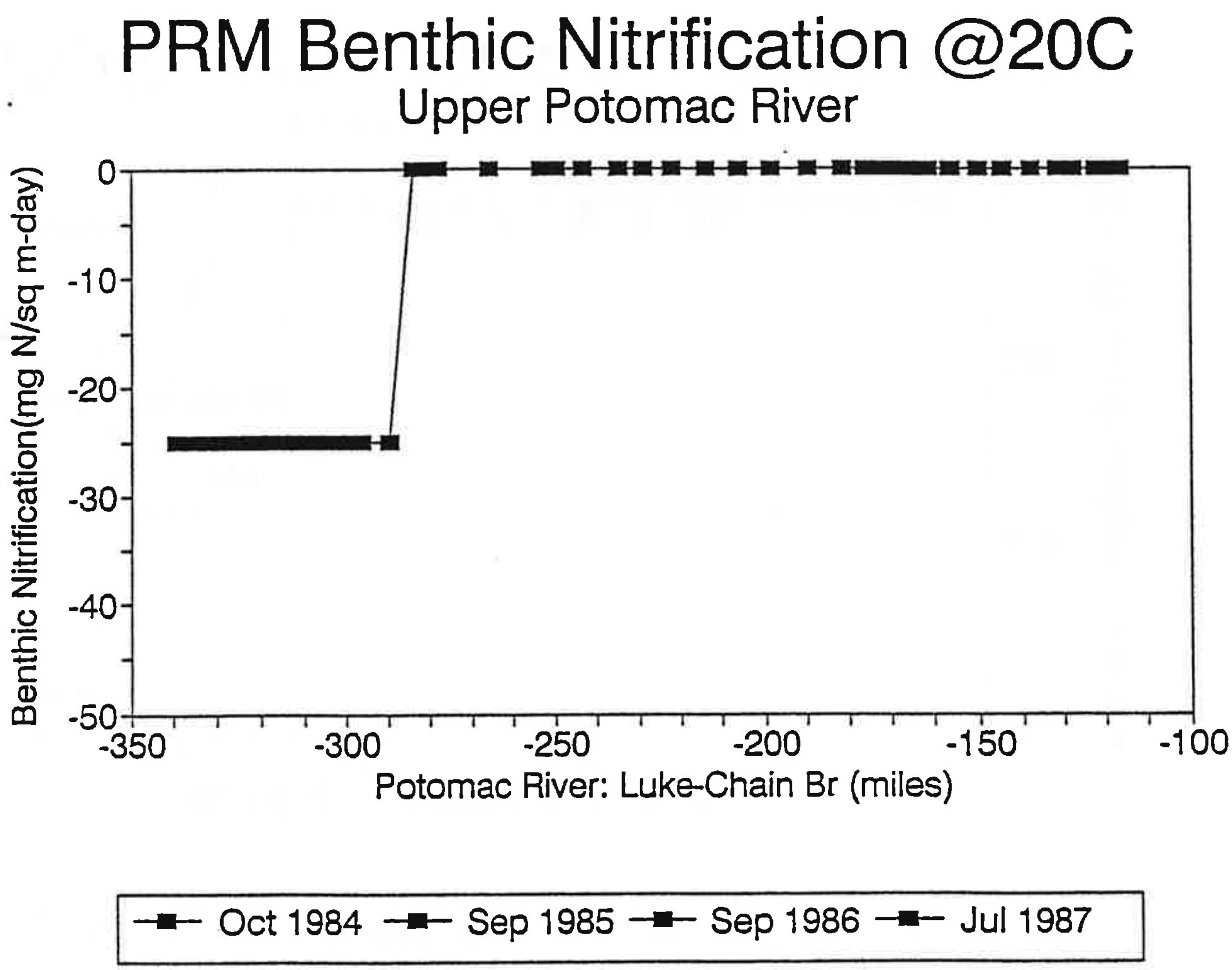


Figure 18b- Model parameterization of benthic nitrate loss rates (as mg N/sq m-day): October 1984, September 1985, September 1986 and July 1987

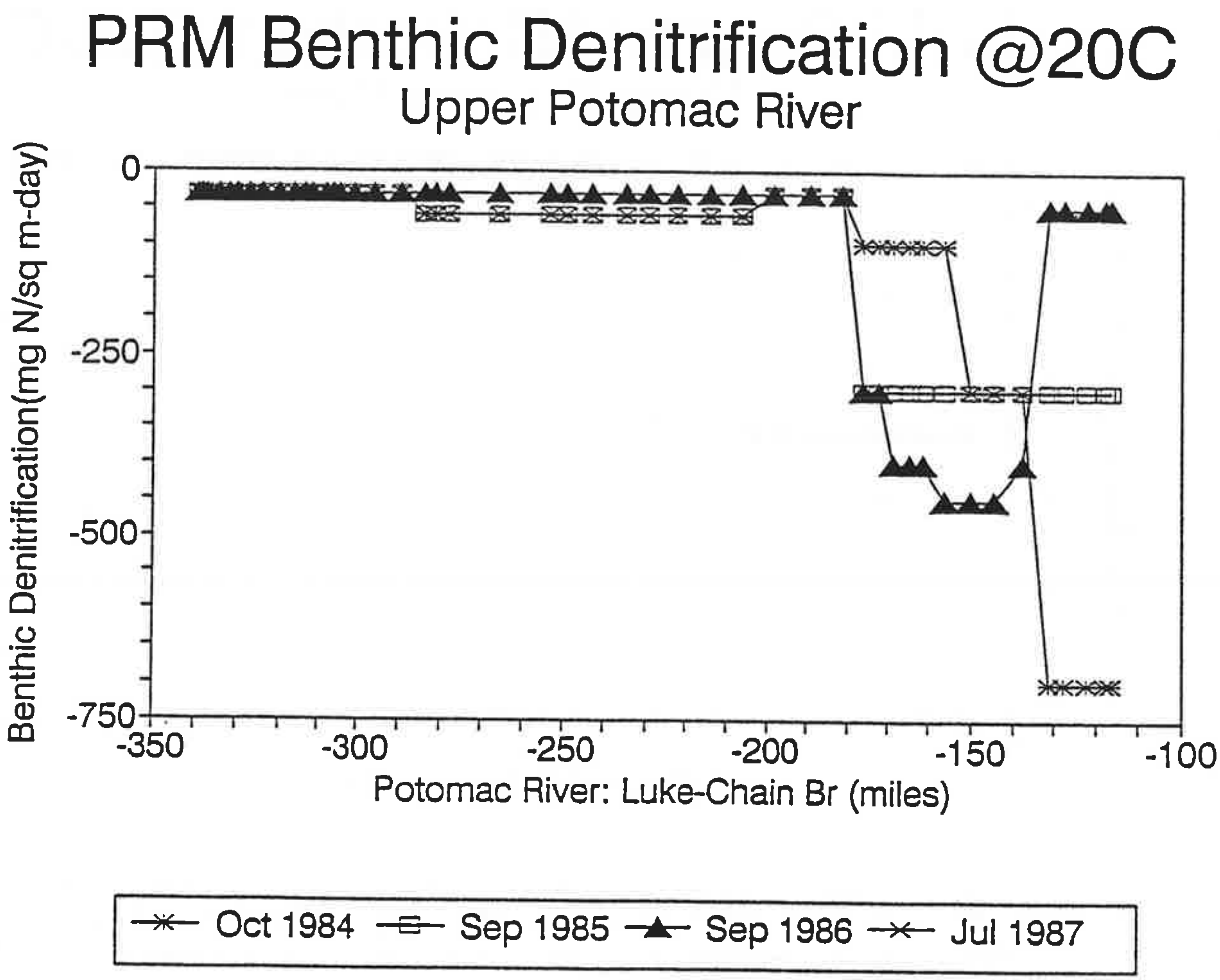
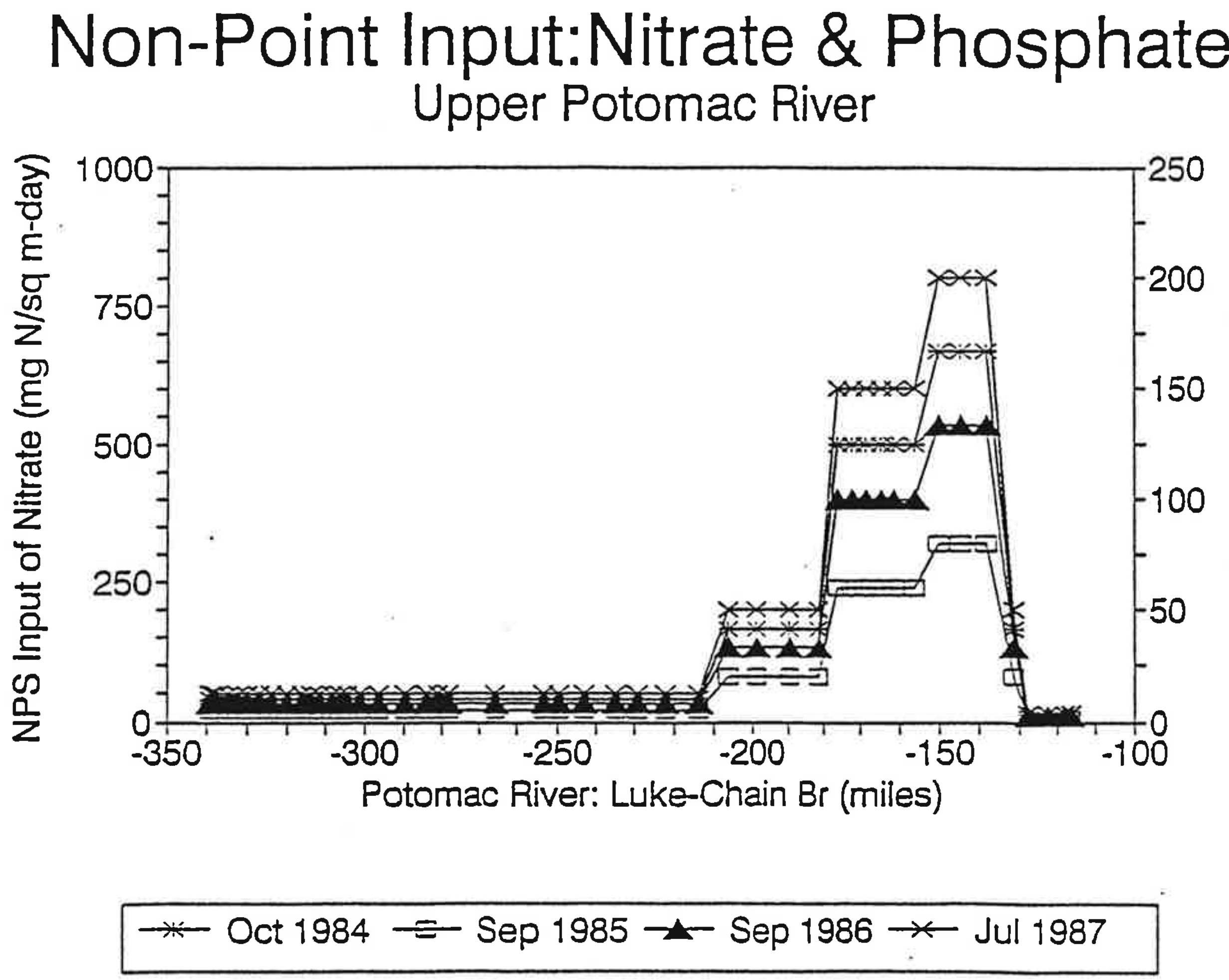


Figure 19- Spatial distribution of non-point input of nitrate and phosphate: October 1984, September 1985, September 1986 and July 1987



6.8 Data Group H- Chemical and Kinetic Constants

Parameter values described in ICPRB (1991) were generally used in the final calibration and verification of the model. A constant flux representing atmospheric deposition of nitrate, ammonia, organic nitrogen, phosphate and organic phosphorus was specified using parameter values reported for the 2D Chesapeake Bay water quality model (HydroQual, 1987). To account for the required non-point loading of organic nutrients during the high flow cases (1984,1987) and the low flow cases (1985,1986), a constant source flux representing non-point organic nitrogen and phosphorus loading was incorporated as an additive component of the "atmospheric deposition" constant. Table 10 summarizes the kinetic coefficients used for the PRM simulation cases.

6.9 Data Group I- Time Varying Forcing Functions

Time varying, spatially constant forcing functions were defined on the basis of available field data and best estimates from the literature. Time variable functions included: water temperature; solar radiation; photoperiod; wind velocity; air temperature; extinction coefficients; sediment flux temperature and time dependent multipliers for sediment oxygen demand; benthic regeneration of ammonia and phosphate and benthic denitrification. In addition, parameter values were specified for the WASP4 velocity functions, salinity and herbivorous zooplankton. For this steady state analysis, time varying parameters were set as a constant value for each 25 day simulation interval (see Table 11).

Solar radiation, photoperiod, wind velocity and air temperature were specified as constant values based on observed or estimated data for each simulation period (Table 25). Solar radiation, photoperiod and air temperature data are based on NOAA/NWS climatological observations at Dulles Airport in Sterling, Virginia. Wind velocity is based on long term monthly average data (1949-1985) recorded at Washington National Airport (MWCOG, 1987). The remaining time forcing functions were set to a value of 1.0 since the time variable nature of these forcing functions was not required for the steady state analysis.

6.10 Data Group J- Initial Conditions

Initial conditions for each PRM case, presented in Appendix L through Appendix M, were based on linear interpolation of the longitudinal distribution of the observed water quality data averaged over each simulation time period. Specification of the dissolved fraction for each state variable was based on parameter values reported for the Potomac Estuary Model (PEM, Thomann and Fitzpatrick, 1982). Constant dissolved fractions for each segment were set as follows:

State Variable	Dissolved Fraction
1-ammonia	1.0
2-nitrate+nitrite	1.0
3-phosphate	0.7
4-phytoplankton	0.0
5-CBOD5	0.8
6-oxygen	1.0
7-organic N	0.8
8-organic P	0.1

The assumption of 80% dissolved fraction for organic nitrogen and CBOD5 needs to be verified with actual field data. Field data were not available to estimate these model parameters. In contrast, water quality and flow data (1978-1986) for observations at Chain Bridge suggest that most of the total phosphorus delivered across the fall line is in the particulate form (MWCOG, 1987; MWCOG, 1989). Based on Chain Bridge boundary conditions used to represent 1977 conditions for the Potomac Estuary Model (PEM, Thomann and Fitzpatrick, 1982), the dissolved fraction of organic phosphorus was set as 10% while the dissolved fraction of inorganic phosphorus was set at 70%.

Table 10 -Kinetic coefficients for the Potomac River Model

NO.	CONST	Units	PRM Value	Sys#	Description	Data Source
011	K12C	1/day	0.5000	1	Nitrification rate @20C	Bowie et al. (1985); EPA Draft WLA Book II (1990)
012	K12T	no units	1.0850	1	Nitrification temperature coeff.	Bowie et al. (1985); EPA WLA Book II (1990)
013	KNIT	mg 02/l	2.0000	1	Half saturation :nitrif. 02 limit	Ambrose et al. 1988; Stenstrom & Poduska 1980
014	ATM_NH3	mgN/sq m-day	0.9490	1	Atmospheric deposition of NH3	HydroQual (1987) Ches Bay Model
021	K20C	1/day	0.0450	2	Denitrification rate @ 20C	Ambrose et al. 1988; Thomann and Mueller 1987
022	K20T	no units	1.0450	2	Denitrification temperature coeff.	Ambrose et al. 1988 pp 80
023	KNO3	mg 02/l	0.1000	2	Half saturation:Denitrif. 02 limit	Ambrose et al. 1988 pp 80
024	ATM_NO3	mgN/sq m-day	2.3590	2	Atmospheric deposition of NO3	HydroQual (1987) Ches Bay Model
031	ATM_PO4	mgP/sq m-day	0.0530	3	Atmospheric deposition of O_PO4_P	HydroQual (1987) Ches Bay Model
041	K1C	1/day	2.5000	4	Phyt#1 max growth rate @20C	Canale & Vogel 1974;Eppley 1972;Thomann & Mueller 1987
042	K1T	no units	1.0680	4	Phyt#1 growth temperature coeff.	Ambrose et al. 1988; Eppley 1972;Thomann & Mueller 1987
043	LGHTS	1=Smith; 2=DiToro	2.0000	4	Phyt#1 light formulation switch	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
044	PHIMX	mgC/mole photon	720.0000	4	Phyt#1 max quantum yield constant	Ambrose et al. 1988; used only when LGHTS =1
045	XKC	(sq m/mg chl)	0.0170	4	Phyt#1 self shading extinction	Ambrose et al. 1988; Parsons &Takahashi 1973 pp 87
046	CCHL1	ug C/ug Chl-a	70.0000	4	Phyt#1 Carbon/chlorophyll ratio	Thomann and Mueller 1987; Bowie et al 1985
047	IS1	ly/day	350.0000	4	Phyt#1 optimal light saturation	Ryther 1956; Thomann & Mueller 1987; Bowie et al 1985
048	KMNG1	mg/l	0.0280	4	Phyt#1:Half Sat. Constant for N	Thomann & Mueller 1987 pp 427; Bowie et al (1985)
049	KMPG1	mg/l	0.0020	4	Phyt#1: Half-Sat. Constant for P	Thomann & Mueller 1987;Bowie et al 1985
050	K1RC	1/day	0.1750	4	Phyt#1 endogenous respiration @20C	Thomann & Mueller 1987;Bowie et al 1985
051	K1RT	unitless	1.0800	4	Phyt#1:respiration temp. coeff.	DiToro et al. 1977; Thomann & Mueller 1987
052	K1D	1/day	0.0200	4	Phyt#1 death rate:non-zoo predation	Ambrose et al. 1988; Kremer & Nixon 1978
053	K1G	1/mg C-day	1.0000	4	Phyt#1 zooplankton grazing rate	DiToro et al. 1977; Thomann & Mueller 1987
054	NUTLIM	0=min;1=mult	0.0000	4	Nutrient limitation option 0-1	Ambrose et al 1988; Lehman et al 1975
055	KPZDC	1/day	0.0200	4	Phyt#1 decay rate in sediments @20C	Ambrose et al. 1988 ; Thomann & Fitzpatrick 1982
056	KPZDT	unitless	1.0800	4	Phyt#1 temp coeff sediment decay	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
057	PCRB	mg P/mg C	0.0250	3	Phyt#1 Carbon/phosphorus ratio	Bowie et al. 1985;O'Connor et al 1973
058	NCRB1	mg N/mg C	0.2500	1	Phyt#1 Carbon/nitrogen ratio	Bowie et al (1985); O'Connor et al. (1973)
059	KMPHYT	mg C/l	1.0000	7	Phyt#1 Half-Sat for recycle of N,P	Ambrose et al. 1988;Thomann & Fitzpatrick 1982
071	KDC	1/day	0.0870	5	CBOD decay rate @20C;U/5=2.84	Leo et al. (1984);Thomann & Mueller(1987)
072	KDT	no units	1.0470	5	CBOD oxidation temperature coeff	Bowie et al (1985)
073	KDSC	1/day	0.0004	5	CBOD decay rate in sediments @20C	Ambrose et al. 1988 pp 93
074	KDST	no units	1.0800	5	CBOD sediment decay temp. coeff.	Ambrose et al. 1988 pp 93
075	KBOD	mg 02/l	0.5000	5	CBOD Half-sat. for 02 limitation	Ambrose et al. 1988 pp. 87
081	OCRB	mg 02/mg C	2.6700	6	Oxygen/carbon stoichiometric ratio	Ambrose et al. 1988 C + 02 = C02 (2.67 = 2*16/12)
082	K2	1/day	0.0000	6	atmospheric reaeration rate	Ambrose et al. 1988;Thomann & Mueller 1987

Table 10 (continued) -Kinetic coefficients for the Potomac River Model

091	K71C	1/day	0.0050	7	mineralization rate of DON @20C	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
092	K71T	no units	1.0800	7	DON mineralization temp. coeff	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
093	KONDC	1/day	0.0004	7	Org N decay rate in sediments@20C	Ambrose et al. 1988
094	KONDT	no units	1.0800	7	Org N sediment decay temp. coeff	Ambrose et al. 1988
095	FON	fraction	0.5000	7	fract. phyt.death recycled to OrgN	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
096	ATM_ON	mgN/sq m-day	2.8010	1	Atmospheric deposition of Org_N	HydroQual (1987) Ches Bay Model
096a	NPS_ON	mgN/sq m-day	40.0000	1	Non Point Load of Org_N:1984,1987	PRM calibration
096b	NPS_ON	mgN/sq m-day	20.0000	1	Non Point Load of Org_N:1985,1986	PRM calibration
100	K83C	1/day	0.2000	8	mineralization rate of DOP @20C	Ambrose et al. 1988 pp. 75
101	K83T	no units	1.0450	8	Org P mineralization temp. coeff	Ambrose et al. 1988 pp. 75
102	KOPDC	1/day	0.0000	8	Org P decay rate in sediments	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
103	KOPDT	no units	1.0800	8	Org P sediment decay temp. coeff	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
104	FOP	fraction	0.5000	8	fract. phyt.death recycled to OrgP	Ambrose et al. 1988; Thomann & Fitzpatrick 1982
105	ATM_OP	mgP/sq m-day	0.2470	1	Atmospheric deposition of Org_N	HydroQual (1987) Ches Bay Model
105a	NPS_OP	mgP/sq m-day	4.0000	1	Non Point Load of Org_P:1984,1987	PRM calibration
105b	NPS_OP	mgP/sq m-day	2.0000	1	Non Point Load of Org_P:1985,1986	PRM calibration

Table 11- Solar radiation, photoperiod, wind velocity and air temperature: October 1984, September 1985, September 1986 and July 1987

Parameter	Units	10/84	9/85	9/86	7/87
Solar radiation	Ly/day	223	394	335	527
Photoperiod	f24 hr	0.25	0.33	0.25	0.39
Wind velocity	M/sec	3.913	3.688	3.688	3.688
Air temperature	Deg C	18.5	22.3	21.7	28.3

7.0 Model Calibration and Verification

7.1 Introduction

In the analysis of nutrients and oxygen for the Potomac River, major emphasis has been placed on the development of the various kinetic interactions, functional formulations and estimates of point and non-point loading of nutrients and oxygen.
Extensive data sets are required to specify initial and boundary conditions, spatial and temporal external forcing functions and kinetic and stoichiometric parameter values. Data and information that was readily available to characterize the Potomac River was used in the development of the model. Where specific data were not available for the Potomac River, the scientific literature was used in conjunction with best engineering judgement to estimate required input data for the model.

Based on water quality and effluent data availability and the persistence of approximately steady state hydrologic conditions, October 1984 and September 1986 were chosen as calibration periods while September 1985 and July 1987 were selected as verification periods (see ICPRB, 1991). The data sets for 1984 and 1985 represent conditions prior to the phosphorus ban for Maryland treatment plants while 1986 and 1987 represent conditions following implementation of the detergent ban. Median monthly streamflow measured at the downstream boundary (Little Falls USGS station) and total nutrient loading from the upstream boundary at Luke, Maryland; tributaries; and waste treatment plants for the four cases is summarized in Table 12.

The overall objective of the analysis is to demonstrate the credibility of a consistent model framework under varying conditions of flow, temperature and nutrient loading for the Upper Potomac River. The initial step in the calibration procedure consisted of a series of trial and error model runs using the October 1984 dataset to evaluate various numerical estimates for model forcing functions and parameter estimates. During the initial calibration phase with the October 1984 dataset, it became apparent that estimates of benthic nitrification, benthic denitrification, nutrient uptake and net oxygen production of attached periphyton were significant components in successfully reproducing the observed spatial distribution of nutrients and oxygen.

Table 12- Median Monthly Flow at Little Falls and Total Nitrogen (TN) and Total Phosphorus (TP) Point Source Loading from Upstream Boundary, Tributaries and Waste Treatment Discharges (Segment 1-47): October 1984, September 1985, September 1986 and July 1987

PRM Case	Little Falls Flow	TN (kg/day)	TP (kg/day)
October 1984	3200 cfs (2068 MGD)	12,099	1,098
September 1985	1560 cfs (1008 MGD)	10,067	1,418
September 1986	931 cfs (602 MGD)	2,378	410
July 1987	3549 cfs (2294 MGD)	14,814	1,011

In applying the forcing functions and parameter values determined for the October 1984 case to the September 1985 case, it became apparent that further refinements of parameter value estimates for the benthic and non-point source spatial forcing functions were required to adequately reproduce the observed data for the different dataset. Preliminary testing of model parameter values was also performed using the 1986 and 1987 datasets to determine the extent of interannual consistency in matching the observed data.

Final calibration and verification required about 70 model runs to obtain consistent sets of model coefficients and spatial forcing functions that are reasonable (based on the literature) and reproduce the major trends in the observed data for all state variables considered. The major factors in determining an appropriate set of consistent benthic and non-point source forcing functions appeared to be streamflow and total nutrient loading (see Data Tables in Appendices L-O). One set of spatial forcing functions approximately described the higher flow and nutrient loading conditions of October 1984 and July 1987 while a second set of spatial forcing functions described the lower flow and nutrient loading conditions of September 1985 and September 1986.

In the calibration and verification of the Potomac River Model, comparisons of observed data and simulation results were made using two approaches: (1) qualitative (i.e. visual) agreement of spatial gradients of observed and model data; and (2) quantitative statistical comparison of observed and model data using linear regression analysis over the entire spatial domain of the model (see Thomann and Fitzpatrick, 1982).

The various components of the model input datasets have been described and summarized in the previous section of this report. The comparison of observed data to model results is presented for the two calibration periods of October 1984 (higher flow; pre-phosphorus ban) and September 1986 (low flow; post phosphorus ban) and the two verification periods of September 1985 (low flow; pre phosphorus ban) and July 1987 (high flow; post phosphorus ban). In presenting the results of the model calibrations, qualitative and quantitative comparisons of the observed data with the model results are used to demonstrate the ability of the model framework to reproduce the observed spatial distributions of nutrients, phytoplankton and oxygen.

As a scientific methodology, a model represents a set of hypotheses incorporated in the state equations that describe the complex interactions of numerous physical, biological, chemical and benthic processes. Where the model results are not in good agreement with observations, the specific hypothesis (or sub-model) is examined to: (1) determine possible reasons for the discrepancy; (2) suggest alternative hypotheses for the model; and (3) suggest additional field data collection efforts to provide key datasets for refinements of the parameterization of the model.

Graphical comparisons of model results to the observed data are presented in the following appendices to this report:

Appendix A- Calibration Results: October 1984
Appendix B- Calibration Results: September 1986
Appendix C- Verification Results: September 1985
Appendix D- Verification Results: July 1987

7.2 Model Calibration: October 1984

Table 13 summarizes the point source and tributary loads for the October calibration case.

Table 13- Summary of Total Tributary and Waste Treatment Loads (as kg/day): October 1984

PRM Seg#	Qr(MGD)	NH3_N	NO3+NO2_N	O_PO4	CBOD_5	DISS_O2	ORG_N	ORG_P	Total N	Total P
1-29	960.3	497.0	1552.7	331.4	10744.3	39169.7	1477.6	202.3	3527.3	533.7
30-47	1108.0	484.1	6009.8	492.3	9329.2	40112.5	2077.3	71.4	8571.3	563.8
1-47	2068.3	981.1	7562.5	823.7	20073.5	79282.2	3554.9	273.8	12098.5	1097.5

Nitrogen. The observed distributions of inorganic nitrogen (nitrate and dissolved inorganic nitrogen, DIN) reflect the influence of the dominant agricultural component of non-point nutrient loading downstream of Conococheague Creek (RM 210-RM 115) and lower loading rate associated with forested land use upstream of Conococheague Creek (RM 340-210). With the exception of the observations at Chain Bridge where the model results overestimate nitrate, the agreement between the model and observed data is quite good. The good match between the model and observations suggests that the parameterization of the spatial forcing functions specified for benthic productivity, non-point source loading of nitrate and nitrate loss via denitrification to the sediments are reasonable approximations for a nitrogen balance of the Upper Potomac River. In particular, the non-point input of nitrate downstream of Conococheague Creek is an essential component for reproducing the observed distribution of nitrate.

Since observed ammonia (~20-100 ug N/L) accounts for a minor fraction of observed dissolved inorganic nitrogen (~500-2500 ug N/L), the underestimate in ammonia downstream of RM 250 is not strongly reflected in the model representation of DIN. The rapid decline of ammonia in the upper segments (RM 340-RM 330) of the North Branch is attributed to high rates of benthic uptake by attached periphyton and benthic nitrification. Loading from the Cumberland POTW (RM 304) results in a large increase of ammonia followed by a rapid reduction downstream to the vicinity of the confluence of the South Branch (RM 285) and Paw Paw (RM 275). The sharp decline downstream of Cumberland is attributed again to high rates of benthic algal uptake and benthic nitrification that could possibly be enhanced because of organic loading from the Cumberland POTW. Downstream of Paw Paw (RM 275), ammonia is underestimated in the model as a result of insufficient benthic regeneration via the estimated SOD distribution. A sensitivity analysis of the SOD distribution used for the 1984 case suggests that an overall increase of the 1984 SOD maximum rates of ~ 10-50% could result in an improved match between the model and observed ammonia.

The computed distribution of organic nitrogen reflects point source loading from tributaries and waste treatment plants and non-point loading from atmospheric deposition and overland runoff. Since it was not possible with the current version of WASP4 to represent a spatially distributed input of organic nitrogen, non-point loading of organic nitrogen was accounted for as a constant mass flux rate (40 mg N/sq m-day) for the entire model domain. The model results suggest that a spatially distributed input of organic nitrogen is needed to improve the agreement with the observed data.

The distribution of total nitrogen, similar to that of nitrate and DIN, is in good agreement with the observed data with the exception of overestimating the load at the downstream boundary near Chain Bridge. The discrepancy in total nitrogen and nitrate is attributed to an underestimate of the sediment nitrate loss rate downstream of the Monocacy River (RM 153). An improved match for the model results could probably be obtained by increasing the rate of sediment denitrification in those segments.

Phosphorus. The observed distributions of phosphate and total phosphorus reflect the influence of the dominant agricultural component of non-point nutrient loading downstream of Conococheague Creek (RM 210-RM 115) and the lower loading rate associated with forested land use upstream of Conococheague Creek (RM 340-210). Overall, the agreement between the model results and observed data is quite good for phosphate and total phosphorus. The good match between the model and observations suggests that the parameterization of the spatial forcing functions specified for benthic productivity, non-point source loading of phosphate and settling losses are reasonable approximations for a phosphorus balance of the Upper Potomac River. In particular, the non-point input of phosphate downstream of Conococheague Creek is an essential component for reproducing the observed distributions of phosphorus.

Although the phosphorus load is significant, the relatively low levels of simulated phosphate in the upper segments (RM 340-RM 330) of the North Branch is attributed to high rates of benthic uptake by attached periphyton and high rates for settling losses to the sediments. Similar to ammonia, loading from the Cumberland POTW (RM 304) results in a large increase of phosphate followed by a gradual reduction downstream to the vicinity of the confluence of the South Branch (RM 285) and Paw Paw (RM 275). The decline downstream of Cumberland is attributed again to high rates of benthic algal uptake and settling losses that could possibly be enhanced because of particulate organic loading from the Cumberland POTW. Downstream of Paw Paw (RM 275), the results for phosphate are consistent with ammonia since phosphate appears to be underestimated as a result of insufficient benthic regeneration via the estimated SOD distribution.

The computed distribution of organic phosphorus reflects point source loading from tributaries and waste treatment plants and non-point loading from atmospheric deposition and overland runoff. Since it was not possible with the current version of WASP4 to represent a spatially distributed input of organic phosphorus, non-point loading was accounted for as a constant mass flux rate (4 mg P/sq m-day) for the entire model domain. The model results suggest that a spatially distributed input of organic phosphorus is needed to improve the agreement with the observed data as well as refinements in the mineralization rate and settling loss rates.

The model's overestimate of total phosphorus in the North Branch (RM 340-300) is attributed to the overestimate of the organic phosphorus component. At the downstream boundary, total phosphorus is in very good agreement with the observed data suggesting that the model framework is a useful tool for evaluations of the impact of nutrient control measures on changes in fall line loading. Reflecting the relatively good agreement between the model and the observations, the computed ratio of inorganic N/P is also in good agreement with the observed data. In particular, the sharp decrease in N/P in the North Branch of the Potomac (RM 340-330) is attributed to benthic uptake of nutrients from the attached periphyton with processes similar to a case study described in Thomann and Mueller (1987).

Chlorophyll and Primary Productivity. While chlorophyll data are available only for stations downstream of Point of Rocks, Maryland (RM 159), primary productivity data are not available for any region of the Upper Potomac River for comparison with model results. Observations for October 1984 as well as long term (1978-86) summaries of chlorophyll observations at mainstem stations near Point of Rocks, the Monocacy River, Whites Ferry and Chain Bridge (MWCOG, 1984; 1989) (see Table 14) suggest an increase in chlorophyll downstream of the Monocacy River with peak biomass levels recorded near Chain Bridge. Although a sampling station is not located in Seneca Pool, it is probable that the increased biomass observed at Chain Bridge results from physical accumulation (long residence time) and enhanced growth in Seneca Pool.

Table 14- Long Term Interannual Chl Observations: 1982-86 (after MWCOG, 1989)

Station	N	Mean	Median	Range
		-------- ug Chl-a /L	------------------	
Chain Br	105	14.8	6.5	<1 - 79
Upstream of Chain Br	319	9.4	4.0	<1 - 142

The agreement between the sparse observed data set and the model results is quite good. In particular, the model reproduces the increase of chlorophyll observed at the Chain Bridge station with the model biomass in good agreement with the mean chlorophyll level. Improvements in the model results could be obtained by a finer tuning of the phytoplankton settling rate downstream of the Monocacy River (RM 153). Computed primary productivity appears to be a reasonable estimate of free-flowing production with relatively low productivity (~0.05 - 0.2 g C/sq m-day) computed as far downstream as the Monocacy River (RM 153). The significant increase in primary productivity (and chlorophyll biomass) downstream of the Monocacy River (~0.2 - 0.8 g C/sq m-day) is attributed to the increased availability of nutrients and to the increased hydraulic residence time of the slow-moving, broad and relatively deep segments near Whites Ferry, Goose Creek and the Seneca Pool.

Figure 20a presents the hydraulic flushing rate computed in the model for comparison to the model computation of the net phytoplankton growth rate (Figure 20b). The model clearly demonstrates the effect of physical factors on the observed accumulation of chlorophyll downstream of the Monocacy River since upstream of the Monocacy, the net algal growth rate (i.e. net growth = growth - respiration - settling - non predatory death) is much lower than the physical turnover time of the river segments. In contrast, the reduced velocity and increased depth of the segments downstream of the Monocacy River result in reduced physical flushing rates and a positive net growth rate (Figure 20b) that results in an accumulation of biomass rather than physical wash out since sufficient time is available for the biological reactions to occur.

CBOD5 and Dissolved Oxygen. For model calibration, CBOD5 data are limited to a few mainstem stations downstream of Point of Rocks, Maryland (RM 159). Dissolved oxygen data, however, is available at a number of mainstem stations from the North Branch of the Potomac to Chain Bridge. CBOD5 data were available for a few tributary stations that was used to estimate boundary conditions for CBOD5 for tributaries and the upstream boundary of the North Branch. Tributary CBOD5 was typically ~1 - 2 mg/L upstream of Point of Rocks and ~2-6 mg/L downstream of Point of Rocks.

In all cases, the upstream boundary condition for CBOD5 was specified as 4.0 mg/L. The CBOD5 decay rate of 0.087/day (@ 20C) and a corresponding CBODU/CBOD5 ratio of 2.84 was based on a composite data set (Leo et al. 1984) for secondary waste treatment plants that is summarized in Thomann and Mueller (1987). A constant low settling rate of 0.05 m/day was specified for the particulate (20%) component of CBOD. The model results are in fair agreement with the observations with the model falling in the middle of the observed range of ~2-5 mg/L from Point of Rocks to Chain Bridge. Although the underestimate of the results for CBOD5 is consistent with the caveat of Ambrose et al. (1988), the results suggest that an additional non-point source input of CBOD5 resulting from agricultural land uses downstream of Conococheague Creek (RM 210) might improve the match with the observed data.

The spatial distribution of oxygen reflects point source inputs of organic carbon as well as benthic demands from SOD and net oxygen production of attached algae. Overall, the agreement between the model results and observed data is quite good for dissolved oxygen. The good match between the model and observations suggests that the parameterization of the spatial forcing functions specified for benthic productivity, SOD and P/R ratios are reasonable approximations for an oxygen balance of the Upper Potomac River. In particular, the benthic component of the net photosynthetic processes of benthic algae is an essential sub-model for reproducing the observed distributions of oxygen. Improvement in agreement between the observations and the model could be obtained by further tuning of the P/R ratios specified for each segment.

The sharp reduction of simulated oxygen in the upper segments (RM 340-RM 330) of the North Branch is attributed to high rates of benthic production with P/R < 1 for the attached periphyton and high SOD rates resulting from the characteristic high velocities of this reach. Maintenance of oxygen levels of ~9 - 10 mg/L from the South Branch (RM 285) to Conococheague Creek (RM 210) are attributed to moderate SOD and benthic production rates as well as the assumption of generally autotrophic conditions where P/R > 1. In addition turbulent reaeration from dams and rapids is accounted for in the hydraulic coefficients determined by Hydroscience (1976). The computed drop in oxygen downstream of Point of Rocks from ~10 mg/L to ~8 mg/L is in good agreement with the observed data. Similarly the computed increase of oxygen towards Chain Bridge is also in good agreement with the observations. The decline downstream of Point of Rocks (RM 159) is attributed to benthic algae production with a low P/R <<1 and increased maximum SOD rates that could possibly be enhanced because of particulate organic loading from Antietam Creek and the Monocacy River.

Figure 20a -Hydraulic flushing rate computed in the model: October 1984

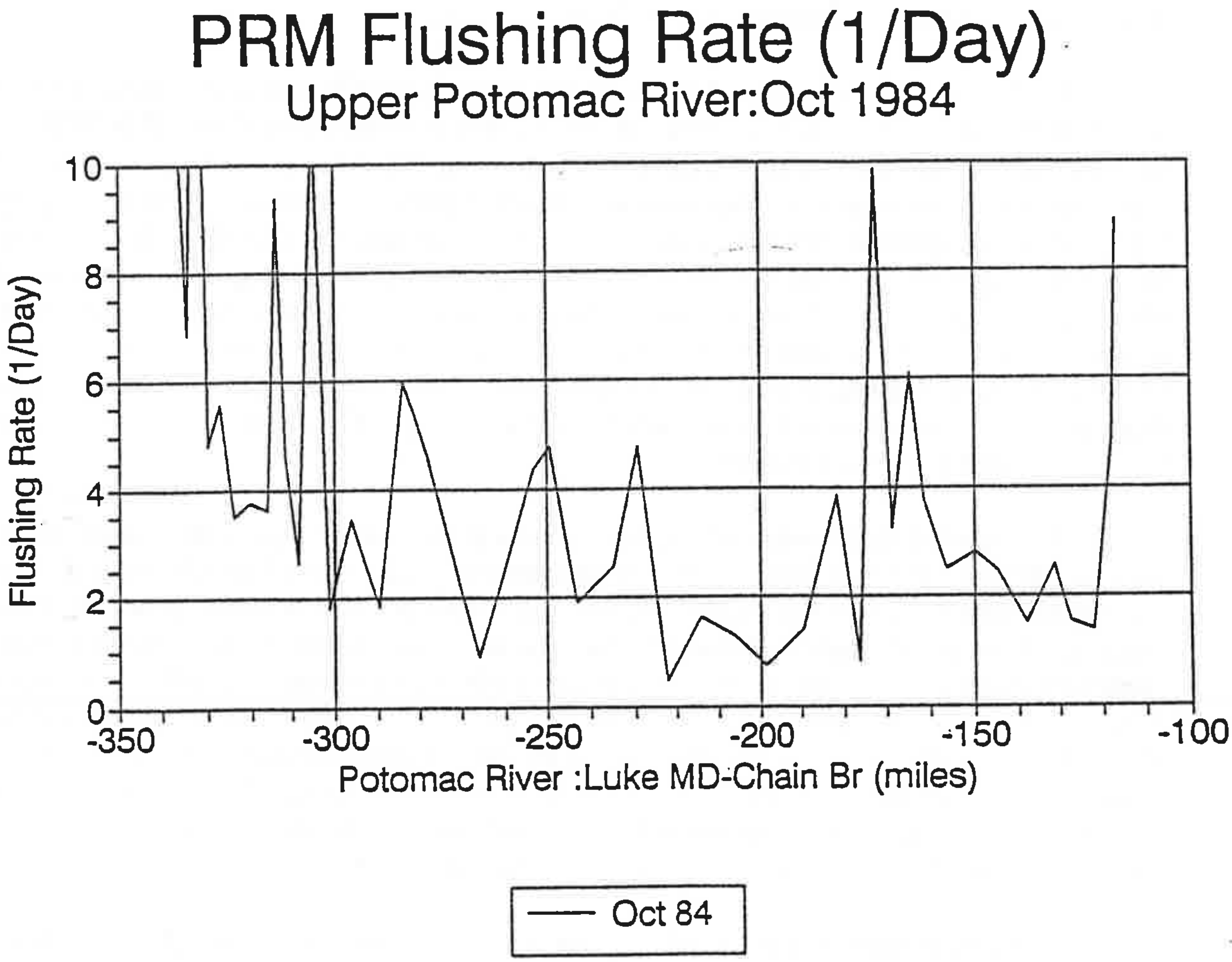
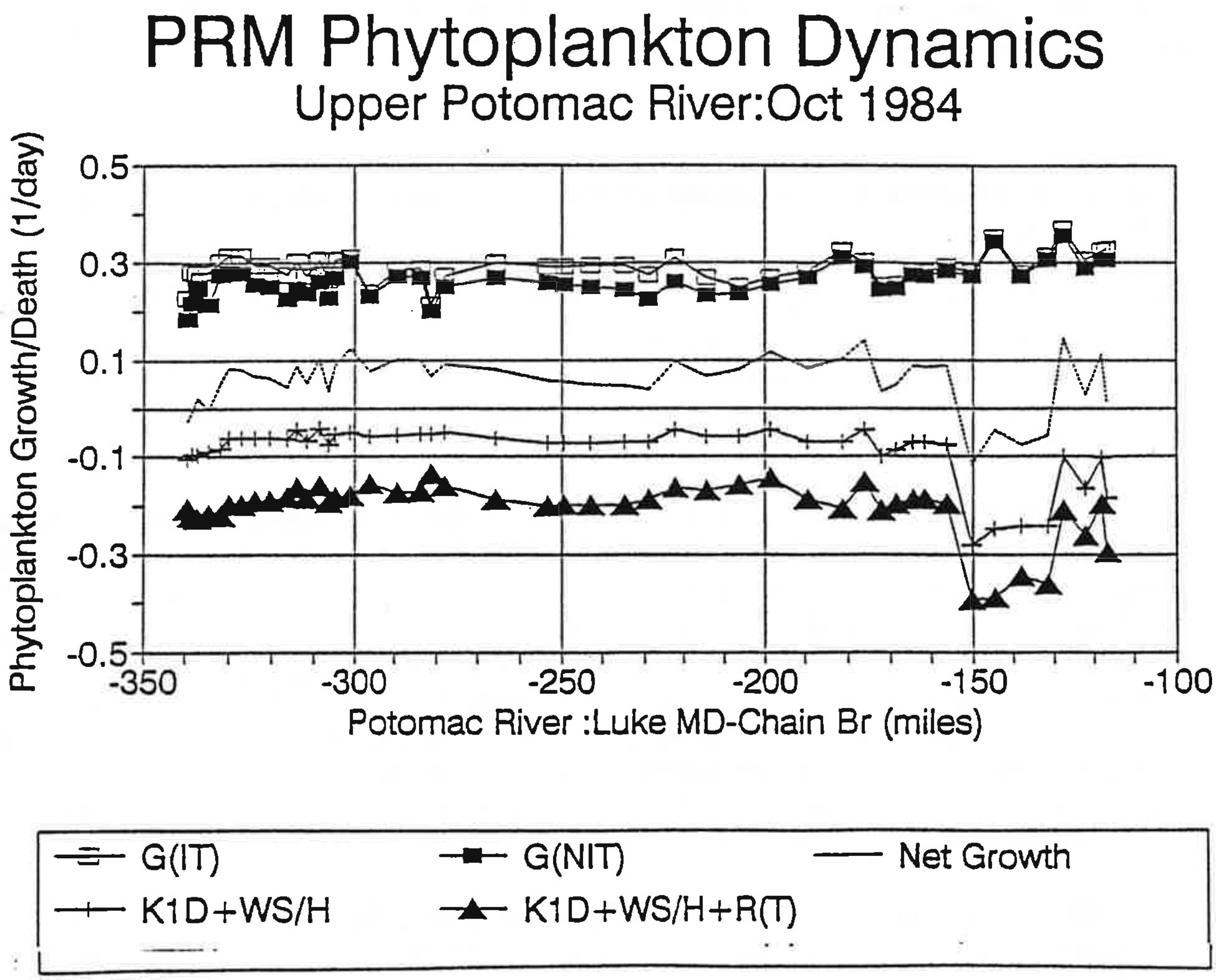


Figure 20b- Computed phytoplankton dynamics: October 1984



7.3 Model Calibration: September 1986

Table 15 summarizes the point source and tributary loads for the September 1986 calibration case. The loading data clearly demonstrates that the September 1986 calibration case is characterized by much lower flow at Chain Bridge (Qr=602 MGD) and total nutrient input (TN= 2378 kg/d; TP= 410 kg/d) than was the October 1984 case (Qr=2068 MGD; TN=12099 kg/d; TP=1098 kg/d). Because of the low flow conditions, flow balance estimates of ungauged tributary inflows downstream from Segment 31 near Conococheague Creek (RM 210) resulted in net diversions of water from the mainstem of the river with an associated loss of mass.

Table 15- Summary of Total Tributary and Waste Treatment Loads (as kg/day): September 1986

PRM Seg#	Qr(MGD)	NH3_N	NO3+NO2_N	O_PO4	CBOD_5	DISS_O2	ORG_N	ORG_P	Total N	Total P
1-29	535.8	449.0	941.6	165.6	10915.1	17797.4	803.7	56.7	2194.3	222.2
30-47	66.6	95.3	600.7	193.1	-639.6	3528.9	-512.1	-5.8	183.9	187.2
1-47	602.4	544.3	1542.3	358.6	10275.6	21326.3	291.6	50.8	2378.2	409.5

Nitrogen. Similar to the October 1984 results, the model distributions of ammonia, nitrate and total nitrogen reflect the dominant influence of agricultural non-point loading downstream of Conococheague Creek (RM 210) and uptake of inorganic nitrogen by benthic algae. Ammonia is in reasonable agreement with the observations particularly downstream of Antietam Creek (RM 179) with good agreement at the Chain Bridge boundary. Nitrate and total nitrogen is consistently overestimated in the model with a relatively larger discrepancy downstream of Conococheague Creek (RM 210). Organic nitrogen, however, is in good agreement with the observations with the exception of the reach from Point of Rocks (RM 160) to the Monocacy River (RM 153) where observed organic nitrogen is characterized by a peak of ~ 1000-1100 ug N/L.

In contrast to the calibration for the October 1984 dataset, benthic ammonia regeneration was reduced by ~50% through an overall 50% reduction in the maximum SOD distribution. The reduction in the maximum SOD was needed to calibrate the ammonia, phosphate and oxygen data for the September 1986 case. Similarly, the non-point load of nitrate (and phosphate) needed for even crude agreement to the observed data for 1986 accounted for ~80% of the non-point source load used for the October 1984 calibration. Calibration values for sediment denitrification rates for the 1986 case were also somewhat different than the calibration values used for 1984 with higher rates from Antietam Creek (RM 179) to Watts Branch (RM 129) and lower rates from Watts Branch to Chain Bridge (RM 115). The constant non-point load of organic nitrogen for the 1986 calibration (20 mg N/sq m-day) was 50% lower than the constant input (40 mg N/sq m-day) used for the 1984 higher flow conditions calibration.

It is clear from the model results for the 1986 calibration that parameterization of the spatial forcing functions for nitrogen is quite different between the 1984 and 1986 calibration datasets. Improved agreement between the model and the 1986 data could possibly be obtained by further tuning of sediment nitrate loss rates and non-point loading of nitrate and organic nitrogen.

Phosphorus. The overall computed distribution of phosphate in 1986 is somewhat similar to the 1984 calibration. The initial low level of phosphate in the North Branch (RM 340-320), in good agreement with the observed data, is maintained by very high settling rates and uptake by benthic algae. Following the input from the Cumberland POTW, the simulated decline of phosphate, again in good agreement with the observations, is attributed to settling and benthic algae uptake. Although the non-point load of phosphate is ~80% lower than that used for the October 1984 calibration, simulated phosphate is overestimated downstream of Antietam Creek (RM 179) with good agreement achieved at Chain Bridge.

Settling rates specified for the 1984 calibration were used without any modification for the 1986 calibration. Specifically for segments downstream of Antietam Creek (RM 179), the settling rate was set as 4.0 m/day. for both calibration cases. An improved match to the observed data could probably be obtained by further tuning of the settling velocity for phosphate adsorbed to solids. The low flow conditions of 1986 most likely resulted in a change in suspended solids inputs and distribution in the river that would have influenced particulate settling losses of adsorbed phosphate.

Unlike the 1984 calibration, organic phosphorus is consistently underestimated for the 1986 calibration. The computed concentration at Chain Bridge is, however, in good agreement with the observed data. Similar to the interpretation of the 1984 results, an improvement in simulated organic phosphorus could be obtained by specifying a spatial forcing function for non-point loading that reflects dry summer conditions.

Chlorophyll and Primary Productivity. During the low flow conditions of September 1986, chlorophyll and primary productivity were considerably lower than for the October 1984 calibration. The model results are in good agreement with the observed chlorophyll data, particularly in the reach from the Monocacy River (RM 153) to Chain Bridge (RM 115) where observed chlorophyll is ~4-6 ug Chl/L. For the September 1986 calibration, the settling velocity for this reach (Segment 40-47) was decreased from 0.25 to 0.05 m/day to match the observed data. Computed primary productivity is considerably lower than the 1984 case with peak rates of only ~0.1 g C/sq m-day downstream of the Monocacy River.

CBOD5 and Dissolved Oxygen. With the exception of one grab sample at Chain Bridge, the model results for CBOD5 are not in good agreement with the sparse observations downstream of Point of Rocks (RM 160). Peak CBOD5 observations of ~6-8 mg/L at stations near Point of Rocks and the Monocacy River are not reproduced with the model. Preliminary calibration runs assigned an upstream CBOD5 boundary condition of 10 mg/L

so that the model results were in agreement with the observations. Since such a high CBOD5 level for the North Branch did not, however, seem realistic, the upstream boundary was set at 4 mg/L for all cases.
Consistent with the 1984 results, the 1986 calibration results suggest that a non-point load of CBOD5 is needed to improve the agreement between the model and the observed data.

In general, the model is in good agreement with the oxygen observations from the North Branch to Chain Bridge. Similar to the 1984 calibration, the reduction in oxygen from ~10 to ~8 mg/L in the North Branch results from high rates of net benthic productivity with P/R <1 (~1.5 - 2.5 g O_2 m^{-2} d^{-1}) and SOD rates (~1.0 g O_2 m^{-2} d^{-1}) driven by the characteristic high velocity of this reach. From the South Branch (RM 285) to the Cacapon River (RM 248), the model overestimates oxygen. For this reach it was assumed that P/R >1 for benthic algae production while SOD was ~0.8 - 1.0 g O_2 m^{-2} d^{-1}. The model reproduces the increasing trend from the Cacapon River (RM 248) to Sheperdstown (RM 183) and Antietam Creek (RM 179) although the results (~8.5 mg/L) are somewhat underestimated in comparison to the observations at Sheperdstown (~8.5 - 10.0 mg/L). Driven by benthic P/R <1 (~1.5 - 2.5 g O_2 m^{-2} d^{-1}) and SOD rates (~1.0 g O_2 m^{-2} d^{-1}), the model reproduces the decline in oxygen from Point of Rocks with good agreement between the model and observations. The model,however, underestimates the recovery in oxygen levels observed at Chain Bridge where benthic P/R was assumed <1.

Similar to the 1984 calibration, the results of the 1986 calibration confirm the significance of net oxygen production from benthic algae and the assumption of parameterizing SOD as an increasing function of velocity. For the 1986 calibration, it was necessary to reduce the maximum SOD used in the 1984 case (6-10 g O_2 m^{-2} d^{-1}) by ~50% to 3-8 g O_2 m^{-2} d^{-1}.

Improved agreement with observed data for the 1986 calibration could probably be obtained by further tuning of the assumed maximum SOD function and the assumed spatial transitions of the benthic P/R ratio. In the absence of actual field data describing benthic processes, however, to guide the calibration efforts for both the 1984 and 1986 cases, it did not seem particularly useful to simply refine the numerical assumptions to improve the model results. The 1984 and 1986 calibration results are significant in demonstrating the significance of benthic processes on the overall oxygen balance as well as on inorganic nutrient distributions.

7.4 Model Verification : September 1985

Table 16 summarizes the point source and tributary loads for the September 1985 verification case. The loading data shows that the September 1985 verification is characterized by lower flow at Chain Bridge (Qr=1008 MGD) than was the October 1984 case (Qr=2068 MGD). Total nutrient input for 1985, however, (TN= 10066 kg/d; TP= 1418 kg/d) was of comparable magnitude to the October 1984 calibration case (TN=12099 kg/d; TP=1098 kg/d).

Table 16- Summary of Total Tributary and Waste Treatment Loads (as kg/day): September 1985

PRM Seg#	Qr(MGD)	NH3_N	NO3+NO2_N	O_PO4	CBOD_5	DISS_O2	ORG_N	ORG_P	Total N	Total P
1-29	498.5	434.8	1026.2	272.5	6025.1	16628.9	777.9	81.7	2238.9	354.2
30-47	509.8	411.3	6178.4	906.2	6707.9	15758.3	1238.1	157.5	7827.8	1063.7
1-47	1008.3	846.1	7204.6	1178.7	12733.0	32387.3	2016.0	239.2	10066.7	1417.9

Nitrogen. For the 1985 verification, both nitrate and ammonia are in good agreement with the observed data from the North Branch (RM 340) to Chain Bridge (RM 115). The good match is attributed to parameterization of the spatial forcing functions describing benthic algae uptake, benthic ammonia regeneration via the assumed SOD distribution, benthic nitrification and denitrification and non-point loading of nitrate. Similar to the September 1986 calibration, the maximum SOD distribution for the 1985 verification was reduced by ~50% in comparison to the October 1984 maximum SOD to match the observed ammonia, oxygen and phosphate distributions. Non-point input of nitrate (and phosphate), lower than the data used for the 1986 calibration, was reduced by 48% in comparison to the 1984 calibration.

In order to match the observed data, verification values for sediment denitrification rates for the 1985 case were also somewhat different than the calibration values used for 1984 with higher rates from Antietam Creek (RM 179) to Watts Branch (RM 129) and lower rates from Watts Branch to Chain Bridge (RM 115). The constant non-point load of organic nitrogen for the low flow 1985 verification (20 mg N/sq m-day) was 50% lower than the constant input (40 mg N/sq m-day) used for the 1984 higher flow calibration.

In general, total nitrogen is in good agreement with the observed data. Discrepancies in total nitrogen are primarily attributed to discrepancies between observed and computed organic nitrogen with the model tending to overestimate organic nitrogen somewhat. Total nitrogen, for example, is overestimated at Chain Bridge because of the overestimate of organic nitrogen at Chain Bridge. Refinements in the settling rate for organic nitrogen and the development of a spatial non-point load of organic nitrogen could probably improve the agreement of organic nitrogen and total nitrogen.

Phosphorus. For the 1985 verification, phosphate, organic phosphorus and total phosphorus are in good agreement with the observed data from the North Branch (RM 340) to Chain Bridge (RM 115). The good match is attributed to parameterization of the spatial forcing functions describing benthic algae uptake, benthic phosphate regeneration via the assumed SOD distribution, settling loss of particulate inorganic phosphorus and non-point loading of phosphate. The dominant processes in the 1985 verification are similar to those described for the calibration cases, i.e. high settling velocity in the North Branch; benthic algae uptake etc. In order to match the decline of phosphate at Chain Bridge, the settling velocity for particulate inorganic phosphorus was decreased from the calibration value of 4.0 m/day to 1.5 m/day for the 1985 verification. The constant non-point load of organic phosphorus for the low flow 1985 verification (2 mg P/sq m-day) was 50% lower than the constant input (4 mg P/sq m-day) used for the 1984 higher flow calibration. In setting the organic phosphorus non-point load, a constant ratio of 10:1 was assumed for the organic N:P non-point loading function.

Reflecting the good agreement between the model and the observations, the computed ratio of inorganic N/P is also in good agreement with the observed data. In particular, the sharp decrease in N/P in the North Branch of the Potomac (RM 340-330) is attributed to benthic uptake of nutrients from the attached periphyton as described in the discussion of the 1984 calibration. The overestimate of N/P near Hancock (RM 238) results from the underestimate of observed phosphate at this station. The good match in the N/P ratio suggests that the relative proportions of point and non-point inputs as well as nutrient uptake by benthic algae and phytoplankton are well characterized in the 1985 model verification.

<u>Chlorophyll and Primary Productivity</u>. Chlorophyll data for the 1985 verification is limited to grab samples at the Chain Bridge station. Based on the very limited data, the model appears to be in reasonable agreement with the data. In order to approximate the observed chlorophyll level of ~ 2 ug Ch/L at Chain Bridge, it was necessary to increase the settling velocity used in the 1984 calibration (0.25 m/day) to 0.75 m/day for the 1985 verification from the Monocacy River (RM 153) to Chain Bridge (RM 115). Preliminary runs with the lower settling rate determined for the 1984 calibration resulted in high accumulations of biomass and unrealistic increases in the computed oxygen levels from photosynthetic oxygen production. Similar to the 1984 calibration results, primary productivity is relatively low (~0.05 - 0.1 g C/sq m-day) from the North Branch (RM 340) to the Monocacy River (RM 153). Peak phytoplankton production rates of ~0.2 - 0.4 g C/sq m-day are computed downstream of the Monocacy River near Whites Ferry and Seneca Pool.

<u>CBOD5 and Dissolved Oxygen</u>. Although the observed data are limited, the model results for CBOD5 appear to be in good agreement with observed CBOD5 from Point of Rocks to Chain Bridge. In contrast to the datasets for October 1984 and September 1986, oxygen during September 1985 is characterized by a steep decline and high variance in the vicinity of the confluence with the South Branch (RM 285) and Paw Paw (RM 276). Although the model results are higher than the observed means, the model tracks the decreasing trend fairly well as a result of the assumption that $P/R < 1$ (net benthic production ~1.0-2.7 g O_2 m^{-2} d^{-1}) from the South Branch (RM 285) to the Cacapon River (RM 248). In contrast, the 1984 and 1986 calibrations are based on an assumption of $P/R > 1$ (~0.15-0.30 g O_2 m^{-2} d^{-1}) for this reach. From Hancock (RM 238) to Point of Rocks (RM 159), the model is in good agreement with the observed data, reproducing the recovery of oxygen downstream of the Cacapon River (RM 248). The model also is in good agreement with the observed

characteristic decline from Point of Rocks (RM 159) to the vicinity of the Monocacy River (RM 153) and the observed increase at Chain Bridge.

In order to match the observed oxygen, ammonia and phosphate data for 1985, maximum biochemical SOD for the 1985 verification was set at ~50% of the 1984 calibration parameter values. The two low flow cases of September 1986 and September 1985 are thus based on identical assumptions of the maximum SOD distribution.

7.5 Model Verification : July 1987

Table 17 summarizes the point source and tributary loads for the July 1987 verification case. The loading data shows that the July 1987 verification is characterized by higher flow at Chain Bridge (Qr=2295 MGD) than either the October 1984 case (Qr=2068 MGD) or the September 1985 case (Qr= 1008 MGD). Total nutrient input for 1987, however, (TN= 14814 kg/d; TP= 1011 kg/d) was of comparable magnitude to October 1984 (TN=12099 kg/d; TP=1098 kg/d) and September 1985 (TN= 10066 kg/d; TP= 1418 kg/d).

Table 17- Summary of Total Tributary and Waste Treatment Loads (as kg/day): July 1987

PRM Seg#	Qr(MGD)	NH3_N	NO3+NO2_N	O_PO4	CBOD_5	DISS_O2	ORG_N	ORG_P	Total N	Total P
1-29	1089.6	498.5	1763.8	220.6	13003.8	30582.0	1393.2	125.8	3655.5	346.5
30-47	1204.9	323.8	7387.8	356.2	12600.9	32620.3	3447.4	308.6	11159.0	664.8
1-47	2294.5	822.3	9151.5	576.9	25604.7	63202.3	4840.6	434.4	14814.4	1011.3

Nitrogen. For the 1987 high flow verification, both nitrate and ammonia are in generally good agreement with the observed data from the North Branch (RM 340) to Chain Bridge (RM 115). As with the other calibration and verification cases, the generally good match is attributed to parameterization of the spatial forcing functions describing sources and sinks of nitrogen. Maximum SOD for the 1987 verification (5-10 g O_2 m^{-2} d^{-1}) was reduced by ~15% in comparison to the October 1984 maximum SOD (6-10 g O_2 m^{-2} d^{-1}) to match the observed ammonia, oxygen and phosphate distributions. The major discrepancy is the pronounced underestimate of ammonia at Chain Bridge. The underestimate is attributed to an underestimate of the maximum biochemical SOD downstream of the Monocacy River. Finer tuning of the maximum SOD for the 1987 verification could result in an improvement of the model for the Chain Bridge observation. Non-point input of nitrate (and phosphate), higher than the data used for the 1984 and 1986 calibrations, was increased by 20% in comparison to the 1984 calibration and 50% in comparison to the 1986 calibration in order to match the observed nitrate data.

In order to match the observed data, verification values for sediment denitrification rates for the 1987 case were different than the calibration values used for 1986 but the same as the values used for the other higher flow case of 1984. The constant non-point load of organic nitrogen for the high flow 1984 calibration and 1987 verification (40 mg N/sq m-day) was twice as high as the constant input (20 mg N/sq m-day) used for the 1985 and 1986 low flow cases.

Phosphorus. With the exception of the large variance associated with the peak concentration of organic phosphorus (~150-550 ug P/L) and total phosphorus (~225-600 ug P/L) observed at Point of Rocks (RM 159), the model results for total phosphorus are in good agreement from the North Branch (RM 340) to Chain Bridge (RM 115). The results for phosphate, however, significantly overestimate the increasing trend resulting from agricultural non-point loading downstream of Conococheague Creek (RM 210) by about a factor of two. Using the 1984 and 1986 calibration value for the particulate inorganic phosphorus settling velocity of 4.0 m/day from Antietam Creek (RM 179) to Chain Bridge (RM 115), however, resulted in good agreement with the observed data at Chain Bridge.

Reflecting the trends in agreement of inorganic nitrogen and phosphorus, the computed N/P ratio is in fair agreement with the observed data pairs. AS with the 1984, 1985 and 1986 cases, the rapid drop in N/P in the North Branch results from nutrient uptake by benthic algae. The overestimate of nitrate near Hancock (RM 239) results in the overestimate of the model N/P. Downstream of Antietam Creek (RM 179), the overestimate of phosphate results in an underestimate of the model N/P ratio.

Non-point input of nitrate and phosphate,. higher than the data used for the 1984 and 1986 calibrations, was increased by 20% in comparison to the 1984 calibration and 50% in comparison to the 1986 calibration in order to match the observed nitrate data for 1987. Consistent with the 1984, 1985 and 1986 cases, it was assumed that a constant N:P ratio of 4.0 characterized the non-point input of phosphate for the 1987 verification. The results of the 1987 verification suggest that an increased N:P ratio for non-point input of phosphate would have resulted in an improved match with the observed data by reducing the mass input of phosphate. Alternatively, increasing the calibrated value of 4.0 m/day for the settling velocity downstream of Antietam Creek (RM 179) could also improve the agreement with the observed data.

Chlorophyll and Primary Productivity. During July 1987 observed chlorophyll at Chain Bridge was characterized by an increase of chlorophyll from Point of Rocks (RM 159) (~2 ug Chl/L) to a mean of ~8 ug Chl/L with a large variance ranging from ~2-12 ug Chl/L. The model reproduces this general trend somewhat with a computed increase in chlorophyll downstream of Point of Rocks from ~4 to 12 ug Chl/L. Similar to the 1985 verification, the settling velocity was increased from 0.25 m/day to 0.75 m/day downstream of the Monocacy River (RM 153) in order to approximate the observed chlorophyll data. Similar to the results of the 1985 verification, preliminary calculations with the 1984 calibration settling rate of 0.25 m/day resulted in unrealistic accumulations of biomass and photosynthetic oxygen production downstream of the Monocacy River. Computed primary productivity for the July 1987 case was significantly higher than the other simulation cases of 1984, 1985 and 1986. Model primary productivity was on the order of ~0.1-0.2 g C/sq m-day from the North

Branch (RM 340) to Point of Rocks (RM 160) with a dramatic increase in peak production to ~0.4-2.0 g C/sq m-day downstream of the Monocacy River (RM 153).

CBOD5 and Dissolved Oxygen. Consistent with the observations for organic nitrogen and phosphorus, CBOD5 is characterized by a high mean (~5 mg/L) with a large variance ranging from ~2.5-7.5 mg/L at Point of Rocks (RM 160). Similar to the model results for the other cases, the model fails to reproduce the observed gradient of CBOD5 in the vicinity of Point of Rocks. Additional non-point loading of CBOD5 that reflects agricultural and forested land use characteristics could improve agreement with the sparse observations.

The model results for oxygen are in generally good agreement with the observed distribution although the model does not reproduce the entire pattern of depletion and recovery that is reflected with the observations. As with the other cases, the decline in the North Branch is attributed to high rates for biochemical SOD (~1.5-2.0 g O_2 m^{-2} d^{-1}) and net benthic algae oxygen production characterized by P/R <1 (~4.5-8.0 g O_2 m^{-2} d^{-1}). As described previously, maximum SOD for the 1987 verification (5-10 g O_2 m^{-2} d^{-1}) was reduced by ~15% in comparison to the October 1984 maximum SOD (6-10 g O_2 m^{-2} d^{-1}) to match the observed ammonia, oxygen and phosphate distributions.

Improvements in agreement with the observed oxygen data could be obtained by further refinement of the maximum SOD and P/R estimates. In the absence of actual field data for characterizing benthic oxygen demand and benthic algae processes, it did not seem fruitful to simply numerically manipulate the spatial forcing functions further to improve the match to the oxygen observations. As will be shown in the discussion of model sensitivity, the computed oxygen balance is strongly coupled to the external forcing functions specified for biochemical SOD and net benthic algae oxygen production.

8.0 Summary Statistics for Model Calibration and Verification

In the calibration and verification of the Potomac River Model, comparisons of observed data and simulation results were made using two approaches: (1) qualitative (i.e. visual) agreement of spatial gradients of observed and model data; and (2) quantitative statistical comparison of observed and model data using linear regression analysis over the entire spatial domain of the model (see Thomann and Fitzpatrick, 1982). The previous section presented qualitative comparisons of the observed data to the Potomac River Model results for the four cases. In general, the qualitative comparison of the observed data with the model suggests that the model can reproduce the spatial trends observed under quite different low-flow summer conditions. The model can be considered an adequate framework for preliminary water quality management planning purposes. Although the qualitative comparisons are an acceptable means of judging the validity of a model, a more rigorous quantitative method is desirable to further characterize the agreement between the observed data and the model.

Statistical methods generally used to compare observed data and model results include: comparison of means; relative error; and regression analyses (see Thomann and Fitzpatrick, 1982). For the Potomac River Model, linear regression was chosen to provide a quantitative measure of model credibility. Statistics were computed for each simulation case based on the observed data and model results for each WASP4 state variable with data from the entire 200 mile domain of the Upper Potomac River pooled for the regression analysis. No attempt was made to characterize the spatial domains of the water quality responses dominated by either forest or agricultural land uses, or point source inputs.

The linear regression testing equation is given by:

$$X = a^* + b^*C + e^*$$

where: X is the observed concentration; C is the simulated concentration; a^* and b^* are the estimated intercept and slope of the calculated and observed data sets; and e^* is the residual error in X, the observed data. The statistics computed by regressing the observed data with the model results include:

(1) the correlation coefficient (r) and (r^2), a measure of the variance in the observed data that is accounted for by the model;

(2) standard error of estimate (SE est); the residual error between the model and the data;

(3) slope (Slope) estimate of b^* and intercept (Intcp) estimate of a^* of the regression equation;

(4) maximum (Mx Err) and minimum (Mn Err) error of the estimates;

(5) standard deviation of the residual error (sd err).

Table 18 summarizes the regression results computed for each of the calibration and verification cases. As shown in this Table, the ability of the model to capture the observed variability in the nutrient systems varies between years and among the nutrients. In general most of the observed variablity of nitrate, total nitrogen (most of which is nitrate), orthophosphate, and total phosphorus is captured by the model. However, these results should be viewed with caution. The observed data sets are very small, and these regression analyses do not consider changes along the river. These results should be compared to the plots of observed and model values in Appendices A-D which indicate spatial variation in model performance. The discussion in Chapter 9 on Sensitivity Analyses provides some indication of sources of error. These regressions are summarized below for total nitrogen and total phosphorus, two key variables for the evaluation of scenarios for nutrient control measures. Figures 22-29 present the residual error (observed-model) and the linear regression (observed vs model) plots for total nitrogen and total phosphorus.

Table 18- Linear Regression Analysis of Model Calibration and Verification Cases: Oct 1984, Sept 1985, Sept 1986 and July 1987

Data Set: prm84068.inp Run Date: 26 Jun 1991 Time of Run: 12:45:41

SY#	SYS VAR---	-Nbr	-----Slope	-----Intcp	-------R^2	----SE est	----Mx Err	----Mn Err	----Sd Err
1	NH3_N	11.	0.453	38.125	0.458	21.856	53.500	8.018	30.981
2	NO3_N	11.	0.954	106.494	0.799	319.944	822.000	63.870	304.898
3	O_PO4_P	8.	1.258	1.621	0.903	18.012	53.000	14.018	19.681
4	TOTCHLA	4.	1.524	-4.345	0.796	4.153	4.600	-0.860	4.097
5	BOD5	4.	0.228	2.701	0.108	0.927	1.860	0.465	1.169
6	OXYGEN	11.	1.059	-0.246	0.660	0.397	0.880	0.285	0.378
7	TON	11.	0.261	372.255	0.175	97.642	213.000	-54.130	152.364
8	TOP	8.	-0.458	78.618	0.126	16.665	30.100	-9.804	24.171
11	TN	11.	0.788	302.110	0.731	391.855	650.000	-37.636	406.789
12	TP	11.	0.960	0.494	0.409	44.695	77.000	-4.418	42.427
14	TEMP	13.	0.862	2.151	0.878	0.510	1.625	0.054	0.531

Data Set: prm85069.inp Run Date: 26 Jun 1991 Time of Run: 12:55:10

SY#	SYS VAR---	-Nbr	-----Slope	-----Intcp	-------R^2	----SE est	----Mx Err	----Mn Err	----Sd Err
1	NH3_N	11.	0.405	21.485	0.306	25.046	10.000	-11.755	33.227
2	NO3_N	11.	0.515	347.019	0.234	166.576	398.000	41.818	178.095
3	O_PO4_P	11.	0.716	13.969	0.873	14.753	33.360	-2.471	20.202
4	TOTCHLA	Too few values for regression:N= 2.							
5	BOD5	4.	0.796	0.306	0.710	0.867	0.440	-0.207	0.763
6	OXYGEN	11.	1.232	-1.935	0.803	0.646	0.720	-0.122	0.656
7	TON	11.	0.301	319.326	0.129	112.683	202.000	-85.636	143.118
8	TOP	11.	-0.715	62.800	0.121	27.512	82.100	-3.882	34.939
11	TN	11.	0.353	738.722	0.243	182.110	270.000	-94.818	248.732
12	TP	11.	0.625	27.646	0.746	21.428	46.400	-9.491	29.159
14	TEMP	12.	0.970	0.818	0.986	0.314	0.700	0.140	0.309

Data Set: prm86069.inp Run Date: 26 Jun 1991 Time of Run: 12:55:59

SY#	SYS VAR---	-Nbr	-----Slope	-----Intcp	-------R^2	----SE est	----Mx Err	----Mn Err	----Sd Err
1	NH3_N	11.	0.103	39.642	0.017	34.734	81.400	-14.754	49.649
2	NO3_N	10.	0.396	351.324	0.509	110.089	150.000	-181.400	191.651
3	O_PO4_P	11.	0.385	15.059	0.420	15.013	24.700	-6.956	24.051
4	TOTCHLA	6.	0.723	1.085	0.563	0.959	2.270	0.491	0.936
5	BOD5	4.	-1.045	8.919	0.555	1.357	5.800	3.035	2.663
6	OXYGEN	11.	0.739	2.177	0.615	0.390	0.740	-0.034	0.406
7	TON	11.	1.394	-148.547	0.546	170.037	371.000	62.364	168.881
8	TOP	11.	1.889	-13.005	0.499	16.379	42.100	19.336	17.167
11	TN	10.	0.645	341.007	0.658	192.422	200.000	-186.500	227.987
12	TP	11.	0.736	30.243	0.738	17.680	39.300	10.782	19.568
14	TEMP	11.	0.975	0.746	0.978	0.578	1.400	0.291	0.556

Data Set: prm87068.inp Run Date: 26 Jun 1991 Time of Run: 12:56:47

SY#	SYS VAR---	-Nbr	-----Slope	-----Intcp	-------R^2	----SE est	----Mx Err	----Mn Err	----Sd Err
1	NH3_N	11.	0.254	39.708	0.472	15.175	44.400	-21.245	42.478
2	NO3_N	11.	0.984	-68.704	0.842	246.909	404.000	-85.545	234.405
3	O_PO4_P	11.	0.553	6.660	0.665	18.069	29.400	-15.896	25.984
4	TOTCHLA	6.	-0.124	4.372	0.082	1.690	4.110	-2.584	4.373
5	BOD5	4.	-0.158	3.799	0.009	2.019	2.870	-0.135	2.019
6	OXYGEN	11.	1.319	-2.394	0.474	0.632	0.990	-0.064	0.615
7	TON	11.	0.666	249.488	0.256	248.461	483.000	38.364	245.662
8	TOP	11.	2.749	-42.317	0.121	92.002	306.000	44.755	89.668
11	TN	11.	0.910	34.877	0.864	284.820	330.000	-128.364	278.526
12	TP	11.	1.584	-36.436	0.605	72.811	240.000	24.618	75.945
14	TEMP	13.	0.980	0.074	0.894	1.111	0.750	-0.422	1.065

8.1 Total Nitrogen

As shown in the residual error plots, the agreement between observed and computed total nitrogen (TN) is a reasonable match for the domain of the upper Potomac River model. (See Figure 22, 23, 24, 25). The results suggest that the model framework can reproduce the overall spatial trend of nitrogen. The consistent discrepancy, however, is the model's overestimate of TN delivered at Chain Bridge, with the relative error ranging from a maximum of -67% for the October 1984 case to a minimum of -2.5% for the October 1984 case to a minimum of -2.5% for the July 1987 case (see Table 33). With correlation coefficients (r) ranging from 0.49 (Sept. 1985) to 0.93 (July 1987), the model accounted for a minimum of 24% (Sept. 1985) to a maximum of 86% (July 1987) of the variance (r^2) in the observations (see Table 18).

In the October 1984, and September 1986 cases the overestimate of TN at Chain Bridge (RM 115) is attributed to the model's overestimate of both nitrate and organic nitrogen. In all four of the simulation cases, organic nitrogen is overestimated with the model at Chain Bridge (RM 115). The results for nitrate suggest that an increase in the benthic denitrification loss rate is needed for the region downstream of the Monocacy River (RM 151) to improve the match with the observed date. The slow velocity, and pools that are characteristic of this region create physical conditions conducive to deposition of solids and resultant high rates of benthic organic mineralization, nitrification and denitrification.

The results for organic nitrogen reflect the constant parameterization used to describe non-point loading and settling of organic nitrogen. Development of spatially varying functions for these terms would improve the agreement between the model and the observations.

8.2 Total Phosphorus

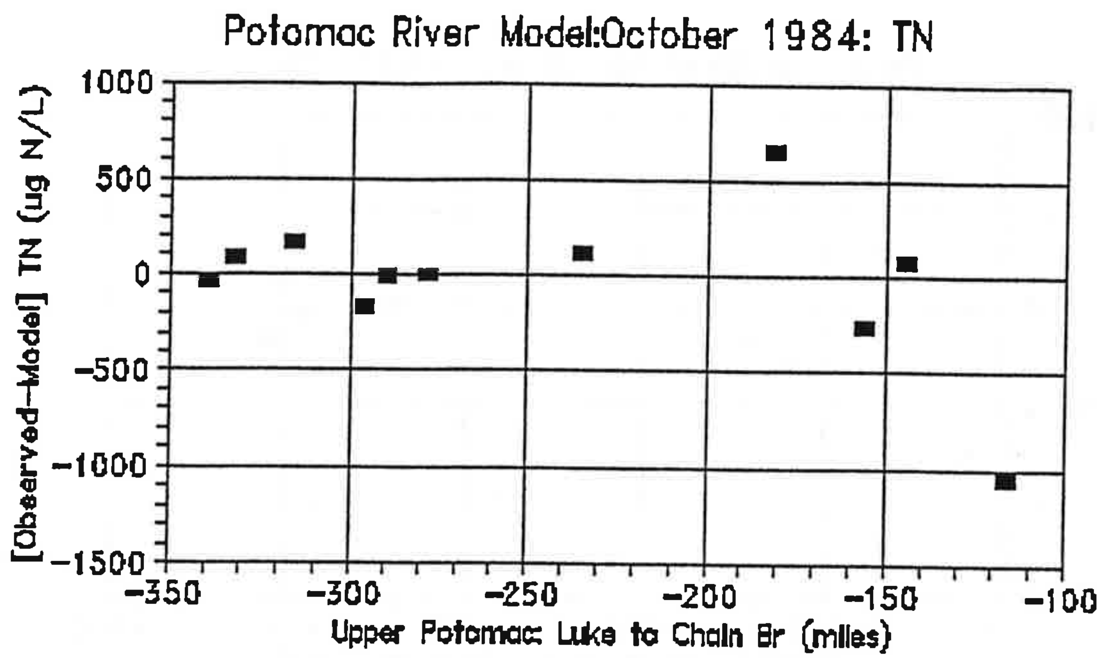
As shown in the residual error plots for the calibration and verification of total phosphorus (TP) (see Figure 26, 27, 28, 29), the model reproduces the overall spatial trends of observed TP quite well. These results suggest that the model framework used to describe inorganic phosphate and organic phosphorus is a reasonable approximation to actual conditions in the upper Potomac River. In particular, with a relative error of 20% to 35% the model's estimate of TP delivered across the fall line at Chain Bridge (RM115) is in good agreement with the observations (see Table 33).

In general, the model tends to slightly underestimate TP with the relative error ranging from +19% to +35% for the October 1984, September 1986 and July 1987 cases. For September 1985, the model overestimated TP somewhat with a relative error of -22% comparable in magnitude to the other cases. With correlation coefficients of 0.64 to 0.86 the model accounted for 41% to 74% of the variance (r^2) in the observations (see Table 32; Figure 26-29).

Where the model underestimates the data (1984, 1986, 1987) the minor discrepancy between the model and the observations at Chain Bridge (RM 115) is attributed to an underestimate of organic phosphorus in 1984, 1986 and 1987 and a small underestimate of inorganic phosphate in 1984 and 1987. The most dramatic discrepancy in TP is at Point of Rocks (RM156) for the July 1987 verification where observed TP ranged from ~250-600 ugP/L with a mean value of 415 ugP/L and the model predicted only 175 ugP/L. This discrepancy in TP is attributed to the organic phosphate. The observed data for organic nitrogen and CBOD5 also is characterized by rather high concentrations at Point of Rocks. The model apparently did not correctly account for the unusually high organic carbon, nitrogen or phosphorus loading from a tributary in the vicinity of Point of Rocks. (e.g. Catoctin Creek, MD; Catoctin Creek, VA; Tuscarora Creek).

Similar to the interpretation of the model computation of organic nitrogen, the incorporation of spatially varying functions for characterizing the non-point input and settling of organic phosphorus could improve agreement between the model and the observed date.

Figure 21- October 1984 Total Nitrogen: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



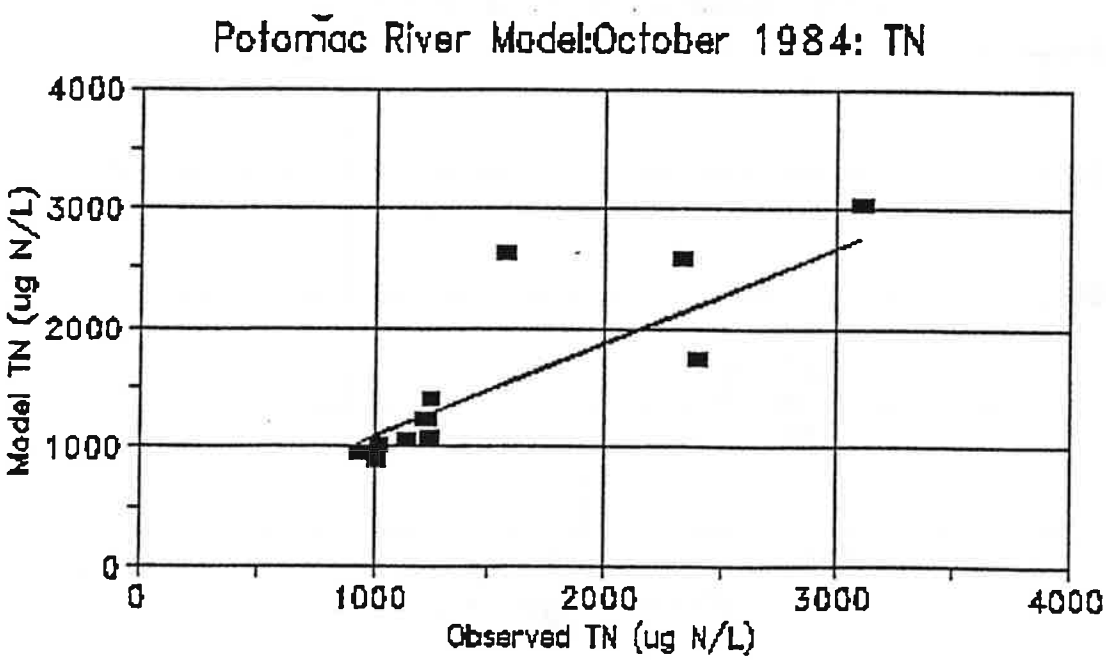
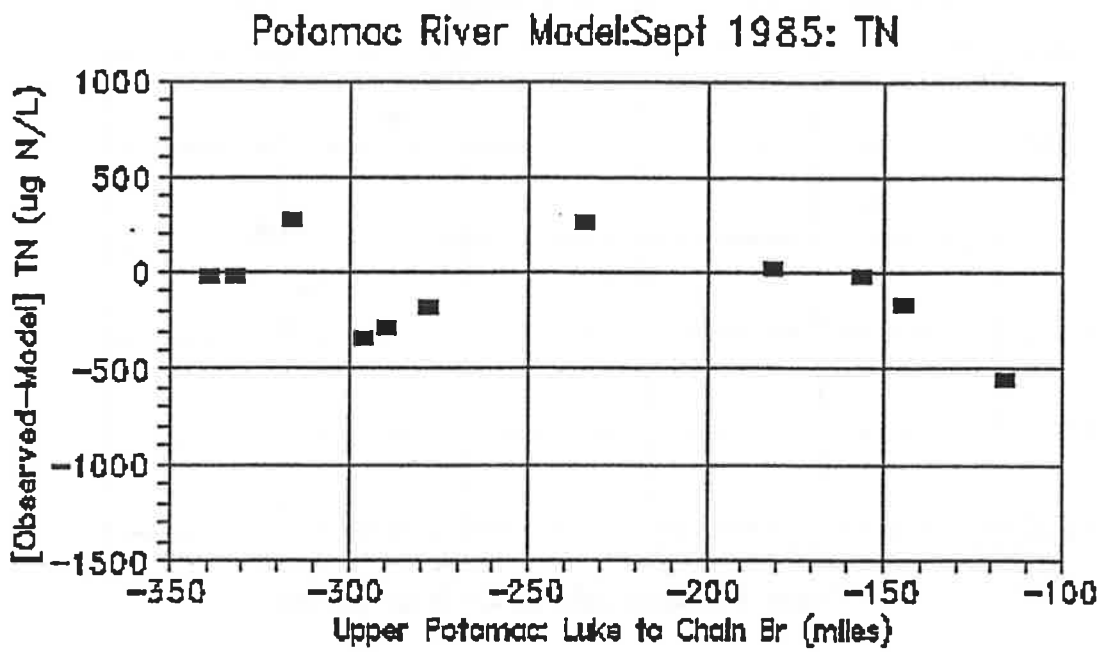


Figure 22- September 1985 Total Nitrogen: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



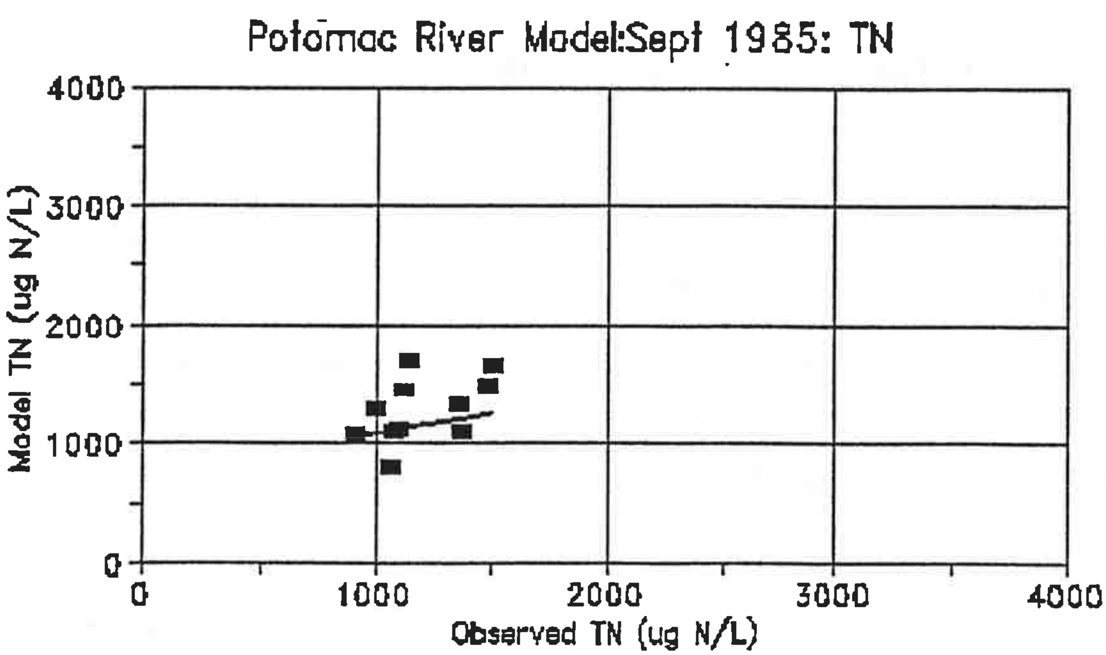
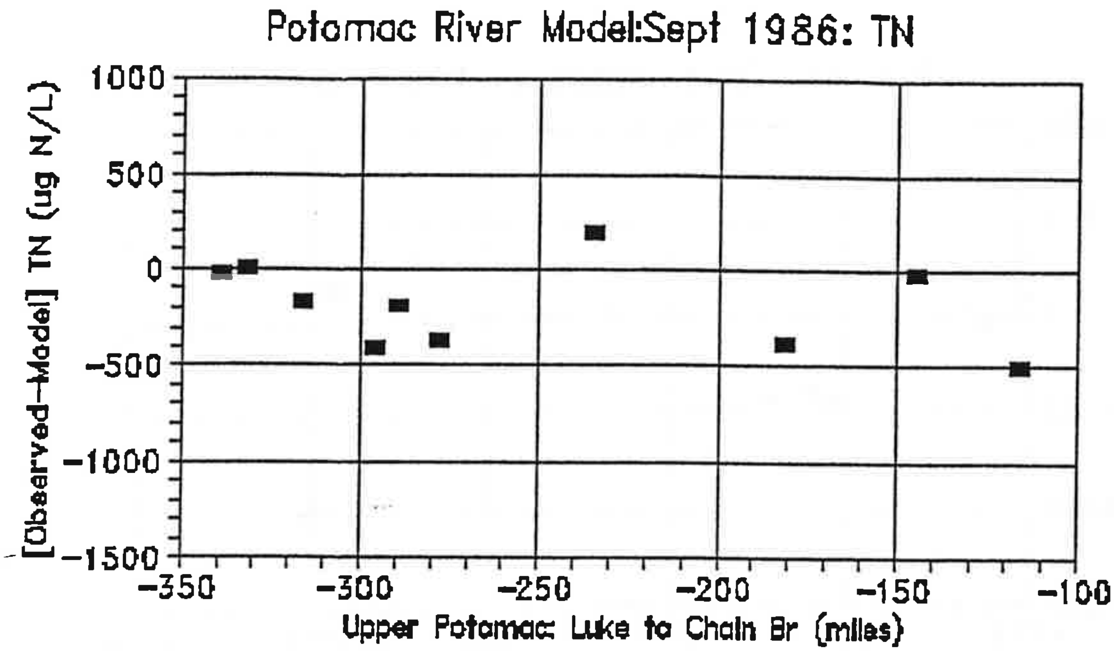


Figure 23- September 1986 Total Nitrogen: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



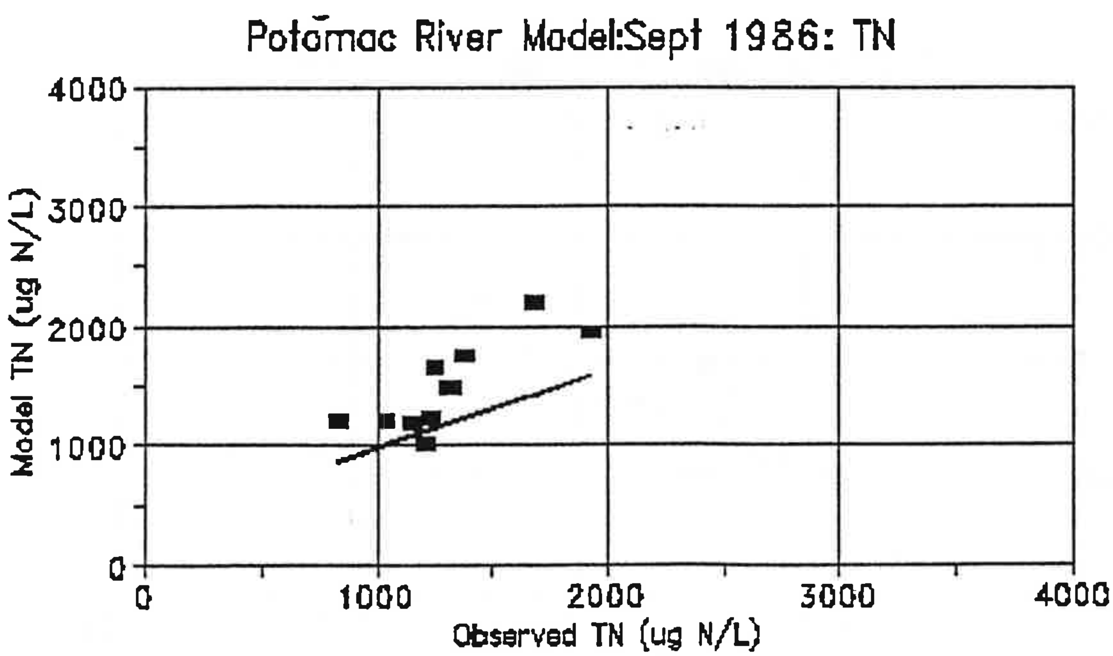
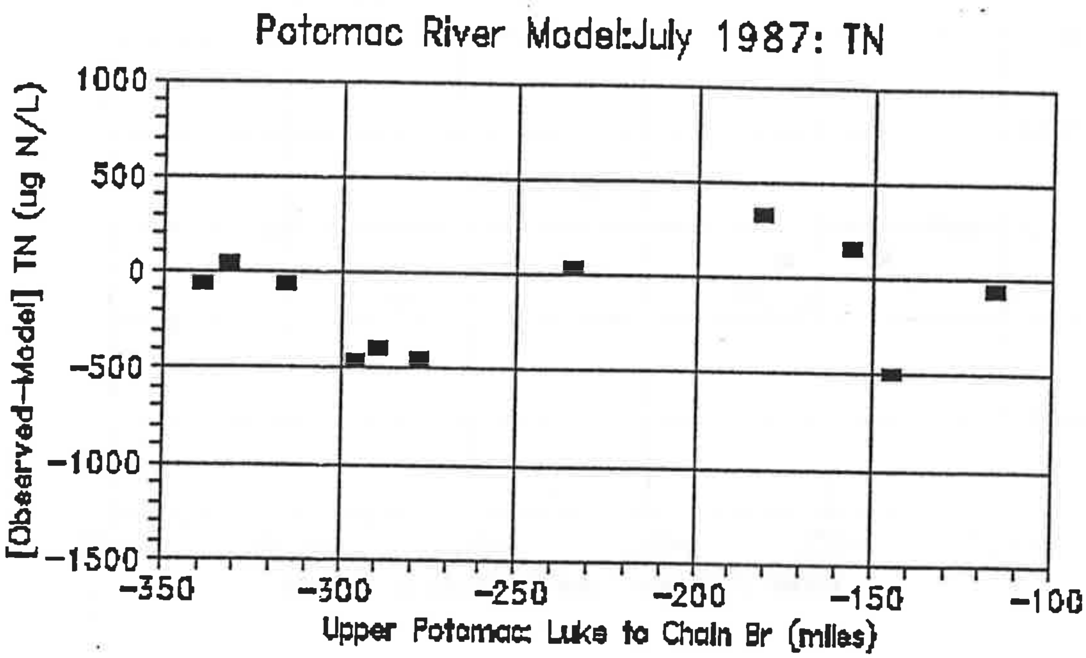


Figure 24- July 1987 Total Nitrogen: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



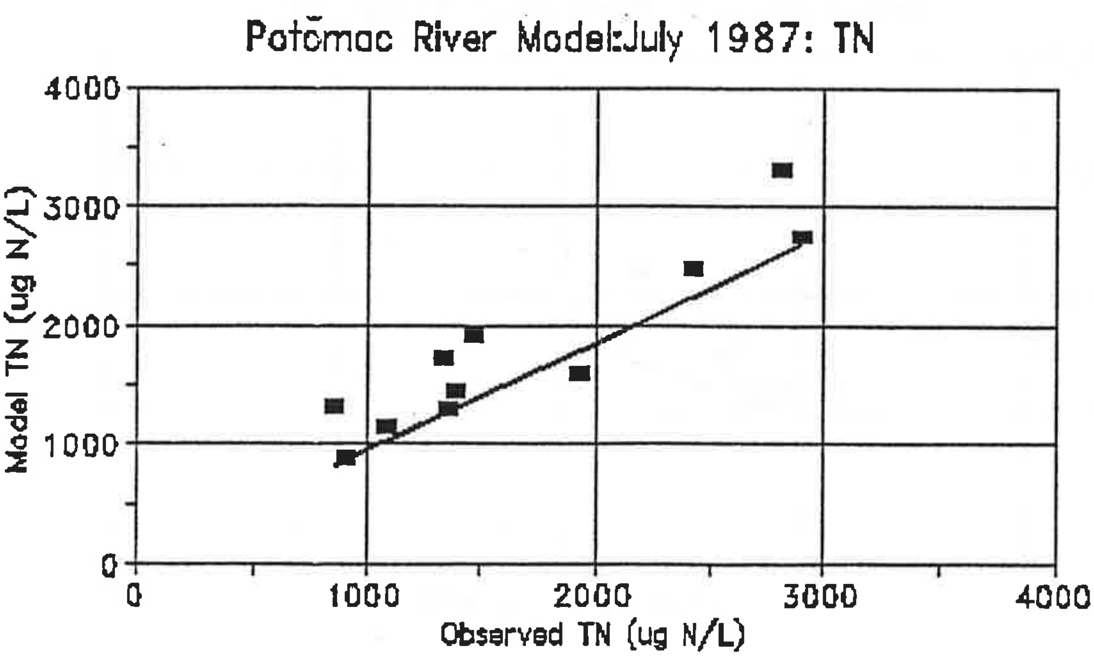
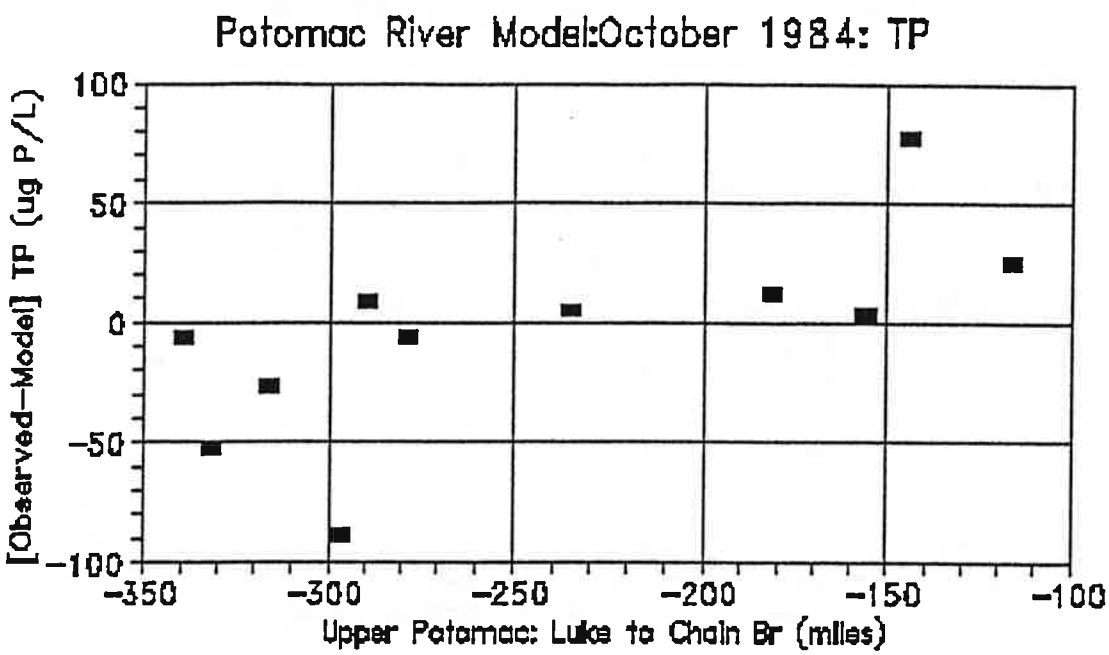


Figure 25- October 1984 Total Phosphorus: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



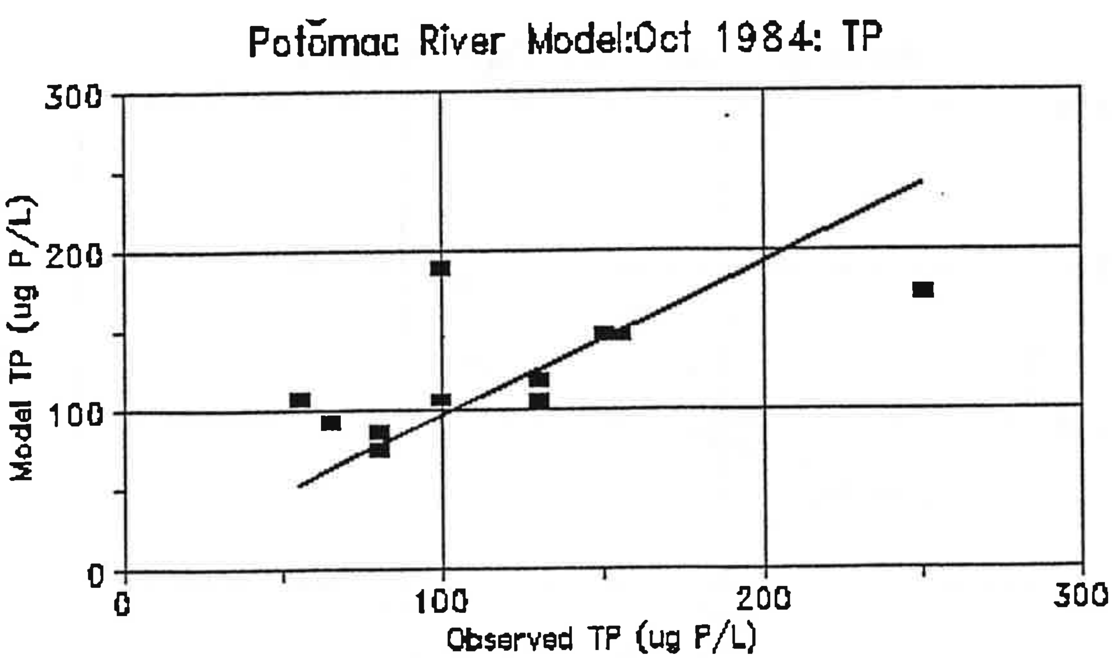
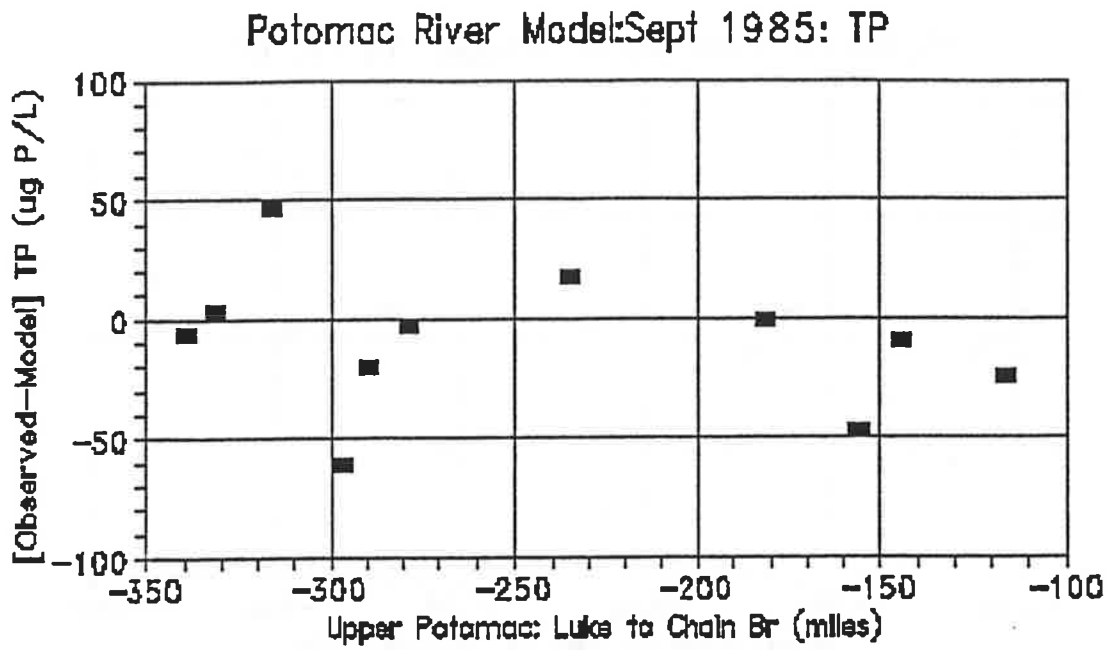


Figure 26- September 1985 Total Phosphorus: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



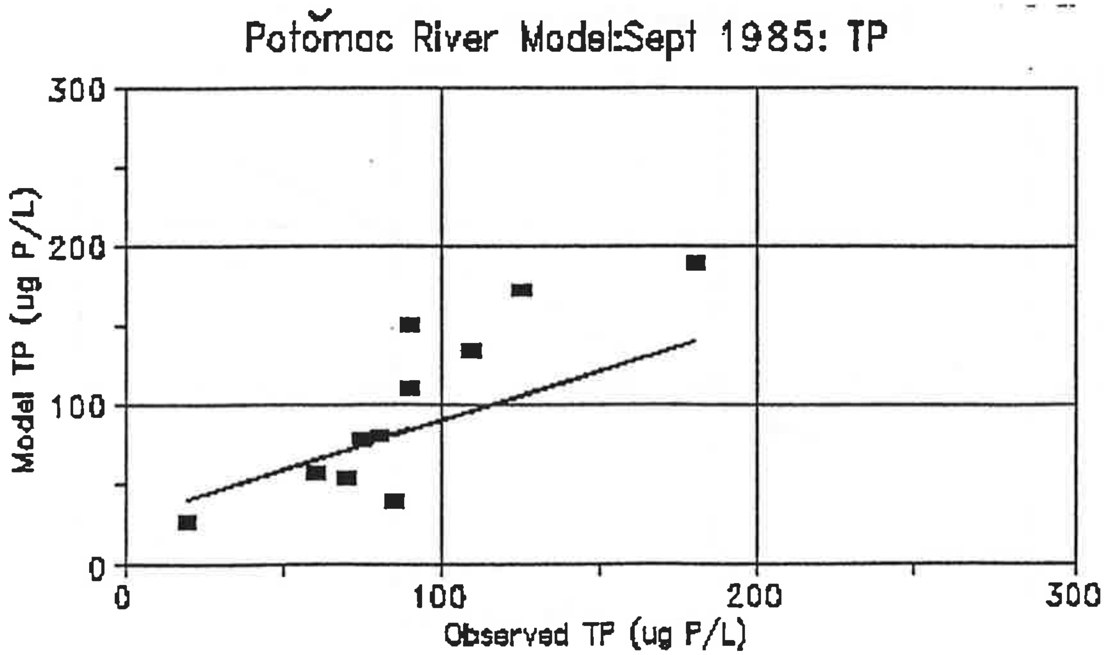
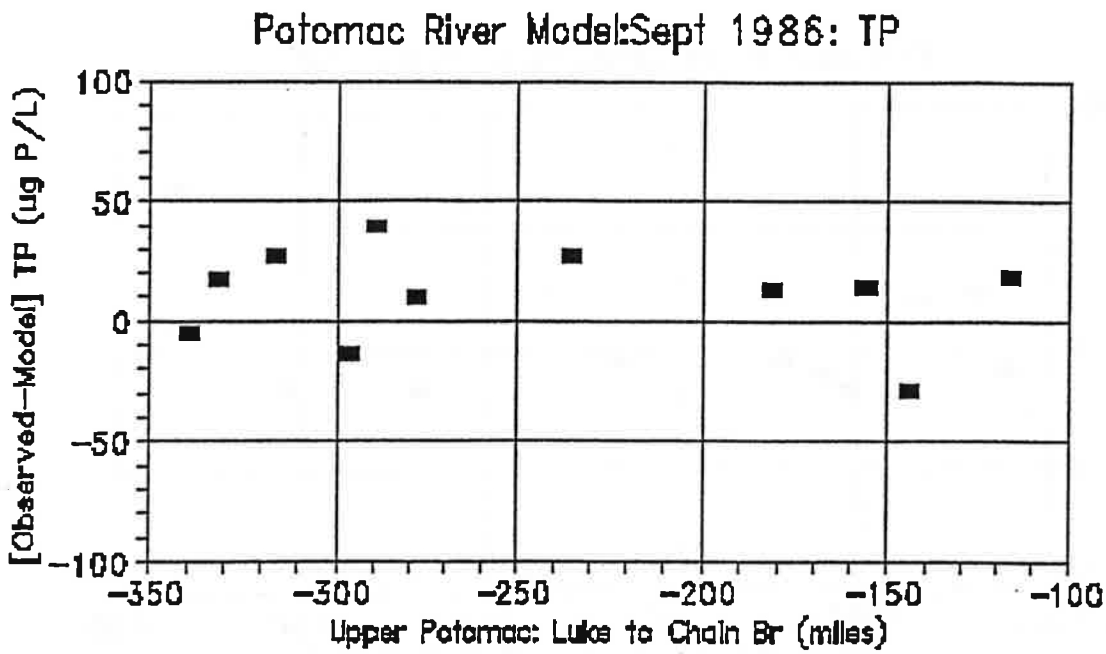


Figure 27- September 1986 Total Phosphorus: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values



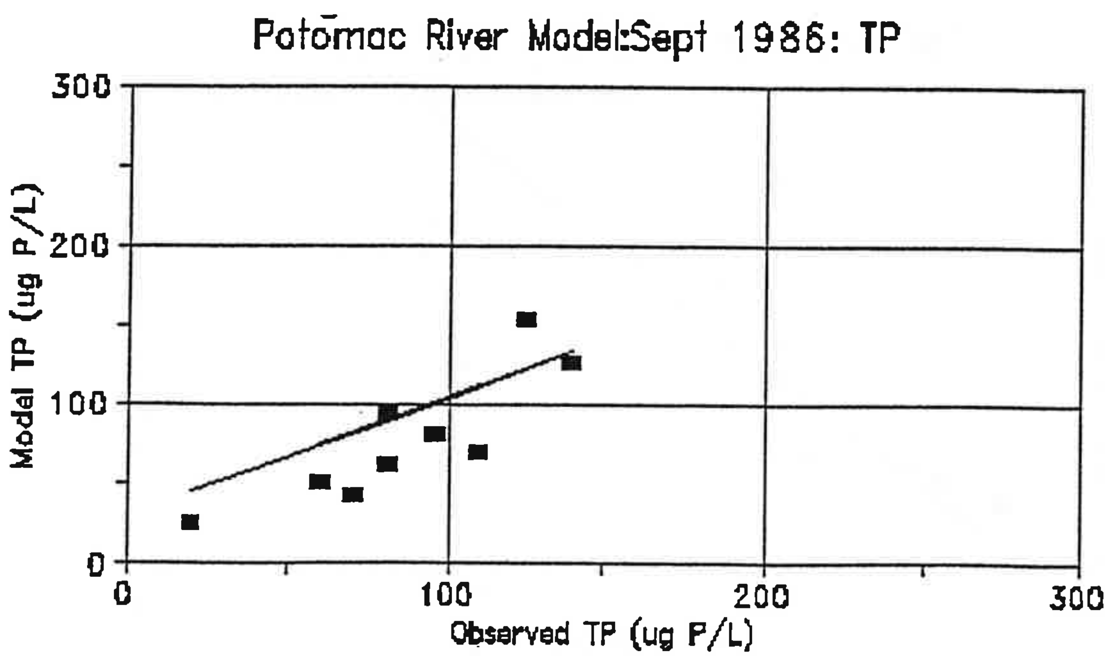
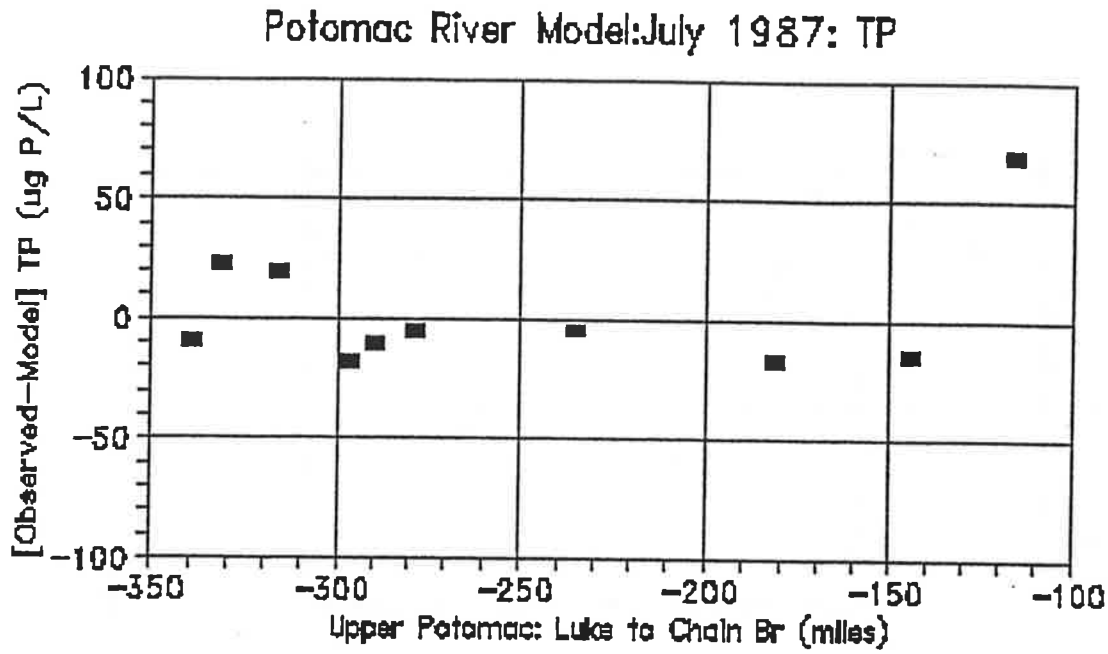
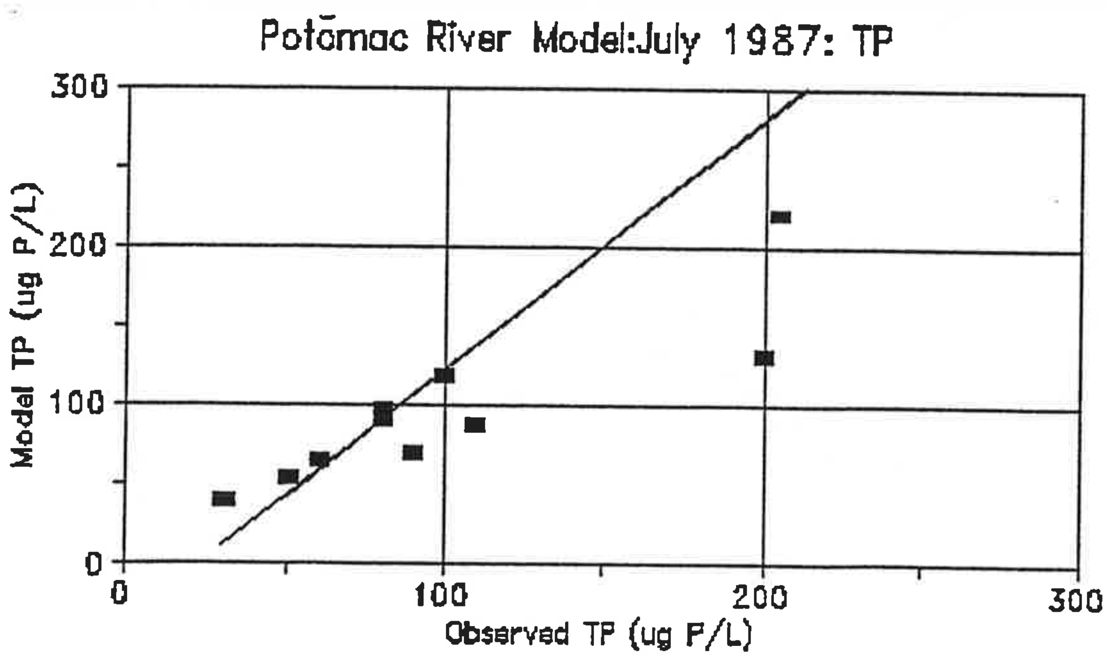


Figure 28- July 1987 Total Phosphorus: Residual Error (Observed - Model) vs River Mile, and Observed values vs Model values





9.0 Sensitivity Analyses

The rate coefficients and kinetic constants described in Section 6 of this report are consistent for the calibration and verification periods. Determined after numerous calibration runs, the set of model coefficients is within reasonable range of reported values based on both experimental observations and other modeling studies (e.g. EPA, 1990; Bowie et al., 1985). Although there is uncertainty in the kinetic coefficients (see Table 10) that is typically explored in a model sensitivity analysis (e.g. Thomann and Fitzpatrick, 1982), the evaluation of the sensitivity of the Potomac River Model focused on the uncertainty of the spatial forcing functions developed to match the observed nutrient and oxygen data.

In the Potomac River Model, the characterization of: sediment oxygen demand and nutrient regeneration; benthic algae production and nutrient uptake; settling rates; and the non-point loading of nutrients is based solely on hypothesized empirical relationships and literature data since field data were not available to describe these processes. Preliminary calibration runs also indicated the significance of these processes on the model results. It was considered essential, therefore, to assess the sensitivity of the model to these very uncertain forcing functions.

Sensitivity analyses were performed using the September 1985 dataset as the base run for comparison to changes in the following seven sets of model parameters:

(1) Water Temperature
(2) Incident Solar Radiation
(3) Sediment Oxygen Demand
(4) Benthic Primary Production
(5) Non Point Source Input of N,P
(6) Nitrification Rate
(7) Inorganic Solids Settling Rate

9.1 Water Temperature

Water temperature specified for each model run was determined as the mean of the observations in the appropriate month for each model segment. For segments with no data, temperature was linearly interpolated. The variability in water temperature during a one month period was estimated using the daily water temperature records from Rockville, WSSC, Washington County, and Williamsport raw water intakes, and the gage at Pinto, for the month of September 1985. The standard deviation in daily water temperature ranged from 1.7 to 3.0 °C. To test model sensitivity to water temperature, the September 1985 case was run with temperatures 2.5 °C higher and 2.5 °C lower than the mean observed temperature (see Figure E-1).

Since water temperature is a key factor in determining biological and chemical reaction rates, it is not surprising that the model is sensitive to the 2.5°C change in water temperature

(see Figure E-1 through E-14) with a temperature coefficient of ~ 1.07 characteristic of SOD (1.065); benthic primary production (1.07) notification (1.08); and denitrification (1.08) a 2.5°C change in ambient water temperature from a reference of 20°C results in about a 20% change in reaction rates.

The major impact of the change in water temperature on ammonia (Figure E-1), nitrate (Figure E-2) and dissolved oxygen (Figure E-7) results from the effects of SOD (Figure 10), denitrification (Figure 18b) and benthic primary production (Figure 15b). The dramatic change in ammonia results from benthic regeneration of ammonia and benthic uptake of ammonia by attached periphyton: The change in oxygen also results from SOD and net benthic production of attached algae.

9.2 Incident Solar Radiation

For each model run, a single incident solar radiation value was used, which was the mean of the estimated daily solar radiation values. To test the sensitivity to these estimates of solar radiation, different (high and low) estimates of daily solar radiation were made and the mean of those values used for model sensitivity runs.

For the calibration and verification model runs, daily solar radiation was estimated using a procedure described in ICPRB (1991) and summarized as:

(a) calculate the theoretical clear sky solar radiation for the day of the year;

(b) multiply the clear sky radiation by a factor based on the observed NOAA/NWS 'cloud cover' value.

The multiplication factors were determined from a 1977-1980 data set which included observed solar radiation and cloud cover values. From this data set, for each cloud cover value, the mean, median, and variance for percent of clear sky solar radiation was calculated. For calibration and verification model runs, the median percent clear sky solar radiation was used as the multiplication factor. For the model sensitivity runs, the multiplication factors, for each cloud cover value, were based on the mean value plus/minus the standard deviation of the percent of clear sky solar radiation. Incident solar radiation values used for the mean base run and the low and high sensitivity runs are summarized below:

Mean Solar Radiation	394 ly/day
Low Solar Radiation	335 ly/day
High Solar Radiation	448 ly/day

Incident solar radiation is assumed constant for the steady-state simulation interval of 22 days. Estimates of maximum and minimum solar radiation levels were used to determine sensitivity to solar radiation. Dramatic changes in ammonia, nitrate, phosphate, oxygen and chlorophyll result from significantly increased primary production stimulated by the availability of additional solar radiation for the maximum case. Primary production increases significantly downstream of RM 220 as a result of the decreasing depth of the shallow water column from ~1-2 meters to ~0.5-2.0 meters. The peak increases in primary production, dissolved oxygen and chlorophyll and sharp declines of nitrogen and phosphorus are related to shallow segments within depths ranging from ~0.5-1.0 meters. The phytoplankton growth rate, and hence primary productivity, is apparently very sensitive to the overall light reduction factor. That factor is, in turn, dependent on water column depth, the extinction coefficient, incident solar radiation and the saturating light intensity used to characterize phytoplankton growth. Extinction in the shallow water column is computed as the sum of the background extinction coefficient and self-shading by phytoplankton biomass. Since chlorophyll data were limited and light extinction data were not available for the upper Potomac River, a constant background light extinction value of 0.04 m^{-1}, characteristic of clean water, was used. The model sensitivity results to the typical range of incident solar radiation levels suggests that a more realistic spatial distribution of the background extinction coefficient is needed to improve the robustness of the model framework for phytoplankton dynamics. Paired bottom light intensity measurements and chlorophyll data are needed to characterize the spatial distribution of the background extinction coefficient.

9.3 Sediment Oxygen Demand

In the model (as in nature), diagenesis of organic matter consumes oxygen and releases nutrients into the overlying water column. The interacting processes are complex with theoretical models (e.g. DiToro, 1990) only beginning to interpret experimental and field survey data sets. In the absence of any sediment oxygen demand (SOD) or nutrient regeneration data for the Upper Potomac River, the sensitivity of the model to changes in the biochemical component of the SOD forcing function was evaluated. Recall that the biochemical component of SOD in the model is empirically determined as a function of velocity, temperature and a maximum SOD specified for each segment (see Section 6). In addition, the total SOD value input to the model also accounts for net oxygen production by benthic algae. For the model sensitivity analysis, the maximum biochemical SOD value was increased by 100% (2X) and decreased by 50% (0.5X) with respect to the distribution of maximum SOD values specified for the base September 1985 run (see Figure 10).

In varying the maximum SOD and estimated SOD, sediment fluxes of ammonia and phosphate also are varied in stoichiometric proportion to the Redfield C:O:N:P ratio. An evaluation of the sensitivity of the model to SOD is quite useful for evaluating the response in ammonia since actual experimental and field data suggests that the ammonia flux rate can vary by a factor of two for a given SOD value (see DiToro, 1986; see Figure 16). The calibrated distribution of ammonia sediment flux rates in the model could thus also vary by a factor of two as a function of a specific SOD estimate.

The September 1985 base run SOD and Benthic P/R distribution, is characterized by peak SOD values of ~1.5-4.0 gO2 m^{-2} day^{-1} (Figure 10) and P/R values of 0.5 (Figure 15b) from RM 300 to RM 240 and from RM 150 to RM 120. Recall that the empirically derived

SOD distribution is the sum of biochemical processes and net oxygen production of the benthic algae. In the SOD sensitivity analysis, only the biochemical component of SOD was varied by a factor of 2. A separate sensitivity run evaluated the model's response to changes in benthic primary production.

Inorganic nutrients and dissolved oxygen were particularly sensitive to the 0.5X and 2X variation in SOD. In the vicinity of the peak SOD distributions, ammonia and phosphate were quite sensitive since the benthic flux of these nutrients was directly computed as a function of SOD and the appropriate Redfield C:O:N:P stoichiometric ratios. Nitrate is also sensitive to SOD because of preferential uptake of ammonia by both benthic algae and the phytoplankton. The increased availability of ammonia results in a decrease in nitrate uptake and a subsequent increase of nitrate in the water column.

As would be expected, oxygen is sensitive to the variation in SOD with a proportionally larger reduction resulting from the higher SOD distribution. It is particularly interesting that the variation of 2.5°C in water temperature resulted in a generally larger magnitude of change in dissolved oxygen because of the combined temperature effect on SOD and net benthic algae oxygen production. Primary productivity and chlorophyll were moderately sensitive to the variation in SOD primarily as a result of changes in the pools of inorganic nutrients.

The impact of the sensitivity analysis for SOD on the nutrient and oxygen balance is sufficiently dramatic to recommend field monitoring efforts to obtain actual data to characterize SOD and benthic nutrient regeneration at appropriate locations from the North Branch of the Potomac to Chain Bridge.

9.4 Benthic Primary Production

As discussed in Section 6, the North Branch of the Potomac River and other sections of the Upper Potomac are undoubtedly characterized by attached periphyton and other benthic algae communities that can be significant components of the oxygen and nutrient balance of the river. In the absence of field data to characterize epiphytic algae, the assumed distributions of gross primary production were varied by a factor of two (i.e. increase by 100%, 2X and decrease by 50%, 0.5X) in relation to the base run September 1985 case. Even though the rates were varied by a factor of two, the benthic production estimates used for the sensitivity runs are within the range of gross benthic production rates reported for field and experimental studies (e.g. Bott et al., 1989). As with the sensitivity to SOD, the maximum benthic production estimate was varied by half and double for the sensitivity runs with the resulting benthic production empirically computed as a function of velocity and temperature.

In calibrating the model, it was necessary to include benthic algae as a major component of the model to account for the observed oxygen and inorganic nutrient distributions. An empirical spatial distribution of gross benthic production and P/R ratios was developed to characterize benthic algae processes for the upper Potomac River. Since no field data were available for the Potomac, values from literature were used to estimate gross benthic algae production. The results of the sensitivity analysis for benthic production are quite dramatic. Ammonia, nitrate, phosphate and dissolved oxygen are very sensitive to the assumed spatial distribution of benthic algae production. Because of the N:P ratio of 10:1 (by weight) assumed for benthic algae, the impact of changes in nutrient uptake from benthic primary production is proportionally greater for nitrate and ammonia than for phosphate.

The regions of greatest change in nutrients and oxygen coincide with the regions of peak values of gross benthic production used for the base run (see Figure 15b) (RM 300-RM 220; RM 150-RM 120).

It is apparent from this sensitivity analysis that benthic production and related nutrient uptake is needed to match the observed data. The effect of decreasing benthic production by 50% results in a computed abundance of ammonia and nitrate that is inconsistent with the observed spatial trends. In particular, the good agreement for inorganic nitrogen and phosphate from the North Branch (RM 340) to Conococheague Creek (RM 206) is seen to be very dependent on the parameterization of gross benthic algae production for the base run simulation.

The effect of increasing benthic production on oxygen is significant in the regions of peak benthic production rats and minimum P/R ratios for the base run (RM 300-220; RM 150-120) (see Figure 15b). Oxygen is reduced by ~0.5-1.0 mg/L in these regions with a doubling of the benthic production rate. The decrease is attributed to the effective increase of net SOD via the parameterization of $P/R<<1$ ($P/R=0.5$). The high degree of variance in observed oxygen in the vicinity of the South Branch possibly results from high rates of benthic production under autotrophic conditions (i.e. $P/R<<1$). The results of the sensitivity analysis suggests that either higher benthic production rates or lower P/R values could, in fact, characterize benthic processes and oxygen dynamics in the vicinity of the South Branch (RM 300-270).

The results of the calibration, verification and this sensitivity analysis of benthic production strongly suggests the need for actual field data to characterize benthic algae biomass, productivity and nutrient uptake for the Upper Potomac River.

9.5 Non Point Source Input of N,P

Non-point source inputs of nutrients can be determined by mass balance difference techniques based on tributary and mainstem water quality and flow data (e.g. Hydroscience, 1976) or by extensive field studies characterizing nutrient runoff for various land uses. In estimating the non-point loading of nitrate and phosphate and organic nitrogen, available data were used to determine the approximate order of magnitude of reasonable values for non-point input of nitrate, phosphate and organic nutrients. The non-point input functions used for calibration and verification were determined by adjusting the forcing function data until the model results agreed reasonably well with the observed data.

Since the parameter estimates for non-point inputs were based on matching the observed data rather than simply assigning an estimate developed in previous studies (e.g. Hydroscience, 1976; Palmer, 1975), it is appropriate to test the response of the model to changes in the parameterization of these input functions. The non-point input of nitrate and phosphate was varied by a factor of two (100% increase; 50% decrease) with respect to the base run distribution of parameter values (see Figure 19). The constant non-point load of organic nitrogen and organic phosphorus was also varied by a factor of two for these sensitivity runs (see Table 10).

As shown in Figure 19, four different non-point source loading functions for nitrate and phosphate were developed to obtain reasonable agreement with the observed data sets for each simulation case. The forcing functions used to describe nitrate and phosphate non-point loading for the September 1985 case were approximately half the loading rate used for the October 1984 case. The 2X sensitivity run for the 1985 base run thus resembles the non-point loading function used for the October 1984 case. The results for nitrate, (Appendix I-2) and phosphate (Appendix I-3) clearly demonstrates that a factor of 2 increase and decrease of the non-point input function is inconsistent with the observed nitrate and phosphate trends for 1985. Halving the nitrate input, for example, results in a rapid depletion of nitrate from Antietam Creek (RM 176) to Seneca Creek (RM 131) that severely underestimates observed nitrate. Doubling the nitrate and phosphate non-point input results in substantial increases within the same region (RM 176 to RM 131) that greatly overestimates the observed trends.

The variation in non-point input of nitrate and phosphate results in a small change in chlorophyll and primary productivity as a result of the change in the availability of nutrients for phytoplankton growth. Organic nitrogen and phosphorus (Appendix I-7; I-8) are moderately sensitive to doubling and halving the spatially consistent non-point load. These results demonstrate the need for characterizing non-point loading and settling with spatially varying forcing functions.

9.6 Nitrification Rate

Because of its significance in oxygen and nutrient balances, nitrification has been well documented in the literature (e.g. Thomann and Mueller, 1987). Although most water quality models assume first-order nitrification occurs in the water column (Ambrose et al., 1988), the benthos often accounts for dominant populations of nitrifying organisms and the resultant transformations of nitrogen (see Cerco, 1981; Williams and Lewis, 1986). Since lab and field studies of upper water column nitrification generally are <u>not</u> characterized by very high rates of nitrification (e.g. tidal freshwater Potomac estuary, Shultz, 1989), it is probable that reported high rates of nitrification (> 1.0/day) used in calibrating water quality models for relatively shallow systems to obtain agreement with observed data are, in fact, implicitly accounting for a dominant benthic component of nitrification (e.g., Deb and Bowers, 1983, South Fork of Shenandoah River; and Williams and Lewis, 1986).

Benthic nitrification was included in the calibration and verification runs as a relatively low mass flux rate of 25 mg N/sq m-day from the North Branch (RM 340) to the South Branch (RM 283) and 0 mg N/sq m-day from the South Branch to Chain Bridge (see Figure 18a). Preliminary calibration runs suggested that the ammonia calculations were very responsive to changes in the benthic nitrification rate. Since calibration was very difficult using high rates for benthic nitrification, it was decided to specify a low benthic nitrification rate in conjunction with a moderate water column nitrification rate of 0.5 /day (@20°C). Model sensitivity to nitrification was evaluated by varying the water column nitrification rate by a factor of two (1.0/day = 100% increase; 0.25/day = 50% decrease).

The overall sensitivity of the model to the change in the water column nitrification rate is limited to a significant variation in ammonia (Appendix J-1) and a small change in nitrate (Appendix J-2). The 2X increase of the nitrification rate to 1.0 day^{-1} results in a significant underestimate of the observed data. While the 0.5X decrease to 0.25 day^{-1} results in a computed ammonia distribution that is higher the observed trend for the Upper Potomac River.

Based on other studies, the model representation of nitrification as a water column and benthic process is a credible framework to characteristic ammonia dynamics within the upper Potomac River. Actual field data are needed, however, to properly describe partitioning of nitrification between the water column and the benthos. Both benthic, and water column nitrification undoubtedly are characterized by spatial variation in the respective flux rates that reflects change in depth, velocity and nitrogen inputs.

9.7 Inorganic Solids Settling Rate

Since inorganic phosphate can adsorb on solids (see Thomann and Fitzpatrick, 1982), particulate deposition can represent a major loss mechanism for phosphate that can be accounted for by specifying spatially varying settling rates. Preliminary calibration runs demonstrated that very high settling rates in the North Branch and relatively lower velocities elsewhere in the Upper Potomac (see Table 6) were required to match the observed gradients of phosphate. Settling rates were determined solely by "tuning"; i.e. adjust the settling velocity until the model results were in reasonable agreement with the observed data. Since no field data were available to check the parameterization of particulate deposition, it is very appropriate to evaluate the sensitivity of the model to changes in the settling rate for adsorbed phosphate. The distribution of settling rates for F#5, particulate inorganic solids, presented in Table 6 were doubled (2X) and halved (0.5X) as shown below:

Seg#	F#5 Sep 1985	F#5 Sep 1985	F#5 Sep 1985 Base Run	2X	0.5X
01-04	25.00	50.00	12.50		
05-15	5.00	10.00	2.50		
16-21	3.00	6.00	1.50		
22-33	3.00	6.00	1.50		
34-47	1.50	3.00	0.75		

Phosphorus, chlorophyll and primary productivity are the variables that are most sensitive to variations in the inorganic solids settling rate. (see Appendix K-3, K-12, K-4 and K-13) for deposition of phosphate absorbed onto solids over the entire model domain. By contrast, ammonia and nitrate are only slightly sensitive to changes in the solids settling rate in the region downstream of Conococheague Creek (RM 206). The sensitivity of chlorophyll, primary productivity and inorganic nitrogen is attributed to the changes in the availability of phosphate for phytoplankton uptake.

In the North Branch of the Potomac (RM 340-RM310) relatively low concentrations of phosphate are maintained in the base run by a balance of: high solids settling rate (25 m/day); high uptake rates by the benthic algae (See Figure 15b) high benthic regeneration rates via SOD (see Figure 10); and the upstream boundary and UPRC waste water inputs. Although the base run settling rate of 25 m/day would appear quite high, for shallow segment depths on the order of 0.5-1.0m (see Figure 6b), the deposition loss rates ($\sim$25-50 day^{-1}) are of the same order as the flushing rates ($\sim$40 day^{-1}) for the steep gradient, high velocity, reaches of the North Branch (see Figure 6a).

In the upper reaches of the North Branch, the moderate response to doubling the settling rate to 50 m/day is attributed to the balance of the characteristic high flushing rate of this region and the enhanced solids deposition rate.

The most dramatic responses to changing the inorganic solids settling rate is in the region downstream of RM 220, reaches of the Upper Potomac that are influenced by agricultural non-point loading (see Figure 19) and a decreasing trend in velocity (see Figure 6a) and travel time (see Figure 4).

The marked response of phosphate is attributed to the combined impact of increasing non-point loading and shifting the mass flux balance between the solids deposition rates (Ws/H) and the hydraulic flushing rate (U/X) (see Figure 4) as characterized by segment depth (H), settling rate (Ws), segment length (X) and segment velocity (U).

Deposition loss resulting from adsorption of phosphate onto solids is a significant mechanism in the description of a phosphorus balance for the Upper Potomac River. Since phosphorus is a key factor in water quality management planning, collection of additional field data is warranted to improve the model characterization of phosphorus dynamics in the Upper Potomac River. Actual field data are needed to improve the credibility of model estimates of inorganic solids settling rates that are based solely on calibrating the model to the observed phosphate data.

Phosphorus loss mechanisms in the model include: phytoplankton uptake; benthic algae uptake and solids deposition. In reaches characterized by fast flushing rates (e.g., North Branch), phytoplankton uptake is a negligible component of the overall mass balance. Computed decreases in phosphate thus result from benthic phosphate uptake and solids deposition. Since both of these processes are described by literature and calibration estimates, field data should be collected to properly characterize the significance of each process on the overall observed trends of phosphorus.

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