Chapter Four: Nutrients (including Sulphates and Chlorides), Riverine Export Fluxes, and River Concentration Relationships with Landscape Input Loadings

Upper Basin Landscape Inputs and Riverine Export Fluxes

We investigated the relationships of TN, TP, K, SO_4, and Cl loadings onto the landscape of the Upper Basin with the riverine export fluxes for four five-year periods (1980-84, 1985-89, 1990-94, and 1995-99). For the four five-year periods, TN riverine export fluxes remained fairly level—about 850 kg/km^2/yr or about +18% of the landscape inputs, including a background flux of 100 kg/km^2/yr (see below).

	TN Upper Basin Inputs kg/km^2/yr	TN Riverine Export kg/km^2/yr	% Inputs Exported %
1980-84	4,389	875.2	19.94
1985-89	4,064	736.5	18.12
1990-94	4,307	833.4	19.35
1995-99	4,465	842.7	18.87

For the four five-year periods, TP riverine export has decreased from 71 to 45 kg/km^2/yr, or only about 5% of the landscape inputs. The decrease in TP riverine export was probably due to the large decrease in wastewater inputs (see below).

	TP Upper Basin Inputs kg/km^2/yr	TP Riverine Export kg/km^2/yr	% Inputs Exported %
1980-84	925	71	7.7
1985-89	867	60	6.9
1990-94	881	44	5.0
1995-99	918	45	4.9

The average landscape loading input for TP for the 1980-99 period was about 900 kg/km2/yr, with a background flux of about 10.5 kg/km^2/yr.

For the four five-year periods, potassium riverine export has increased slightly—from 940 to 1,000 kg/km^2/yr, or about 43% to 50% of the landscape inputs, including the background fluxes of about 370 kg/km^2/yr.

	K Upper Basin Inputs	**K Riverine Export**	**% Inputs Exported**
	kg/km^2/yr	kg/km^2/yr	%
1980-84	1,871	942	50.35
1985-89	1,781	766	43.02
1990-94	1,883	902	47.89
1995-99	2,016	1,002	49.72

Because K is a conservative chemical element, it can be used as a tracer for TP and TN, which are the nutrients of concern in the over-enrichment of the Potomac Estuary. About half of the K inputs were either being stored within the Upper Basin or were exported out of the watershed in agricultural and forest products.

For the four five-year periods, the riverine sulphate export fluxes have decreased from 11,000 to 8,900 kg/km^2/yr.

	SO_4 Upper Basin Inputs	**SO_4 Riverine Export**	**% Inputs Exported**
	kg/km^2/yr	**kg/km^2/yr**	**%**
1980-84	10,753	12,319	114.56
1985-89	9,942	10,144	102.03
1990-94	11,120	9,914	89.15
1995-99	8,922	9,794	109.76

The decrease in SO_4 riverine export was in response to a decrease in air deposition, which was the largest source of landscape inputs (see above). We assumed that total deposition (wet & dry) was 1.6 times wet deposition. Coal mines in the North Branch sub-basin contribute about 3,400 kg/km^2/yr of sulphate to the Upper Basin. As shown above, the riverine exports ranged from 89% to 115% of the input fluxes, including background inputs. This suggests that we may have underestimated dry deposition.

For the four five-year periods, the riverine Cl export fluxes increased from 4,880 to over 5,800 $kg/km^2/yr$. The amount of Cl used as road salt was calculated by difference.

	Cl Upper Basin Road Salt $kg/km^2/yr$	Cl Riverine Export $kg/km^2/yr$	Anthropogenic/ Geological Ratio
1980-84	2,997	4,887	13.81
1985-89	2,761	4,559	16.74
1990-94	3,338	5,267	16.92
1995-99	3,757	5,837	13.74

The increase was attributed to possible increase in road salt used for deicing. The ratios of anthropogenic to geological background of Cl ranged from +13 to +16, indicating human impact on riverine Cl export.

Middle Atlantic and Northeast USA Watershed Inputs and Exports

A strong linear relationship was observed in the SCOPE study of the mass balance of nitrogen inputs and TN riverine export fluxes for the 16 watersheds of the Middle Atlantic and Northeast USA (1). The SCOPE study was expanded (2) to include the influence of climate on riverine nitrogen export. This expanded analysis demonstrated that riverine nitrogen export fluxes were greater in years of higher discharges. The expanded study indicated that watersheds with higher precipitation and higher discharge export a greater fraction of the net nitrogen input.

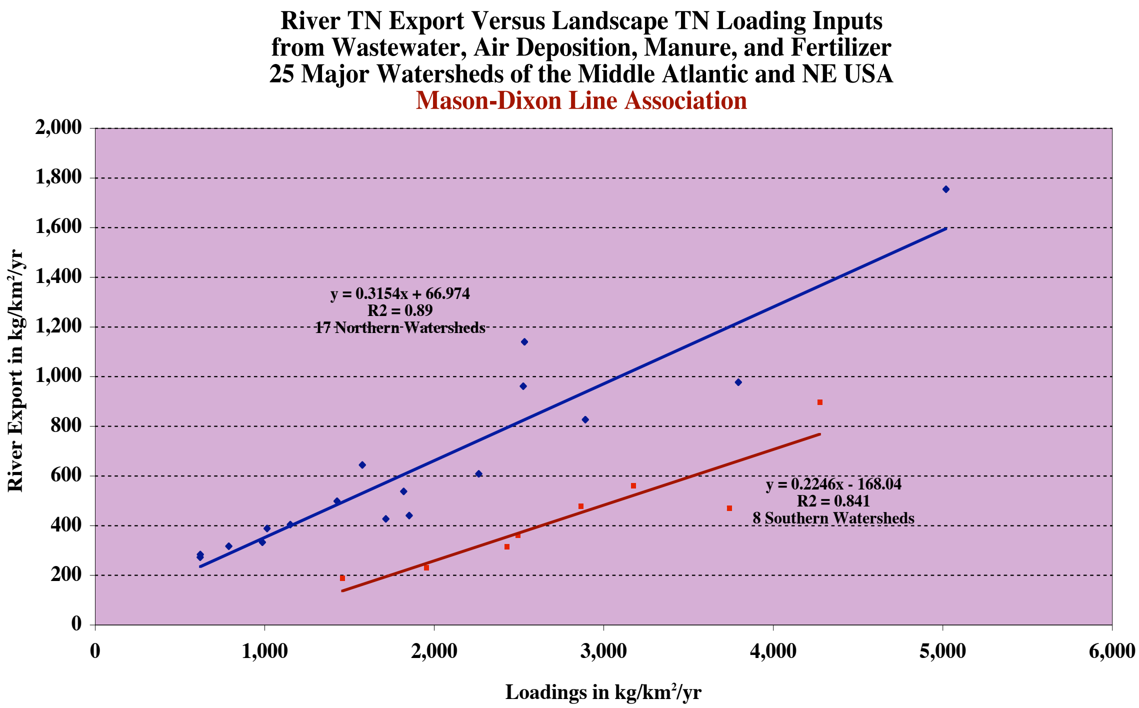
The expanded study suggests that there is a longer-term, steady-state influence of climate on riverine nitrogen fluxes. The percentage of nitrogen inputs that are exported is greater in watersheds with wetter climates.

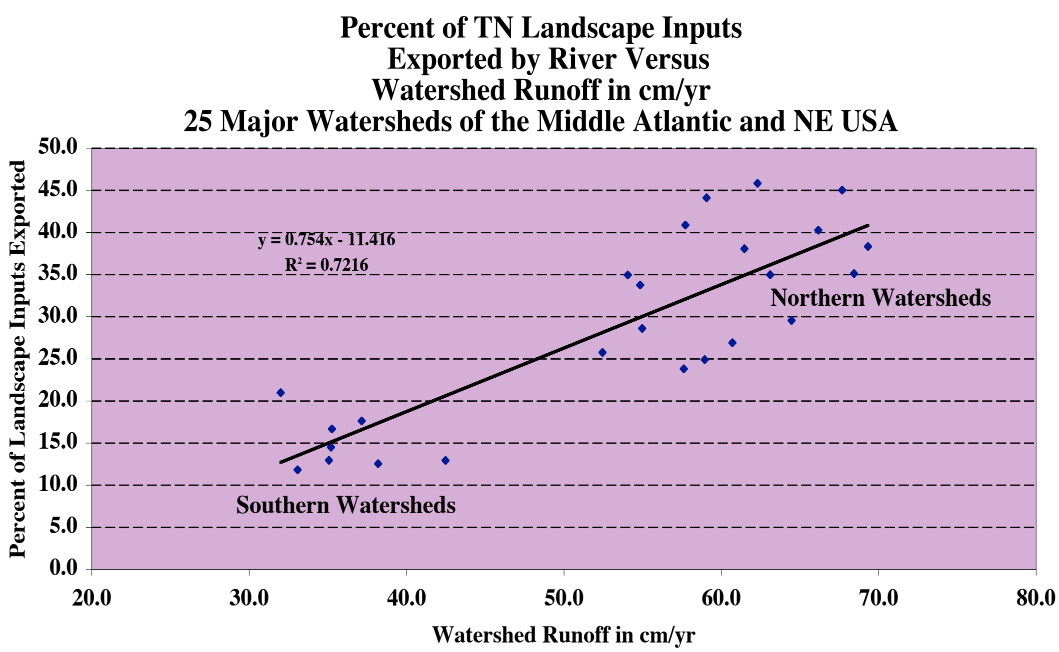
When one carefully examines the SCOPE input/export relationship, it can readily be seen that the three watersheds that were furthest below the trend line were the southern basins: the Potomac, Rappahannock, and James. We added five more southern watersheds and four more northern watersheds because we hypothesized that there was a north-south difference. We calculated the total landscape loading inputs and riverine export fluxes for TN, TP, K, SO_4, and Cl for 17 northern and eight southern watersheds, as presented later in this section.

Using landscape loading of fertilizer, animal waste, air deposition, and wastewater, including a background flux of 100 kg/km^2/yr, the landscape loading inputs and river export fluxes for TN are summarized below.

Northern	TN Landscape Inputs kg/km^2/yr	TN Riverine Export kg/km^2/yr	% Inputs Exported %
St. John	619	273	44.1
St. Croix	620	284	45.8
Penobscot	788	317	40.3
Kennebec	986	333	33.8
Androscoggin	1,151	404	35.1
Saco	1,014	389	38.3
Merrimack	1,426	499	35.0
Charles	1,576	644	40.9
Blackstone	2,532	1,140	45.0
Thames	2,262	609	26.9
Connecticut	1,819	538	29.6
Housatonic	1,852	441	23.8
Upper Hudson	1,714	427	24.9
Mohawk	2,891	827	28.6
Delaware	2,525	961	38.1
Schuylkill	5,019	1,755	35.0
Susquehanna	3,794	977	25.8
Southern			
Potomac	4,274	897	21.0
Rappahannock	3,740	470	12.6
Pamunky	1,954	231	11.8
Mattapooni	1,458	189	13.0
James	2,428	314	12.9
Chowan (BLK)	2,494	362	14.5
Tar	2,864	478	16.7
Neuse	3,175	560	17.6

As can readily be seen in the charts below, there indeed appears to be a north-south or Mason-Dixon Line association.





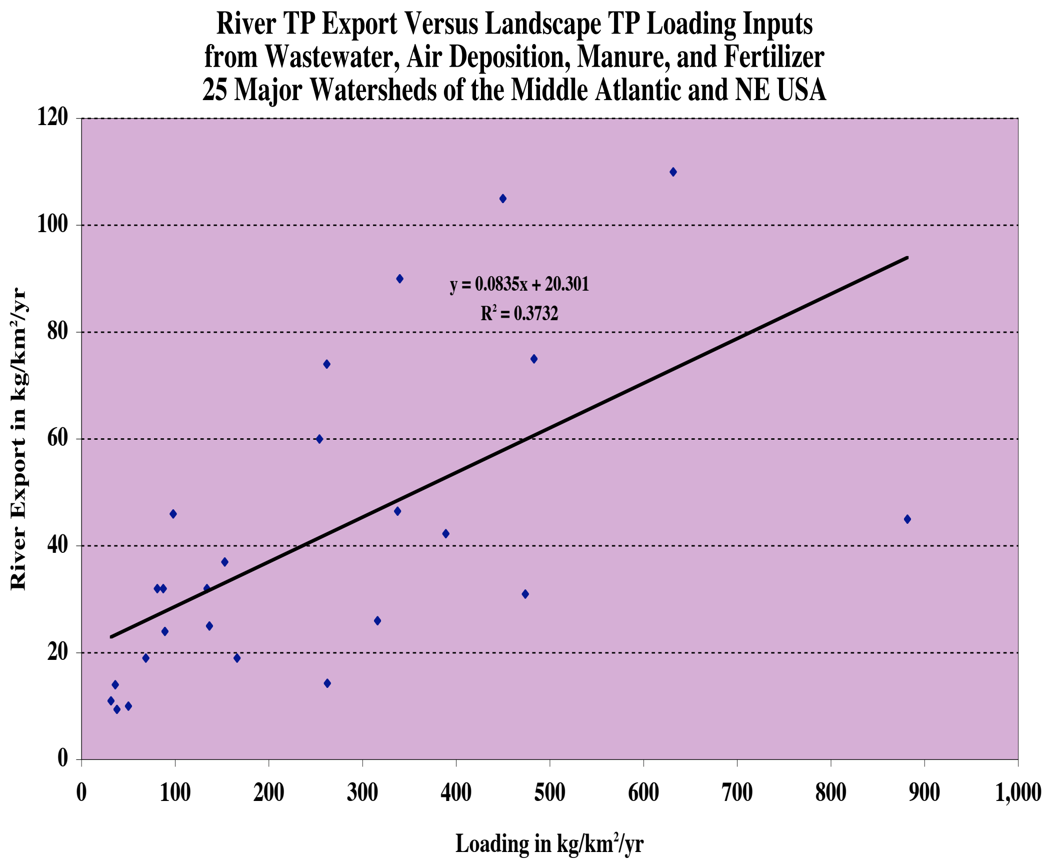
The two TN landscape inputs/riverine export linear relations are very strongly correlated and had slopes of 0.31 for the northern and 0.22 for the southern watersheds (see chart above). Upon further examination, the Mason-Dixon Line separation or "stratification" was due to hydrology, as also presented above. The southern watersheds have an annual river flow runoff ranging from 26 to 44 cm/yr, which is significantly lower than the annual river flow runoff of 53 to 70 cm/yr for the northern watersheds. While the annual precipitation varies from year to year for all 25 basins, the long-term average precipitation is about 100 cm/yr for the 25 watersheds.

For the 25 watersheds, we calculated the four landscape inputs—wastewater, fertilizer, air deposition, and animal waste, (using an estimated background of 10 kg/km^2/yr)—and riverine export fluxes for TP, as summarized below.

Watersheds	**TP Landscape Inputs kg/km^2/yr**	**TP Riverine Export kg/km^2/yr**	**% Inputs Exported %**
St. John	26.4	11.0	41.6
St. Croix	31.0	14.0	45.2
Penobscot	43.5	10.0	23.0
Kennebec	63.1	19.0	30.1
Androscoggin	82.6	24.0	29.1
Saco	34.3	9.4	27.4
Merrimack	88.3	46.0	52.1
Charles	78.5	32.0	40.8
Blackstone	439.9	105.0	23.9
Thames	124.8	32.0	25.6
Connecticut	143.2	37.0	25.8
Housatonic	71.9	32.0	44.5
Upper Hudson	127.4	25.0	19.6
Mohawk	330.7	90.0	27.2
Delaware	244.7	60.0	24.5
Schuylkill	620.8	110.0	17.7
Susquehanna	465.8	31.0	6.7
Potomac	871.2	65.0	7.5
Rappahannock	468.0	75.0	16.0
Pamunky	306.0	26.0	8.5
Mattapooni	156.1	19.0	12.2
James	246.8	12.5	5.1
Chowan (BLK)	252.4	14.3	5.7
Tar	327.4	46.5	14.2
Neuse	378.9	42.3	11.2

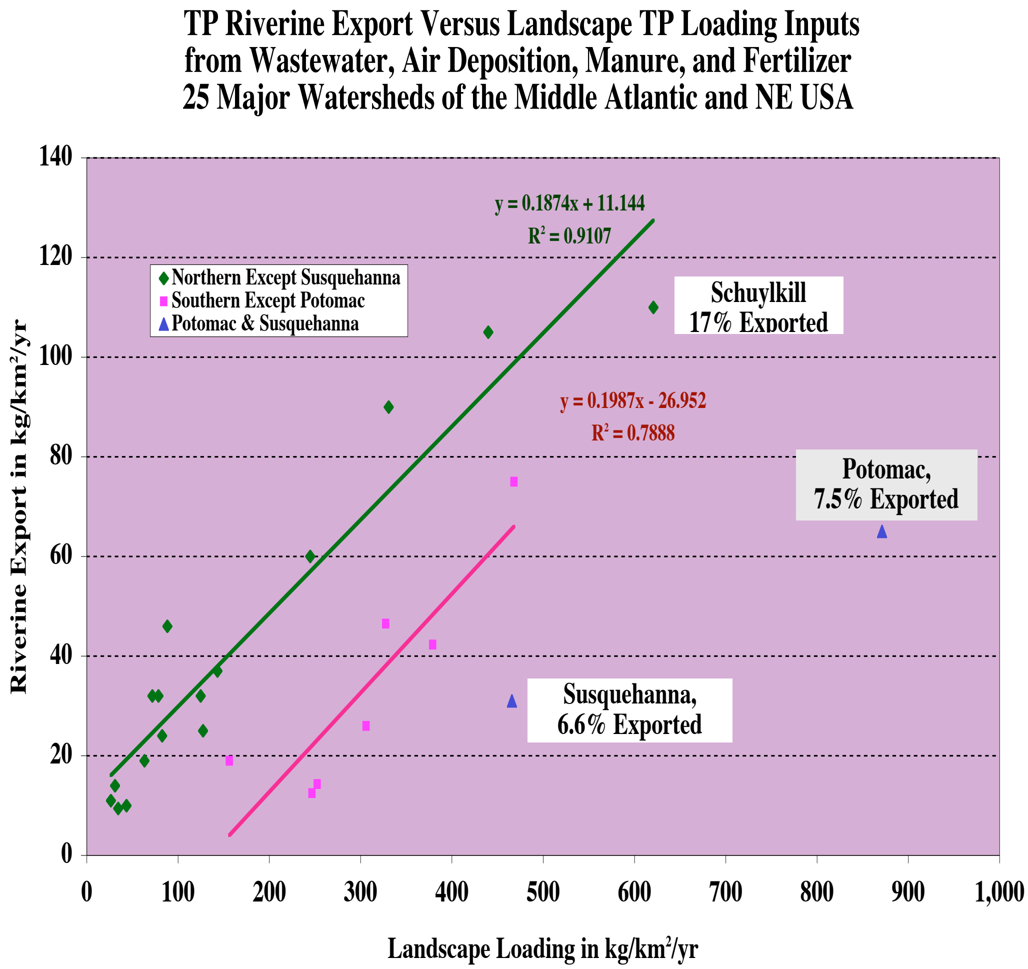
Similar to the percent of TN exported, the percent of TP exported out of the watersheds was highest in the northern watersheds and lowest in the southern watersheds.

For the 25 watersheds, including the Upper Potomac River Basin, the TP landscape loading/ riverine export relationship was not very strongly correlated, as shown below.



The y intercept, which is the average background contribution for the 25 watersheds, was about 20 $kg/km^2/yr$. The relationship has a slope of 0.08, suggesting that about 8% of the landscape inputs were exported out of the basins via riverine export (see above). The 8% is somewhat higher than that of the Upper Potomac River Basin, as presented earlier in this chapter.

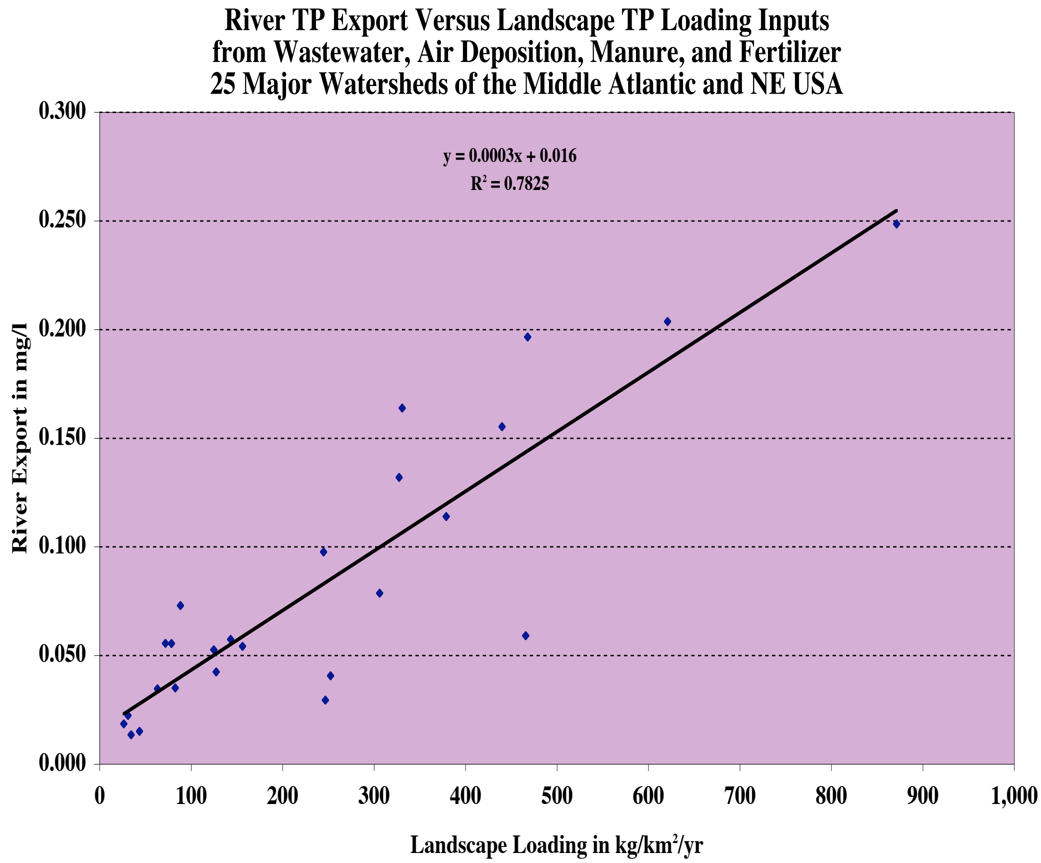
The TP export data for the same 25 watersheds in a stratified Mason-Dixon Line format, as used for TN earlier in this chapter, are presented below.



When we exclude the Susquehanna Watershed from the northern watersheds and the Potomac Watershed from the southern watersheds, there appears to be two distinct linear relationships, as presented above. This is similar to the stratification that was observed for TN, as presented earlier in this chapter.

The low TP export flux for the Susquehanna River can, in part, be attributed to phosphorus sedimentation in the main stem run-of-the-river reservoirs below Harrisburg, Pennsylvania. The low TP export flux for the Upper Potomac River Basin is **unexplainable and needs to be investigated**.

River TP concentration versus landscape loadings input appears to be a better linear relationship for the 25 watersheds, as shown below.



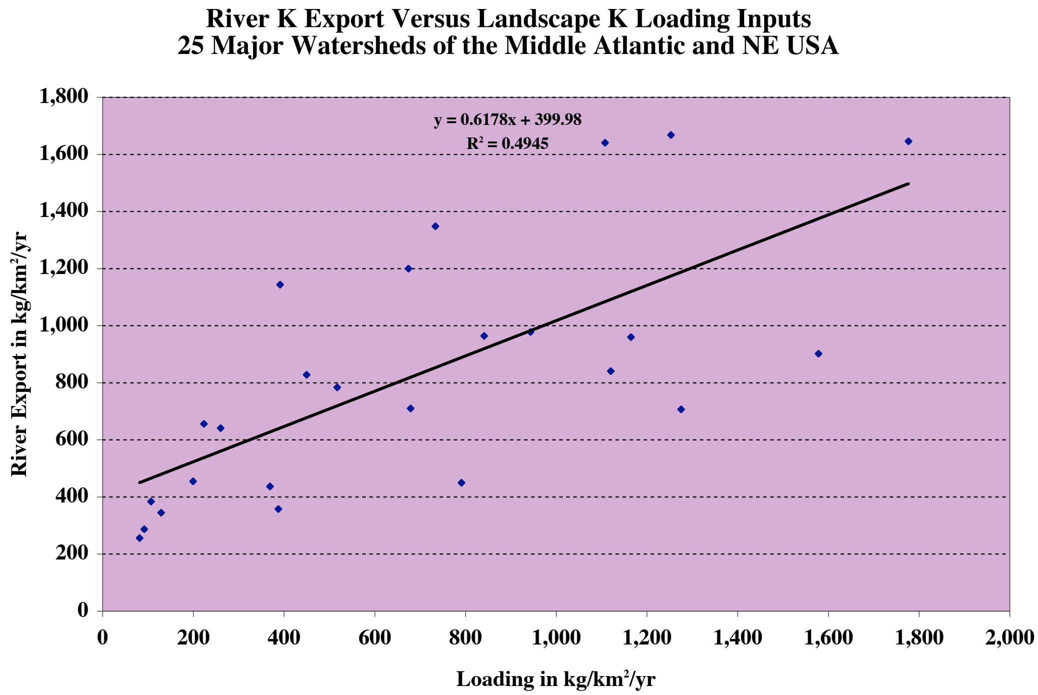
The TP river concentration/landscape input relationship is linear, with a slope of 0.0003 (see above). The y intercept is 0.0216 mg/l, or a TP average background concentration for the 25 watersheds of about 0.022 mg/l. The low river TP concentration for the Susquehanna Watershed can also be seen in the figure above.

Similar landscape inputs and riverine export fluxes for the 25 basins were determined for K, as summarized below. Because we did not have historical chemical analysis data for most of the 25 watersheds, estimates of natural or background contributions could not be made and are, therefore, not included in the total landscape inputs.

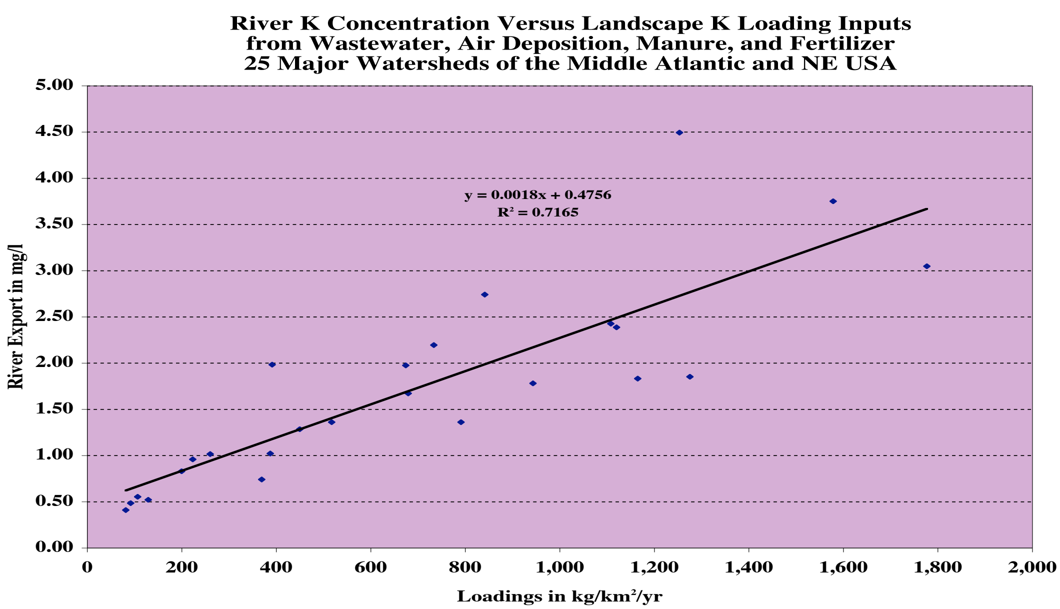
Watersheds	K Landscape Inputs* kg/km2/yr	K Riverine Export kg/km2/yr	% Inputs Exported %
St. John	92	287	313
St. Croix	81	256	315
Penobscot	129	345	268
Kennebec	199	455	228
Androscoggin	223	656	294
Saco	107	384	360
Merrimack	260	641	247
Charles	391	1,144	293
Blackstone	1,108	1,641	148
Thames	674	1,200	178
Connecticut	450	828	184
Housatonic	517	784	152
Upper Hudson	369	437	118
Mohawk	943	978	104
Delaware	733	1,348	184
Schuylkill	1,777	1,646	93
Susquehanna	1,165	960	82
Potomac	1,578	981	62
Rappahannock	1,275	707	55
Pamunky	791	450	57
Mattapooni	387	358	92
James	679	710	105
Chowan (BLK)	841	964	115
Tar	1,120	841	75
Neuse	1,253	1,668	133

* Total landscape inputs do not include any estimate of natural or background contribution.

For the 25 watersheds, the K loading/export relationship was fair and had a slope of 0.62, which means that the riverine export was about 62% of the landscape inputs, as shown below.



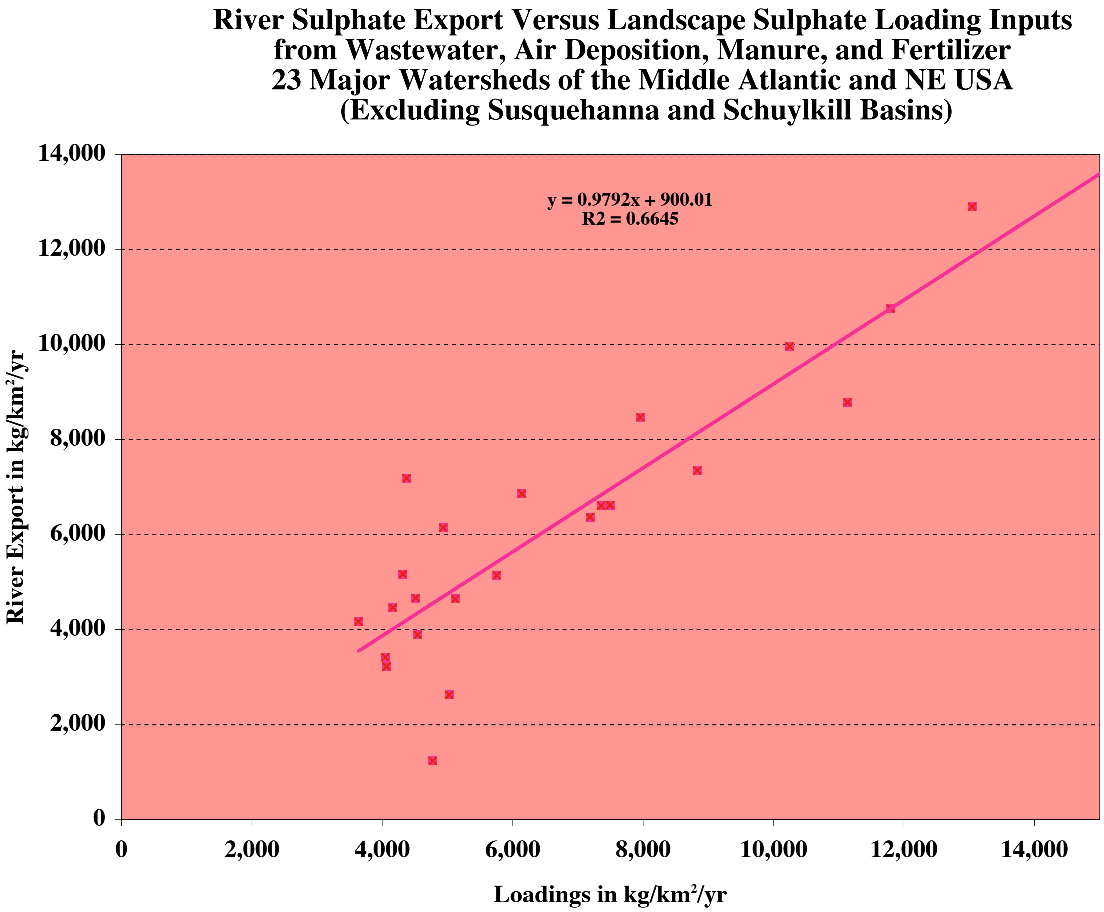
The y intercept, which is the average background contribution for the 25 watersheds, was 400 kg/km^2/yr (see above). Like TP, the river K concentration versus landscape loadings input appears to be a better relationship than the above river export flux versus landscape loading relationship, as shown below.



We determined the landscape inputs for the 25 watersheds, (including estimates from coal mining) and calculated riverine export fluxes for SO_4, as summarized below.

Watersheds	**Sulphate Landscape Inputs kg/km²/yr**	**Sulphate Riverine Export kg/km²/yr**	**% Inputs Exported %**
St. John	4,163	4,460	107.1
St. Croix	4,317	5,165	119.7
Penobscot	4,544	3,889	85.6
Kennebec	4,511	4,664	103.4
Androscoggin	6,139	6,859	111.7
Saco	4,064	3,222	79.3
Merrimack	5,758	5,140	89.3
Charles	7,957	8,470	106.4
Blackstone	11,798	10,756	91.2
Thames	7,356	6,606	89.8
Connecticut	7,187	6,370	88.6
Housatonic	7,494	6,619	88.3
Upper Hudson	8,830	7,346	83.2
Mohawk	10,246	9,960	97.2
Delaware	13,044	12,900	98.9
Schuylkill	28,600	28,600	100.0
Susquehanna	22,000	22,000	100.0
Potomac	11,132	8,783	78.9
Rappahannock	5,024	2,626	52.3
Pamunky	5,118	4,643	90.7
Mattapooni	4,771	1,236	25.9
James	4,930	6,144	124.6
Chowan (BLK)	4,046	3,420	84.5
Tar	3,636	4,165	114.5
Neuse	4,373	7,185	164.3

For the 23 watersheds (excluding the Susquehanna and Schuylkill, which have coal mine drainage), the SO_4 landscape inputs versus export flux relationship was well correlated and had a slope of 0.98, which means that the riverine export was about 98% of the landscape inputs, as shown below.



The y intercept, which is the average background contribution for the 25 watersheds, was 900 kg/km^2/yr. We assumed that total deposition (wet & dry) was 1.6 times wet deposition. The riverine exports ranged from 52% to 124% of the input fluxes, excluding the background inputs. This suggests that our estimate of dry deposition contribution needs to be improved.

Excluding the three watersheds impacted by coal mining (the Potomac, Susquehanna, and Schuylkill), about 50% of the riverine SO_4 export for the 22 watersheds was from atmospheric deposition. For two basins, the Rappahannock and Pamunkey, riverine export was higher than all inputs, suggesting either that the input estimates are too low or that sulfur reduction was occurring.

Similar to the Upper Potomac River Basin chloride inputs and exports, we determined the amount of chlorides from road salt used for deicing by difference, as summarized below.

Watersheds	**Chlorides Road Salt Deicing kg/km²/yr**	**Chlorides Riverine Export kg/km²/yr**	**Anthropogenic/ Geological Ratio**
St. Johns	911.8	1,747.0	1.9
St. Croix	4,950.3	5,799.0	10.0
Penobscot	989.2	1,991.0	1.5
Kennebec	2,472.8	3,073.0	15.7
Androscoggin	6,178.8	7,542.0	9.8
Saco	1,751.1	2,833.0	2.7
Merrimack	7,943.4	10,127.0	6.0
Charles	17,168.6	19,691.0	9.9
Blackstone	12,541.5	28,012.0	12.5
Thames	7,794.0	9,653.0	6.7
Connecticut	5,324.2	7,300.0	4.4
Housatonic	7,215.0	8,687.0	7.4
Upper Hudson	5,747.0	7,204.0	8.4
Mohawk	17,120.4	20,238.0	9.7
Delaware	10,040.1	12,820.0	5.6
Schuylkill	13,851.2	18,256.0	5.5
Susquehanna	3,843.7	6,854.0	2.0
Potomac	3,338.0	5,267.0	16.2
Rappahannock	2,719.5	4,040.0	7.8
Mattaponi	20.0	860.0	0.2
Pamunkey	9.0	1,114.0	0.6
James	2,188.0	3,910.0	4.3
Chowan (BLK)	1,961.0	3,420.0	5.1
Tar	1,130.0	2,658.0	3.5
Nuese	827.0	2,800.0	3.6

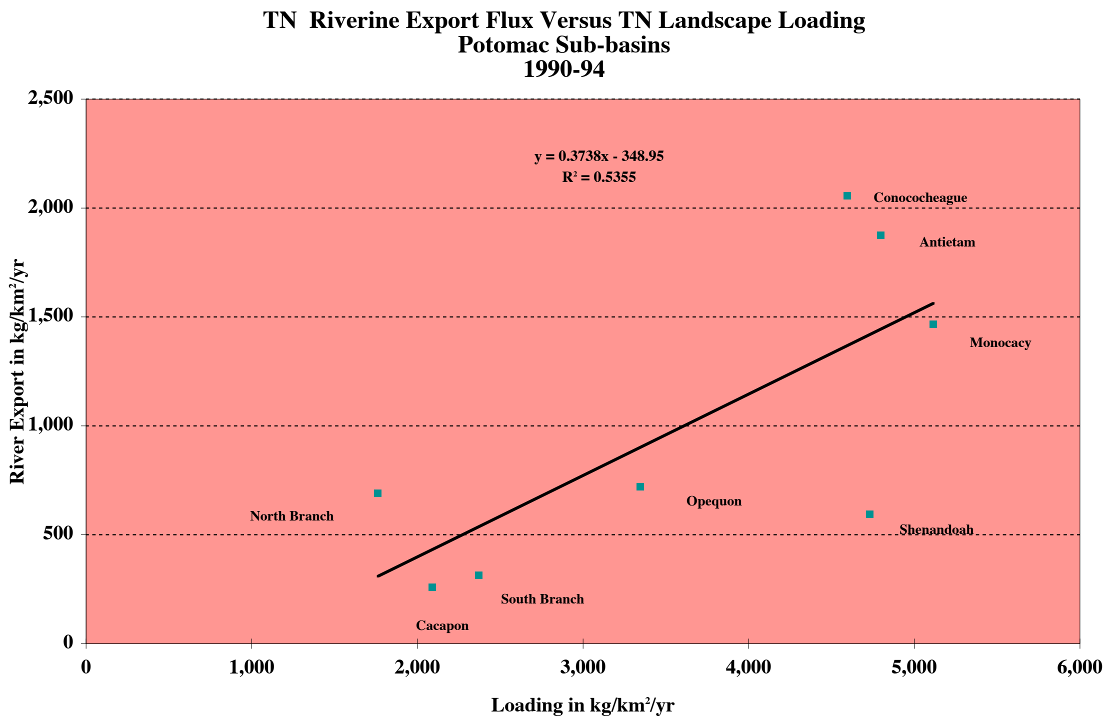
For the 25 watersheds, the average 1990s chloride riverine export was about 8,970 kg/km^2/yr, or six times the export rate from the 1900s. Road salt inputs were about 6,400 kg/km^2/yr, or about 70% of the riverine export fluxes.

Major Sub-basins of the Upper Potomac River Basin

The USGS (3) investigated the relationship of riverine nutrient yields to landscape nutrient inputs for 20 of their 25 surface water-quality monitoring sites in the Upper Basin. In general, the USGS analysis showed that the larger riverine nutrient yields (loads per unit area) corresponded to larger landscape nutrient inputs. For both nitrogen and phosphorus, inputs were the largest in watersheds dominated by agricultural land use.

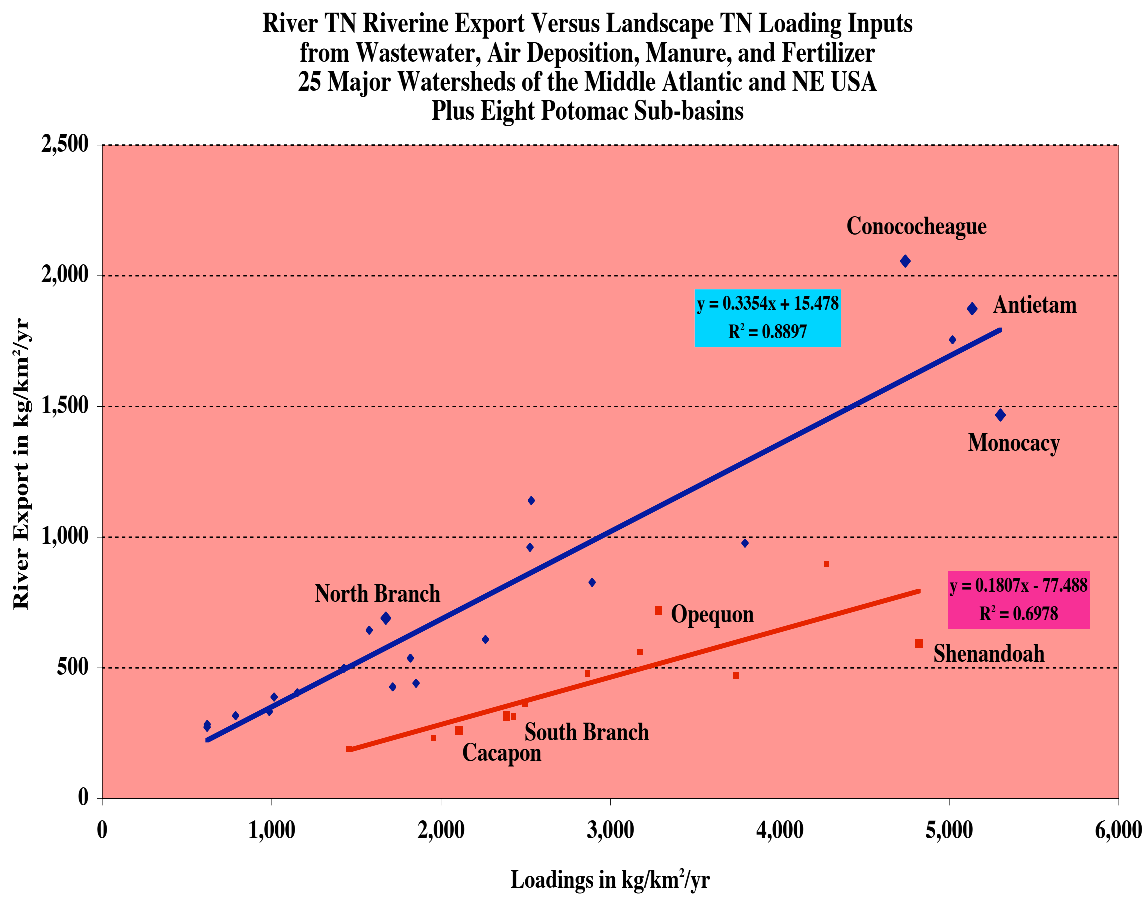
For the eight major sub-basins of the Upper Basin, using mainly the same USGS data (4) as mentioned in the previous paragraph, we attempted to develop relationships between landscape loadings and riverine export for TN, TP, and K. TN and TP data for the Opequon and Cacapon watersheds were extracted from the historical EPA STORET database (5) and the West Virginia Department of Environmental Protection (WVA DEP) electronic databases (6).

For the eight major sub-basins, the TN riverine export versus landscape input relationship was fair, with a slope of 0.37 (see below) and was slightly higher than the eight southern watersheds, which had a slope of 0.22.



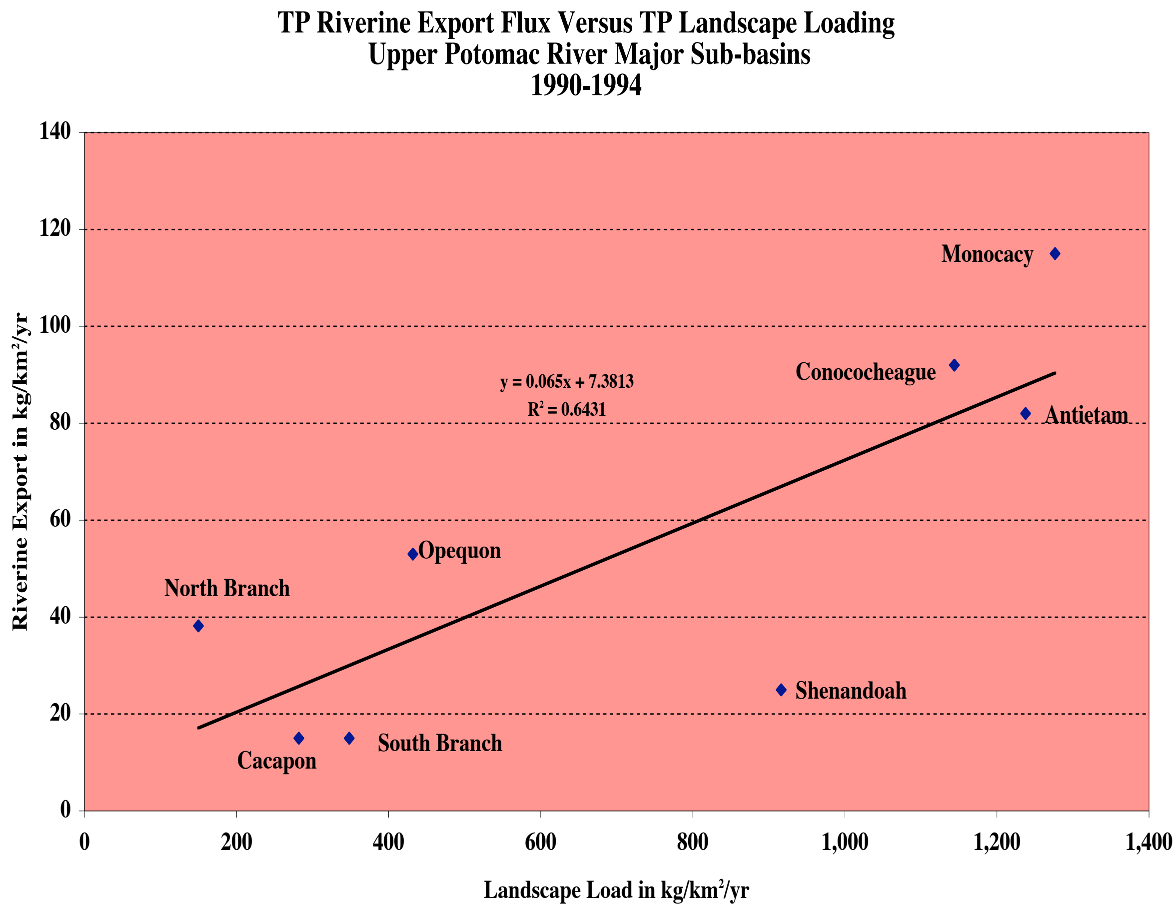
Both the USGS and our analysis of the Shenandoah Watershed found low riverine export fluxes, even though the landscape loading inputs were high. We cannot fully explain why the riverine nitrogen export fluxes for the main Shenandoah and its two main tributaries, the South Fork and the North Fork, were so low. This will be discussed further in Appendix A.

We stratified the eight sub-basins into two stream yields similar to the process used for the 25 northern and southern watersheds of the Middle Atlantic and Northeast USA presented earlier in this chapter. In that there are only four watersheds in each category, we plotted or superimposed the data from the eight sub-basins of the Upper Potomac on the 25 watersheds TN riverine export/landscape loading input plot, as presented below.



The TN riverine export/landscape loading input relationship for the four sub-basins with the higher stream flow yields (North Branch, Antietam, Conococheague, and Monocacy) is very similar to the 17 watersheds north of the Mason-Dixon Line. Likewise, the TN riverine export/landscape loading input relationship for the four sub-basins with lower stream flow yields (South Branch, Cacapon, Opequon, and Shenandoah) are very similar to the eight watersheds south of the Mason-Dixon Line.

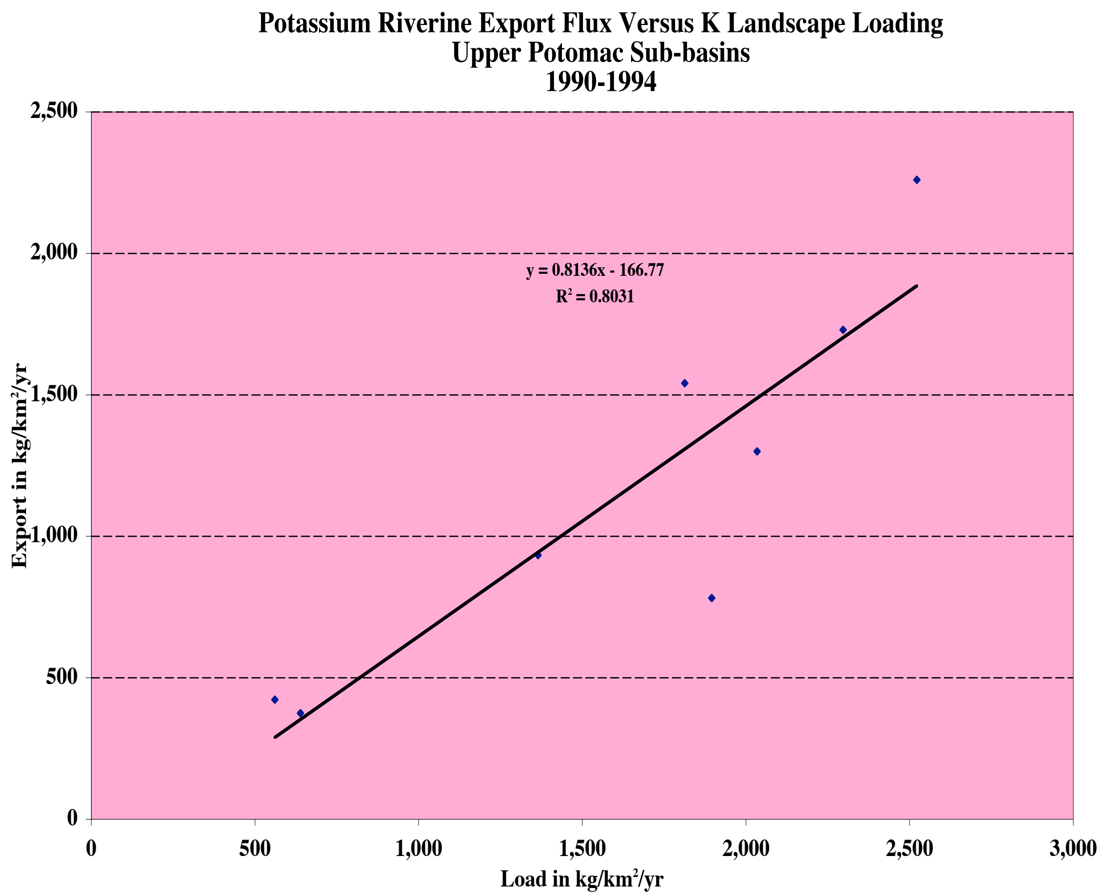
For the eight major sub-basins of the Upper Potomac, the TP landscape input versus riverine export relationship was good (see below), with a slope of 0.065, and was very similar to the 25 watersheds, which had a slope of 0.083.



This suggests that only about 6% to 7% of the landscape TP loading leaves the watershed via riverine export (see above). Most of the TP is being stored within the soils, sediments, and trees of the landscape, or transported out of the Upper Basin in agricultural or forest products.

The y intercept suggests that the average background contribution for the Upper Basin is about 7.3 $kg/km^2/yr$.

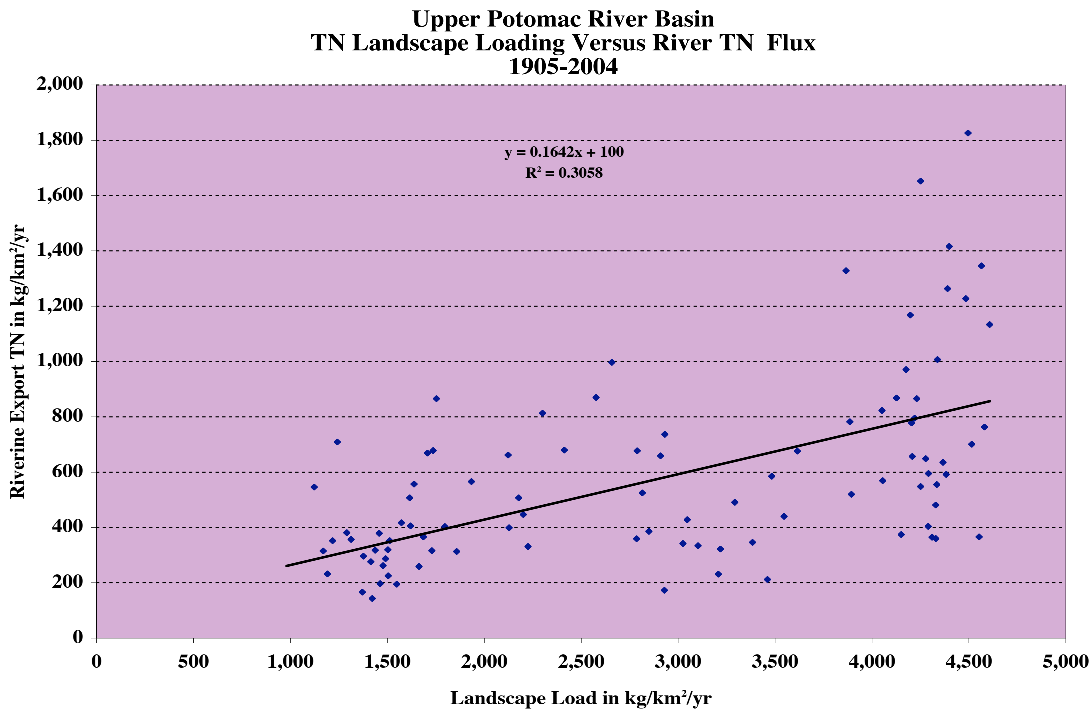
For the eight sub-basins of the Upper Potomac Basin, the K riverine export versus landscape loading input relationship was good (see below), with a slope of 0.62. This compares very favorably with the 25 watersheds, which had a slope of 0.65.



The strong relationship of K loading and K riverine export supports our hypothesis that K is a good conservative watershed tracer for nutrients for those basins that have large landscape loading inputs, like the Upper Potomac River Basin.

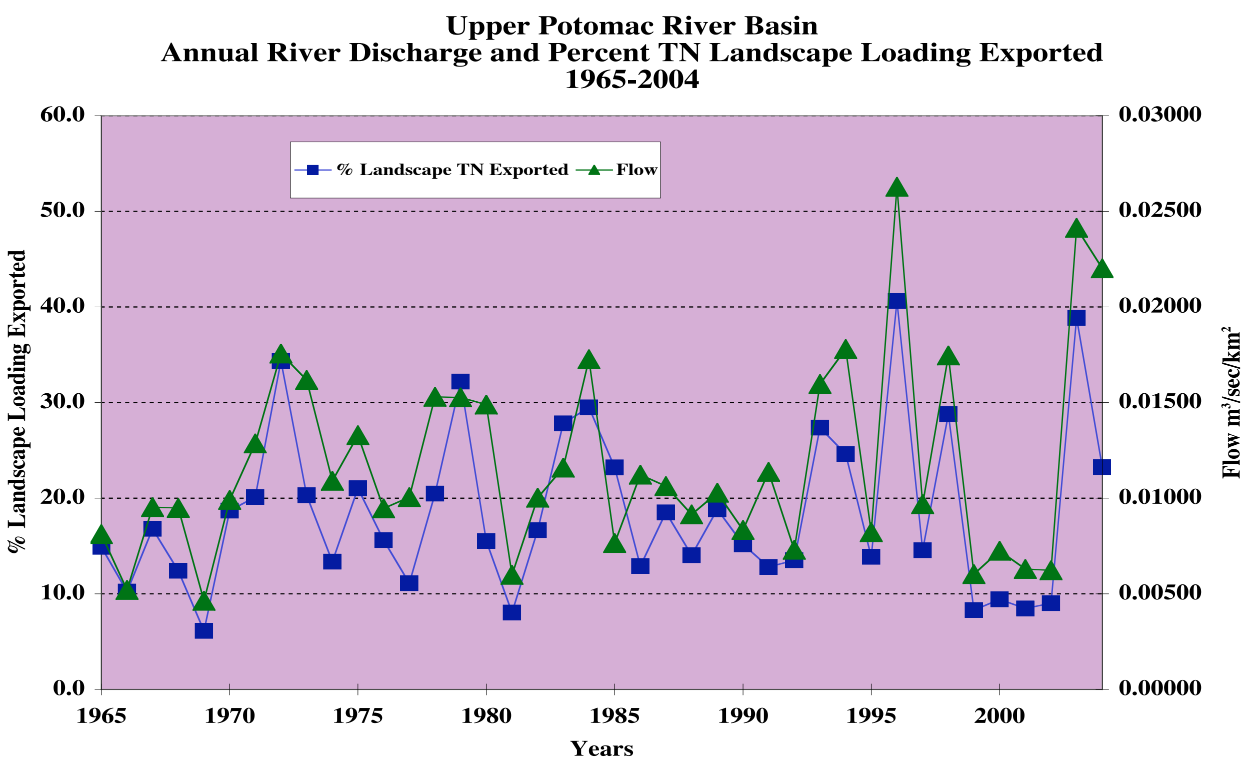
Annual Upper Basin Landscape Loading and Riverine Export Trends

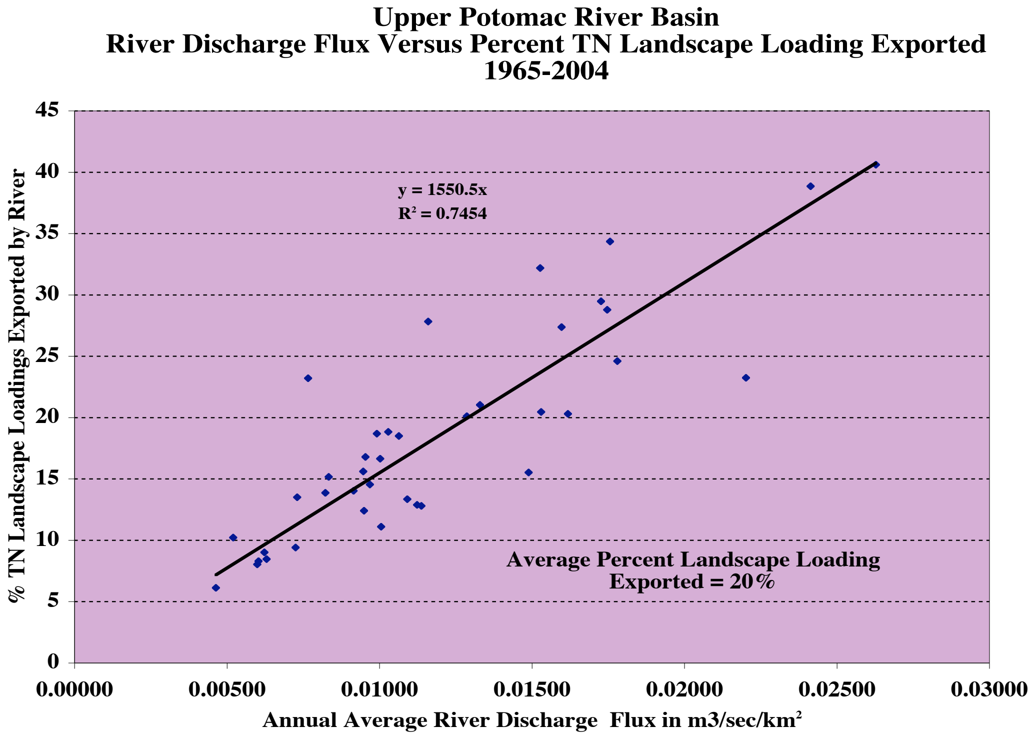
As presented earlier in this chapter, the percent of the TN landscape loading that was exported in the 25 Middle Atlantic and Northeast USA watersheds was closely related to annual river flow in cm of runoff. For the Upper Potomac River Basin, we examined the relationship of the annual landscape loading from 1905 to 2004 versus the TN exported by the river, as presented below. Because there was large variability in annual stream flow,



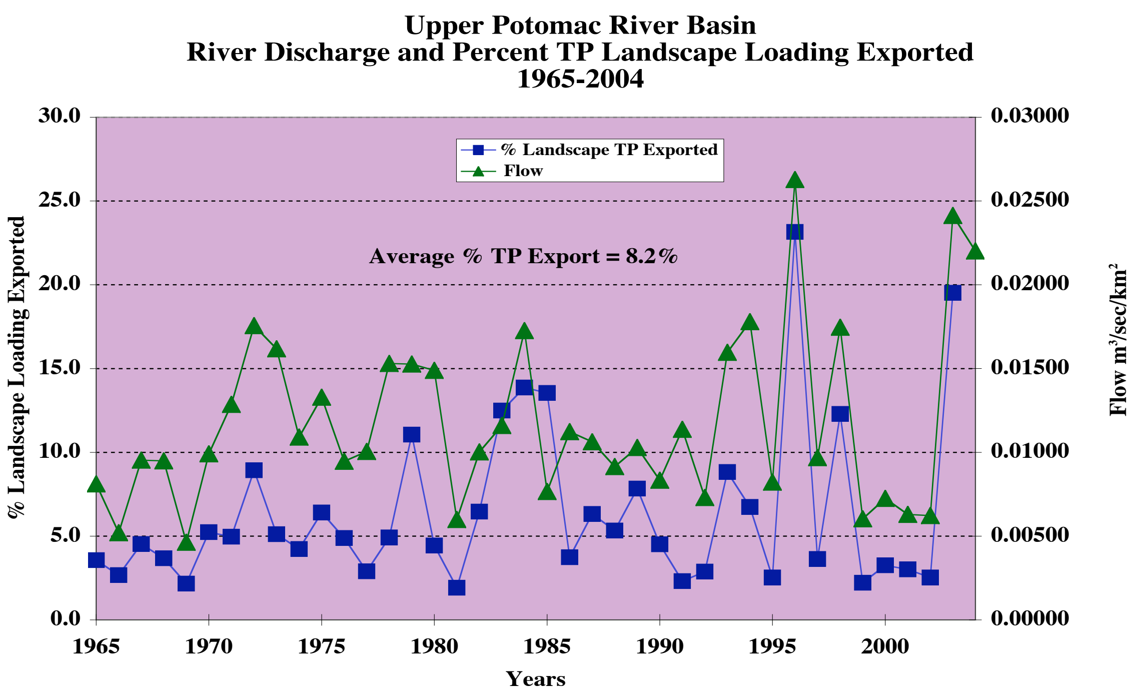
there is also large variability in the graph, as shown below.

While the riverine export flux is a function of the landscape loading input fluxes, the percent of TN landscape loading input that is exported by the river in a given year is also a function of the annual river flow, as presented in the two figures below.





Similar to TN, the average annual percent of TP exported from the Upper Basin is also a function of the annual river flow, with an average of 8.2%, as shown below.

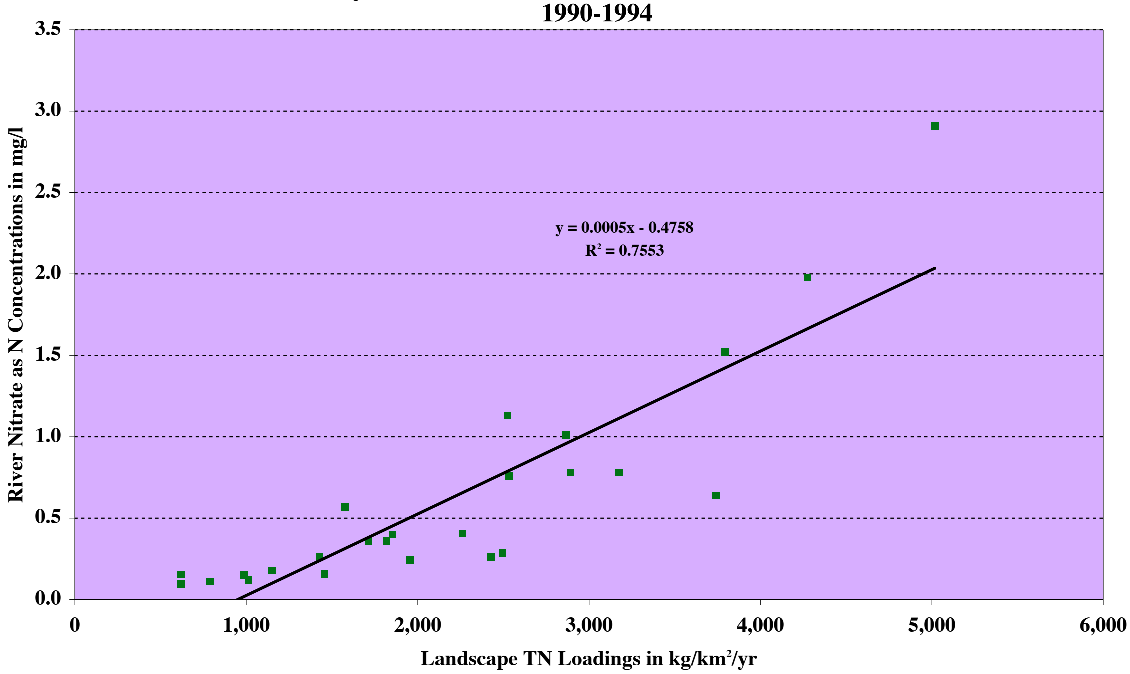


The percent of TN landscape loading inputs exported by the rivers of the sub-basins ranged from about 5% to over 40%, as presented above. The percent of TP landscape loading inputs exported by the rivers of the sub-basins ranged from about 2% to over 23%, as presented above. Similar to the 25 Middle Atlantic and Northeast USA watersheds and to the eight sub-basins of the Upper Potomac River Basin, the percent of TN and TP inputs exported by the rivers appears to also be a function of annual runoff.

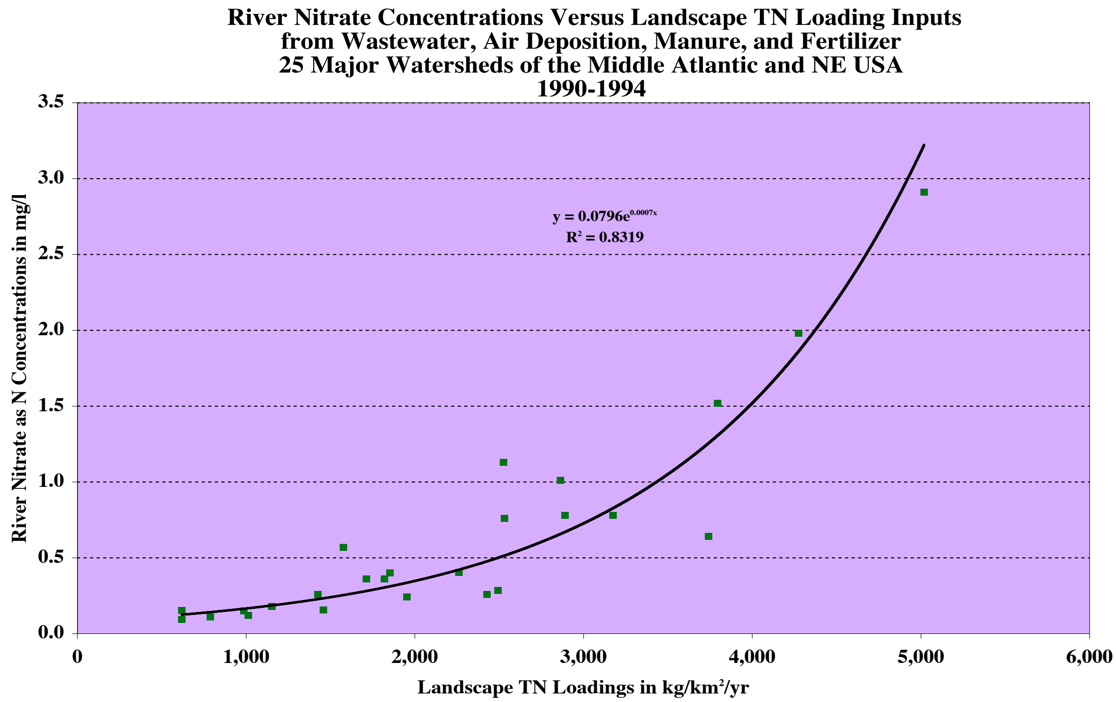
Riverine NO_3 Concentration/Landscape Loading Input Relationships

Based on the strong relationship between river flow and percent of inputs exported by the river, we hypothesized that there should be a strong relationship between riverine nitrate concentrations and landscape loading inputs. For the 25 watersheds, the average annual riverine nitrate concentration/landscape input relationship appears to be linear (see below), with a slope of 0.0005.

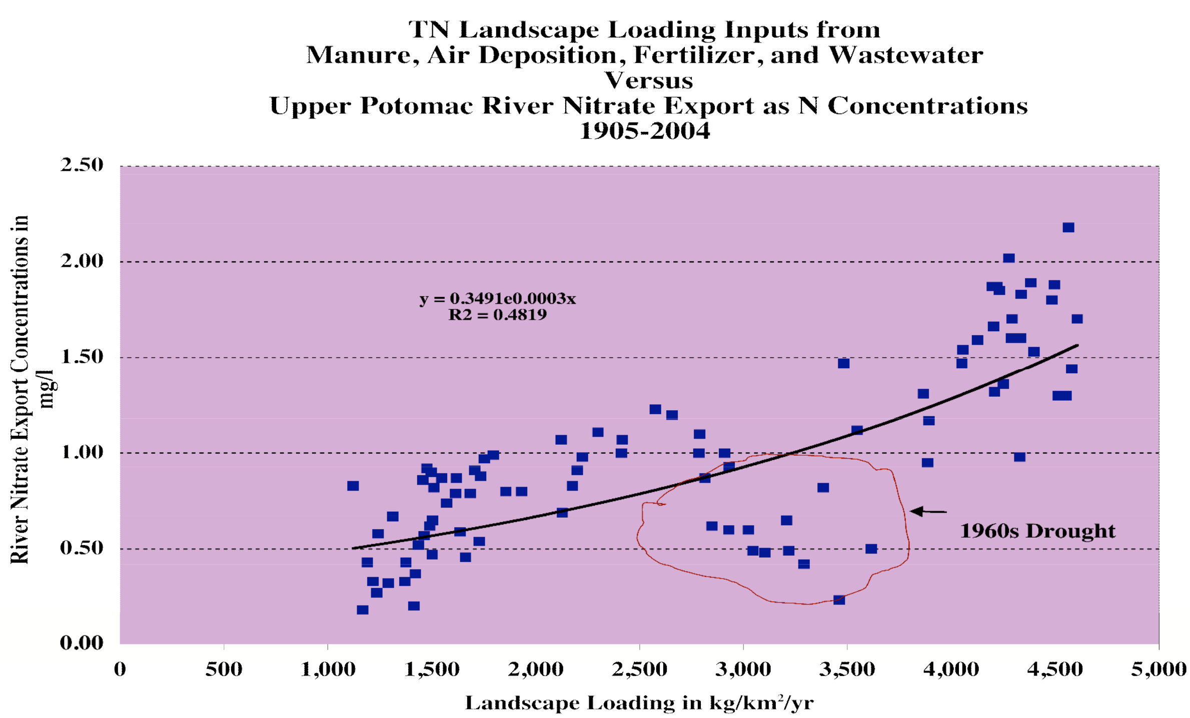
River Nitrate Concentrations Versus Landscape TN Loading Inputs from Wastewater, Air Deposition, Manure, and Fertilizer 25 Major Watershed of the Middle Atlantic and NE USA 1990-1994



We also examined the possibility of whether the relationship above is exponential. The nitrate riverine concentration versus landscape loading exponential relationship appears to be a better general model (see below) that can also be used to estimate the riverine concentration response to landscape loading input changes.

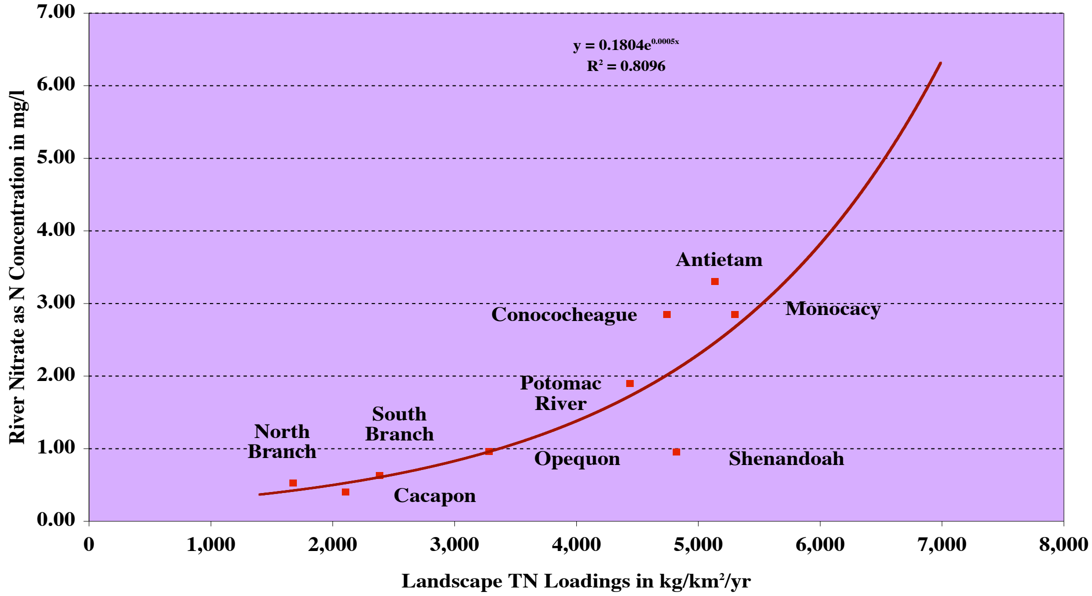


The average Upper Basin annual landscape input/riverine nitrate concentration exponential relationship for the period 1905 to 2004 is presented below.



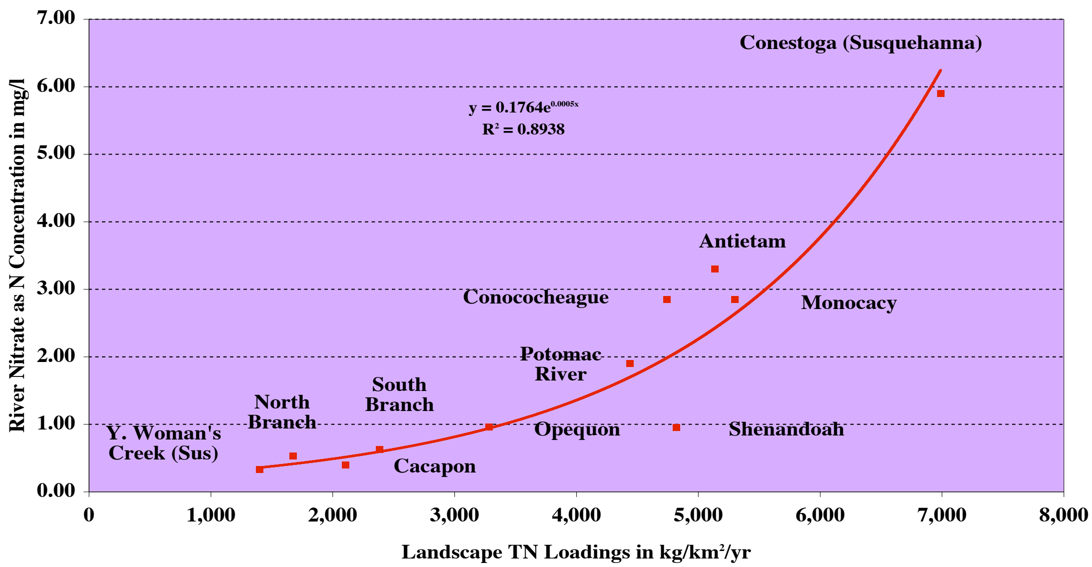
The average annual riverine NO_3 concentration/landscape input exponential relationship (see below) for the period 1990 to 1994 was very good for the eight sub-basins of the Upper Potomac.

Nitrate River Concentrations Versus Landscape TN Loading Inputs from Wastewater, Air Deposition, Manure, and Fertilizer Upper Potomac River and its Eight Major Sub-basins 1990-1994



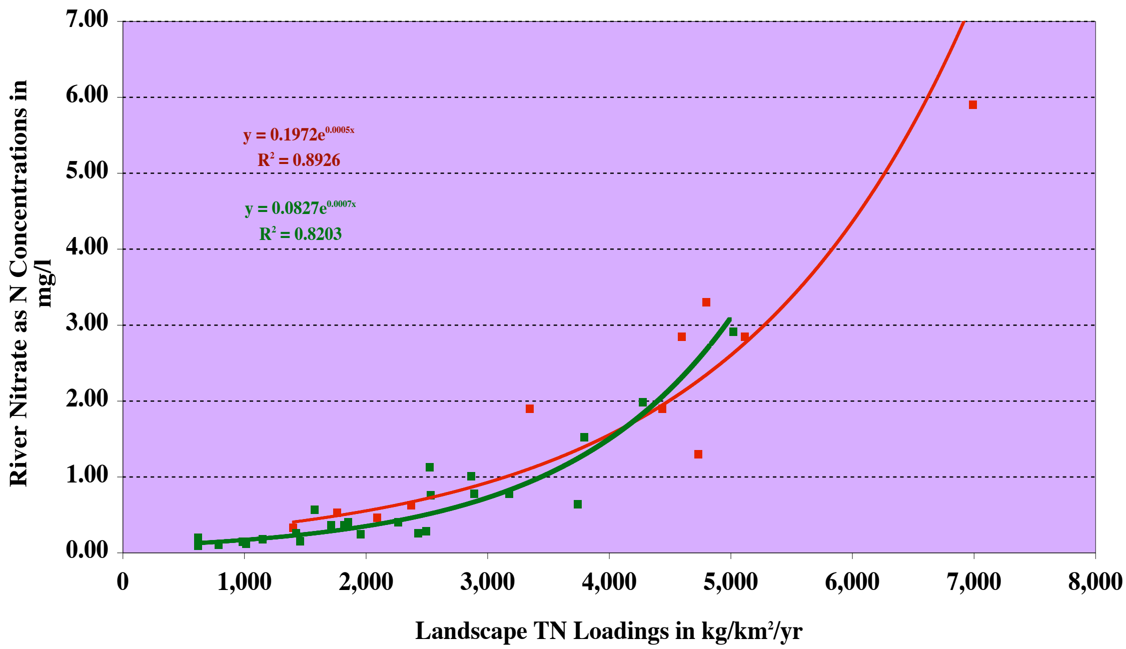
When we add a low and a high landscape loaded sub-basin from the Susquehanna River Basin to the Potomac data above, the exponential relationship improves (see below).

Nitrate River Concentrations Versus Landscape TN Loading Inputs from Wastewater, Air Deposition, Manure, and Fertilizer Upper Potomac River and its Eight Major Sub-basins Plus Conestoga and Young Woman's Creek (Susquehanna) 1990-1994



The strong riverine NO_3 average annual riverine concentration/landscape input exponential relationships overlap. This overlap suggests that the 25 watersheds and the eight Potomac sub-basins plus the two Susquehanna sub-basins are very similar (see below). These relationships can be used to predict how a landscape input reduction will lower the river export NO_3 concentration.

River Nitrate Concentrations Versus Landscape TN Loading Inputs
25 Major Watershed of the Middle Atlantic and NE USA (GREEN)
Upper Potomac River Basin and its Eight Major Sub-basins
Plus Two Susquehanna Watersheds (RED)
1990-1994

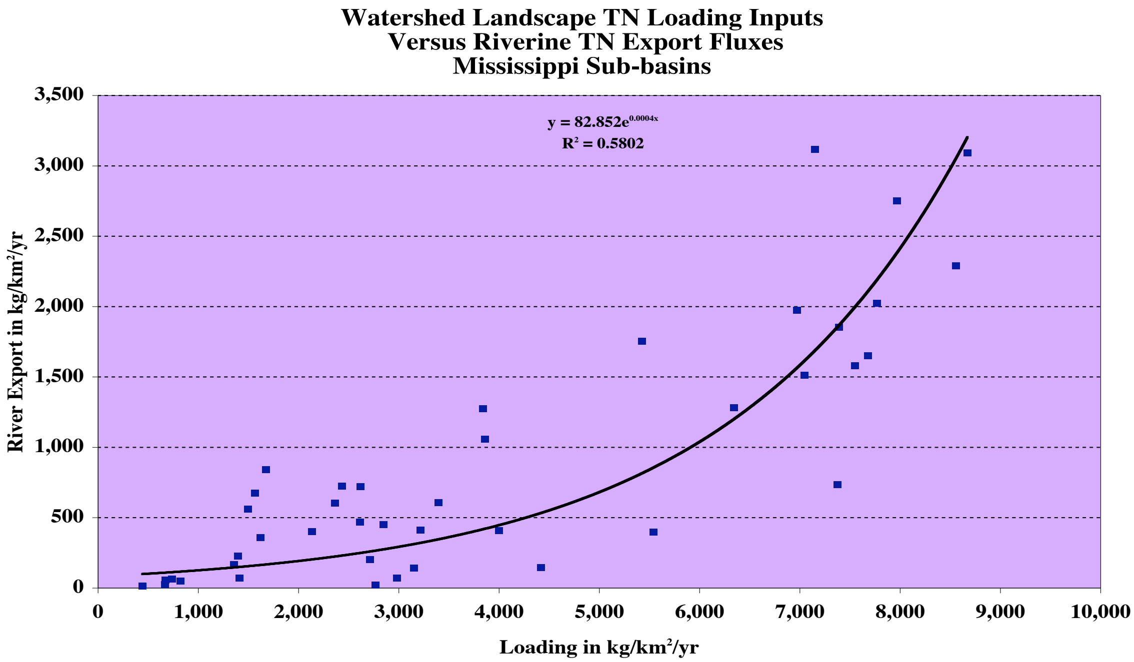


Two general types of statistical models were developed in the expanded SCOPE study of the 16 Northeast USA watersheds (2). The models predict the average annual riverine nitrogen concentrations from the 16 watersheds as a function of the Net Anthropogenic Nitrogen Inputs (NANI) and precipitation or river discharge. Both linear and exponential relationships were investigated.

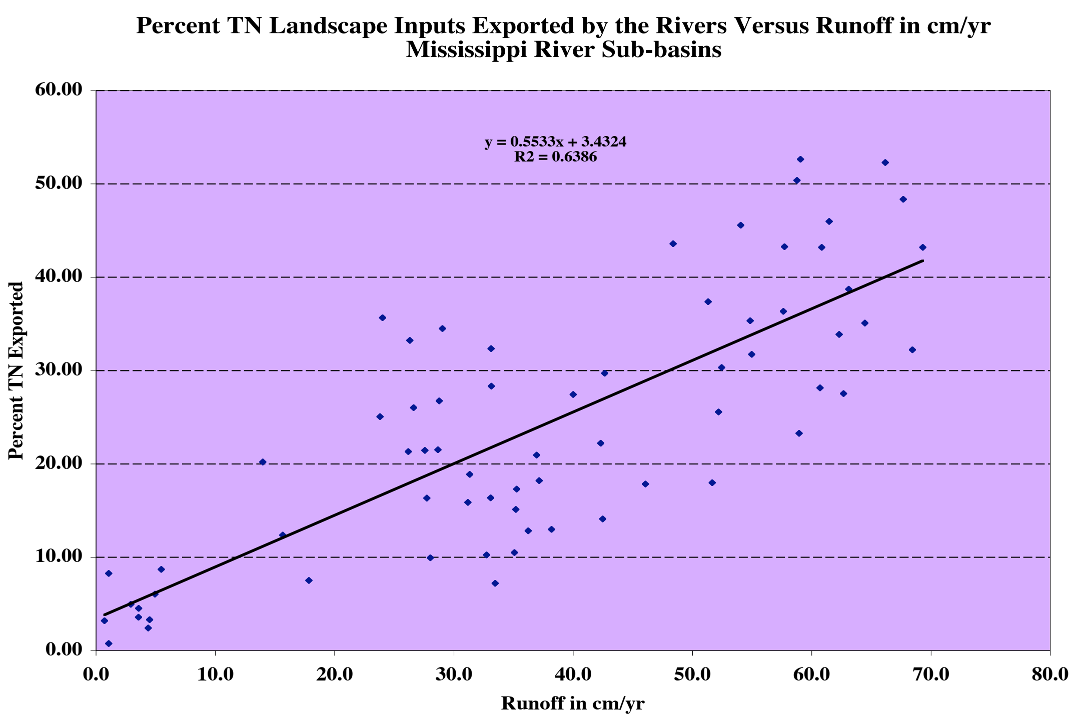
These landscape loadings/nitrogen export relationships provide water quality managers with a means of targeting nutrient control.

Application of Methodology to Mississippi River Sub-basins

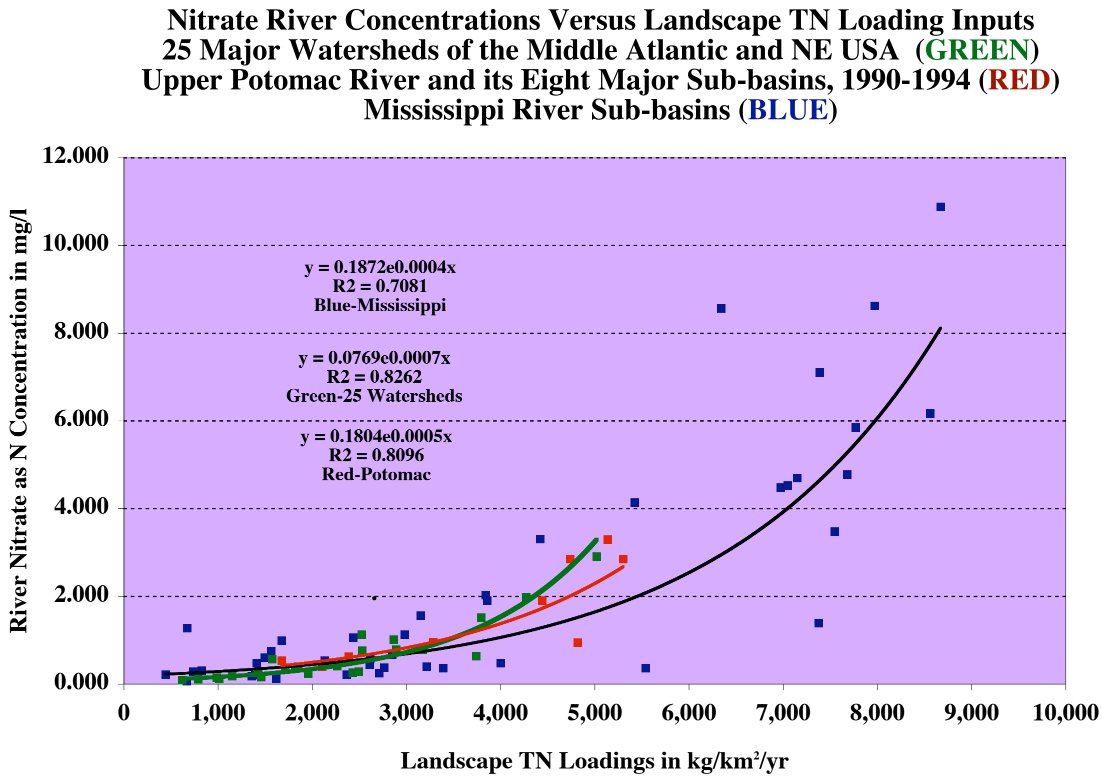
We examined the relationship of landscape loading inputs to riverine TN export fluxes for the 42 sub-basins of the Mississippi River using USGS data (7). As can be seen in the chart below, the relationship appears to be exponential rather than linear.



The percent of TN landscape loading inputs exported by the rivers of the Mississippi sub-basins ranged from about 1% to over 50%, as presented below. Similar to the 25 Middle Atlantic and Northeast USA watersheds and to the eight sub-basins of the Upper Potomac River Basin, the percent of TN inputs exported by the rivers of the sub-basins appears to also be a function of annual runoff (see below).

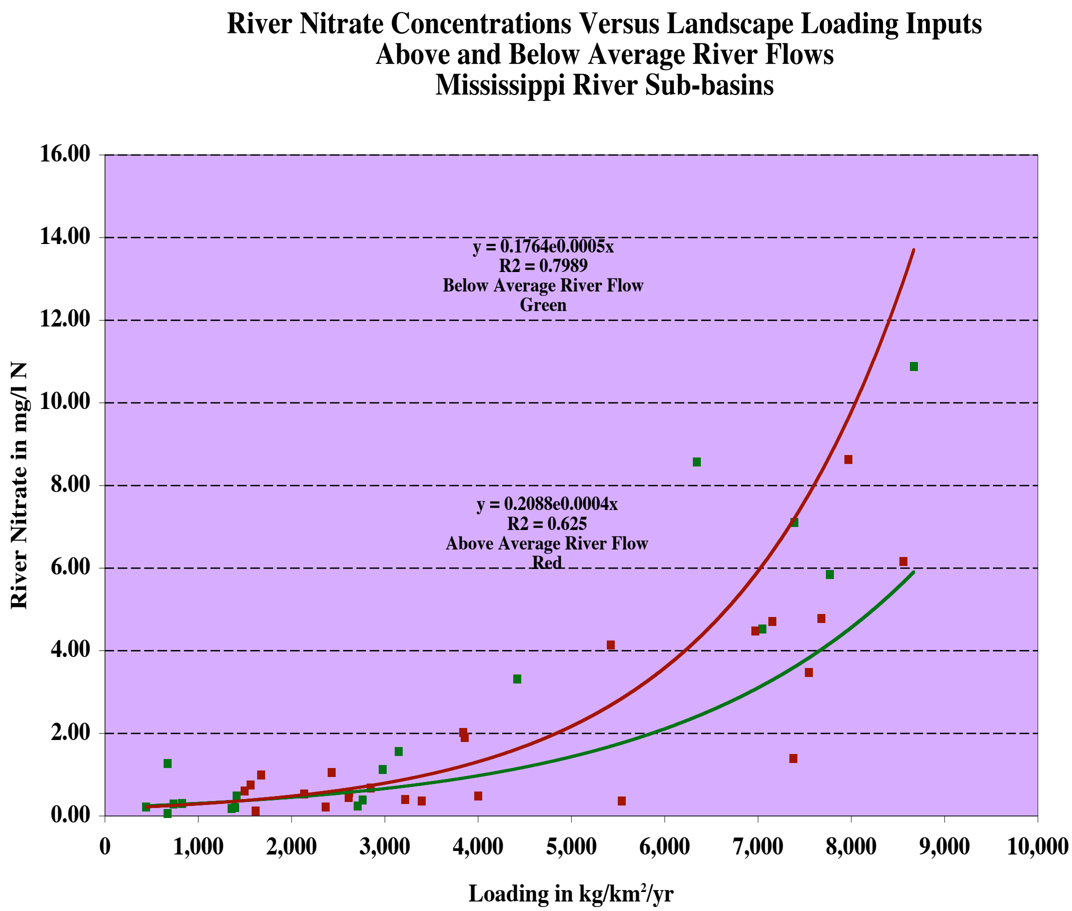


The river nitrate concentrations versus landscape TN loading inputs relationship appears to also be exponential for the 42 sub-basins of the Mississippi River Watershed, as presented below.



The strong riverine NO_3 average annual riverine concentration/landscape input exponential relationships developed for the 25 watersheds of the Middle Atlantic and Northeast USA and for the eight Upper Potomac sub-basins overlap the 42 Mississippi sub-basins relationship, as presented above. These overlapping relationships suggest that the exponential model can be used to predict how a landscape input reduction will lower the river export NO_3 concentration, especially at lower landscape loading inputs.

Because the annual river flow, in cm/yr, can affect the percent of the TN landscape loading input that is exported by the river, we stratified the 42 sub-basins into “above average watershed runoff of the entire Mississippi River” and “below average watershed runoff of the entire Mississippi River,” as present below. The higher nitrate river concentrations usually occurred when the sub-basin river flows were above average.



Mass Balance of the Sum of the Water Quality Constituent Loads of the Individual Sub-basins of the Upper Basin

To aid in establishing nutrient reductions for the major sub-basins of the Upper Potomac River Basin, we attempted to mass balance the sum of major water quality constituent loads from the sub-basins with the water quality constituent loads of the total Upper Basin measured at Chain Bridge.

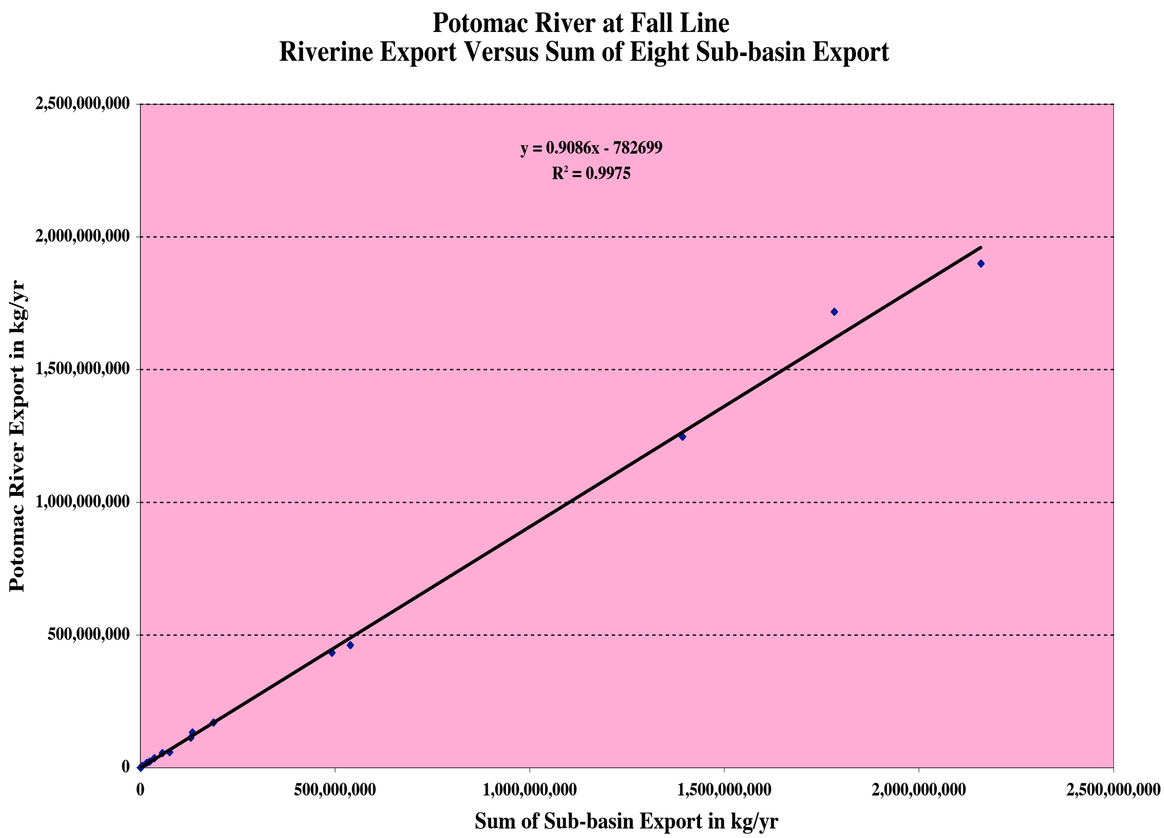
Because the monitored drainage area of the eight major sub-basins of the Upper Basin encompassed only 69% of the drainage at Chain Bridge, we needed a method for estimating the water quality constituents of the unmeasured watersheds. To estimate the contribution of the water quality constituents of the unmonitored drainage area, we increased the area of eight sub-basins by dividing by 0.69.

Similar to estimating the riverine nutrient fluxes, we used the USGS and West Virginia DEP water quality data and the USGS surface water flow data to estimate the fluxes in $kg/km^2/yr$ for the 13 water quality constituents.

We then calculated for each of the 13 water quality constituents, the annual load in kg/yr for the eight expanded areas (see below), the loads at Chain Bridge, and the percent of sub-basin loads with the total loads measured at Chain Bridge.

Water Quality Constituent	Sum of the Sub-basins kg/yr	Potomac River Fall Line kg/yr	Sum of the Sub-basins / Total Basin %
TDS	2,159,418,447	1,899,685,880	113.7
NH_4	686,892	859,080	80.0
Org N	5,198,827	7,171,452	72.5
NO_3	16,765,025	18,135,091	92.4
TN	23,743,901	22,913,732	103.6
TP	1,376,591	1,187,240	115.9
Chlorides	187,999,366	170,321,985	110.4
Hardness	1,782,756,359	1,718,160,372	103.8
SO_4	539,385,673	461,658,274	116.8
Alkalinity	1,392,596,839	1,247,533,835	111.6
Ca	492,287,621	433,275,224	113.6
Mg	129,486,935	113,547,990	114.0
Na	134,037,334	132,941,199	100.8
K	35,996,636	36,448,268	98.8
Silica	74,949,696	58,857,423	127.3
TOC	56,818,093	55,279,942	102.8

For some of the water quality constituents, the estimated contribution from the sum of the individual sub-basins exceeded the load at the Chain Bridge Station, and for other constituents, the sum of the sub-basins was less. The sum of annual loads from the eight expanded sub-basin areas was compared graphically to the estimated load of the Upper Basin at Chain Bridge Station (see below).

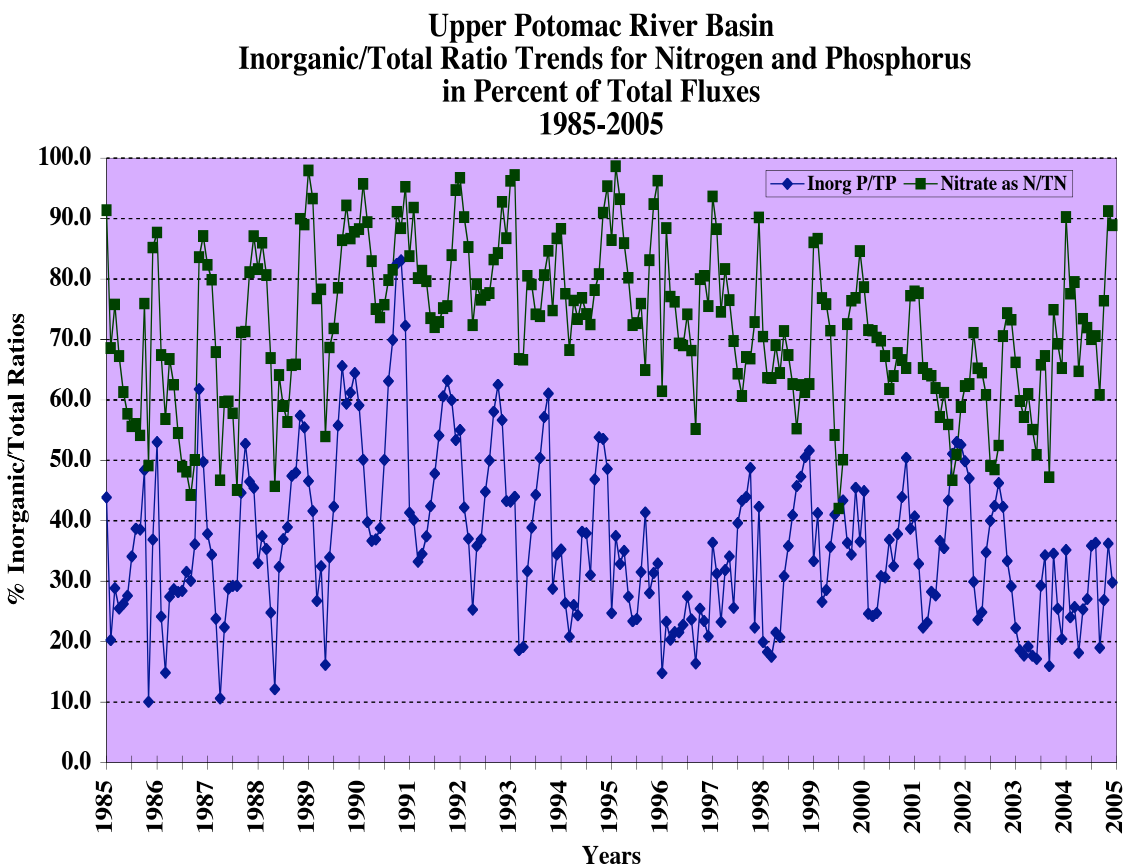


For the more conservative water quality constituents, the percent of the constituent loads for the sum of the eight sub-basins ranged from 73% to 116% greater than that measured at Chain Bridge Station. The high correlation, as shown above with a slope of 0.91, suggests that we can mass balance constituents of the sub-basins, a necessary step in developing the sub-basin nutrient loading reductions.

For the 1990 to 1994 period, about 16% of the sum of TP in the eight sub-basins was lost during transport in the main stem of the Potomac River. The TN loss was about 3%. For a dry period, 1965 to 1966 (5), the TP lost to riverine systems was about 21% of the sum of the sub-basin areas, while TN loss was about 29%.

Changes in Inorganic/Total Ratios for Nitrogen and Phosphorus

The percent of inorganic phosphorous to TP and nitrate nitrogen to TN of the Potomac River at Chain Bridge Station varies monthly and appears to vary annually (see below).



The highest percentage of inorganic TP was usually observed in the late summer-fall months, with the lowest percentage usually occurring in the winter months (see above). The highest percentages of nitrate N were observed in the winter-spring months, with the lowest in the late summer months.

For the period 1985 to 2000, the annual percentage of nitrate N was highest—about 80% in the early 1990s (see above). Since the early 1990s, the percentage of nitrate decreased to about 60%. During the high river flows in the early 2000s, the percentage of nitrates increased to over 70%.

The same is true for TP. The annual percentage of inorganic TP was highest in the early 1990s, with distinct monthly cycles. In the mid-1990s, the annual inorganic percentages decreased and the monthly cycles were not as distinct. **The causes of these annual changes are unknown.**

References for Chapter Four

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