

1 **Defining basin water quality: Land use, tributary input, and downstream dynamics**

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In review following submission to Journal of Environmental Quality

1 **ABSTRACT**

2       During a 1-year period, we sampled surface water in a Chesapeake Bay tributary  
3 stream located in the Valley and Ridge and Blue Ridge provinces. Median nitrate and  
4 chloride concentrations for 7 sites along the mainstem and 5 tributary streams show that  
5 water quality tracks land use patterns and other sub-watershed characteristics. Our  
6 findings corroborate the well-known relationship between land use and solute load. We  
7 can well predict nitrate and chloride concentration with agricultural and urban  
8 development. However, our results show that nitrate loads at downstream sampling  
9 stations are not as high as predicted based on land use. This finding is contrary to  
10 predictability of chloride concentration. Moreover, all of the major predictors of water  
11 quality are inter-correlated, so we unable to separate the effect of land use, topography,  
12 and geology. The data largely confirm the control of water quality by land use practices;  
13 however, the results further indicate that spatial changes of water quality depend on  
14 stream path opportunities for remediation or the geological control of preferential flow  
15 paths

16

17 **INTRODUCTION**

18       Many previous studies have demonstrated the effects of land use on stream water  
19 quality on the basin scale (e.g., Omernik, 1977; Herlihy et al., 1998). These expected  
20 relationships often drive the basis for watershed monitoring design. Much of the  
21 monitoring work has been done by government agencies targeting impaired streams.  
22 Less frequently have citizens initiated sampling programs focused on determining  
23 baseline water quality for their community.

1 Water quality in the mid-Atlantic, particularly non-point source pollution,  
2 increasingly focused on tributary inputs into the Chesapeake Bay. One of the world's  
3 largest estuaries, the Bay is threatened by eutrophication from anthropogenic inputs of  
4 nutrients. Most of the water quality analyses has been done in Coastal and Piedmont  
5 systems (Lowrance et al., 1995), but characterization of the inputs from watersheds in the  
6 Valley and Ridge and Blue Ridge provinces becomes increasingly important as  
7 legislation is proposed to impose land use restrictions on these headwater streams  
8 influencing the Bay. The Maury River watershed that we study is part of the upper James  
9 River basin, which itself is implicated as a major exporter of nutrients and sediment to the  
10 Chesapeake Bay (Sprague et al., 2000; VADCR, 2000).

11 Targeting the sources of non-point source pollution requires understanding the  
12 relationships between water quality and watershed characteristics including land use  
13 patterns. Much work has been done to relate the amounts of anthropogenic nutrient input  
14 (including nitrate and phosphate) to agriculture, with greater proportions of agricultural  
15 land discharging greater amounts of nutrients (e.g. Hill, 1978; Dillon and Kirchner, 1975;  
16 and others). This relationship has become an important factor in many empirical model  
17 of nutrient discharge. Virginia uses land cover data plus animal census numbers in  
18 determining priority watersheds for nonpoint source pollution (Hession et al., 2000)  
19 Spatial modeling suggests that although agricultural land remains a primary source of N  
20 for the James River, urban sources account for more than a third of the load (Sprague et  
21 al., 2000).

22 Other water constituents have been used to indicate stream impairment. The  
23 conservative (non-reactive) anion chloride has often been shown to have strong

1 relationship to the amount of urban land or development within a watershed and has been  
2 used to indicate human disturbance in a watershed including roads, industry and fertilizer  
3 use (Herlihy et al., 1998).

4 For nutrients, riverine inputs occur in two flow systems: baseflow and surface  
5 runoff. Different constituents dominate each of the flow types. For nutrients, the  
6 groundwater source of baseflow enhances the flow of nitrate whereas phosphorous is  
7 found primarily in rapid surface flows or storm flows because it is generally bound to  
8 sediments (Jordan et al., 1997; and references therein).

9 Given the importance of nutrient loads and the fact that they can be well predicted  
10 in source areas by land use, the objective in this paper is to explain the downstream  
11 dynamics of baseflow water quality and to predict changes for varying land use across  
12 variable tributary scales in the Valley and Ridge and Blue Ridge. We use differences in  
13 behavior of conservative and non-conservative constituents to understand the delivery  
14 mechanisms or transport and behavior of pollutant loads in basins of differing size.

15

## 16 **METHODS AND STUDY AREA**

17 The data for this study come from a citizen-volunteer sampling program initiated  
18 with a Chesapeake Bay Program grant. Field data describing pH, temperature, dissolved  
19 oxygen, and conductivity combined with samples analyzed for major ion chemistry and  
20 bacteria were collected biweekly at 11 sites in the Maury River watershed in the upper  
21 James River basin of Virginia. Here we examine the spatial trends in the median nitrate  
22 and chloride concentrations to analyze the effect of spatially concentrated land use  
23 patterns on water quality. Sampling commenced in August 2000 on the Maury River

1 sites, and in January 2001 on the tributary sites and continued biweekly through July of  
2 2001. Air-free, 250 ml samples were collected from below the water surface by  
3 volunteers and analyzed within 24 hours of collection. Nitrate and chloride levels were  
4 measured using ion chromatography. The bulk of the samples are taken at nearly the  
5 same time during each 24-hour long, biweekly period, but individual sampling locations  
6 vary in time of day, from approximately 9 am to 5 pm.

7         The Maury River rises in Paleozoic sedimentary rocks of the Valley and Ridge  
8 province in the headwaters and reaches the igneous and metamorphic rocks of the Blue  
9 Ridge near the confluence with the James River. The steep terrain found in the Blue  
10 Ridge and sandstone ridges of the western part of the basin limits most agricultural  
11 practices to valley floors, which are underlain by shale in the headwaters and limestone in  
12 the southern end of the Great Valley (Figure 1). Land cover in the headwaters and the  
13 extremities of individual subwatersheds is primarily deciduous forest. Agriculture is  
14 primarily pasture and hay, with approximately ten percent under tillage. Unlike the  
15 Shenandoah Valley of northern Virginia, the Maury River watershed has few  
16 concentrated animal feeding operations, particularly few poultry facilities.

17         Flow in the Maury River (Figure 2) is described by gauges near the headwaters  
18 (above sampling station MR02, Figure 1) and the mouth of the basin (above MR05,  
19 Figure 1). Discharge follows a winter increase and summer decline in baseflow with  
20 overprinted storms that occur during any season. Stormflow is more important in the  
21 headwaters, leaving a higher baseflow at the downstream gauge. The peak in baseflow  
22 occurs in March for both gauges. Sampling occurred during the 4<sup>th</sup> year of a 5-year  
23 “drought” in which baseflow has declined. Sampling coincided with only 3 higher flows

1 during November, March, and May, and only two of those occurred very near the peak of  
2 flow. We use the median value to represent base flow water quality for each station,  
3 largely because we only have one year of data, and this year was particularly dry. These  
4 conditions limit our ability to determine a stage-dependent load curve that accounts for  
5 seasonal and temporal variability.

6 Spatial data were investigated using GIS analyses of several data sets. Land use  
7 was examined using 30-meter resolution National Land Cover Data (NLCD, Vogelmann  
8 et al., 2001) for Virginia. The NLCD data reflect land use interpreted from 1992 satellite  
9 images. Although the region is developing through low-density rural housing growth,  
10 land use at the subwatershed scale is stable enough to be predictive. NLCD categories  
11 were merged into a generalized land use map consisting of forest and wetlands (NLCD  
12 codes 41-43, 91, 92), developed (21-23, 85) and agriculture (81, 82). Also at a 30-m  
13 resolution, elevation data were obtained in 7.5 minute quadrangles and mosaiced into a  
14 single layer. Slope was derived from unsmoothed elevations using the standard slope  
15 calculation in ArcView. Road data are U. S. Census Bureau TIGER layers for  
16 Rockbridge, Augusta and Bath Counties, and the cities of Lexington and Buena Vista.  
17 These data are not discriminated by pavement type or size. Road density was  
18 approximated by calculating the average distance to roads for all 30 m grid cells in each  
19 subwatershed. The landscape metrics were calculated for the subwatershed above each  
20 sampling point and cumulated for sampling stations continuing downstream.

21 To assess the impact of the riparian zone on water quality, we use a 100 m buffer  
22 along each side of the streams in the EPA RF3 stream network for the Maury River  
23 watershed. The characteristics of the land use, road density and slope were determined

1 for the buffered area for each subwatershed. The RF3 file represents a digital  
2 compilation of the hydrography of USGS 1:100,000 scale maps. This differs from the  
3 NLCD dataset, which was georeferenced to the 3 arc second topographic information  
4 (1:250,000 scale), and the digital topography, which was at a finer resolution. Therefore,  
5 the stream network is not entirely coincident on the three data sets, leading to some  
6 inconsistency, commonly up to 30 m but never more than 50 m.

7

## 8 **RESULTS**

9       Our findings confirm the well-known relationship between land use and solute  
10 load. As summarized by chloride and nitrate (Figure 3), water with high quality enters  
11 the southern end of the Great Valley or Shenandoah Valley (below MR02) and thereafter  
12 degrades to maximum concentration after passing through Lexington at station MR04.  
13 One can readily see the influence of tributary additions to the general low concentration  
14 flow entering from the headwaters. Hays, Kerrs, and Woods Creek all have significantly  
15 higher chloride and nitrate concentrations than the Maury River. These watersheds are  
16 intensively grazed and are experiencing increasing low-density residential development.  
17 Woods Creek flows through the city of Lexington (population 5500) and is otherwise  
18 pasture.

19       Quantitative investigation of the watershed properties related to the water quality  
20 values indicate relationships with specific land use patterns and aquifer characteristics  
21 (Table 1). The concentrations of nitrate are most strongly correlated with the percent  
22 agriculture in the watershed ( $R=0.954$ ; Figure 4). Other significantly correlated  
23 variables at the 0.05 level were the % of agriculture in the 100m buffer ( $R=0.845$ ), % of

1 carbonate ( $R=0.953$ ), % of carbonate in the 100m buffer ( $R=0.910$ ), % of forest ( $R=$   
2  $0.937$ ), % of forest in the buffer ( $R= -0.906$ ), % urban ( $R= .664$ ), % urban in the 100m  
3 buffer ( $R = 0.649$ ), and the mean slope ( $R=0.807$ ).

4 At all sites, the relationship of chloride concentration at all of the sites is strongest to  
5 the percent development in the watershed (Figure 5A). The value for Woods Creek  
6 skews the regression because it is an outlier in both the amount of chloride and the  
7 amount of urban land in the watershed. For our investigation, we chose to remove that  
8 point from the dataset and to treat the Woods Creek watershed separately. Without the  
9 data point, chloride and urban land are still highly correlated with a slightly different  
10 slope (Figure 5B). The most significant correlation for all sites (with the Woods Creek  
11 outlier removed) is the % of urban in the watershed ( $R= 0.918$ ). Other significant  
12 correlations (at the 0.05 level) are the % of urban in the 100m buffer ( $R= 0.911$ ), area  
13 ( $R=0.624$ ), and the area in the buffer ( $R=0.670$ ). The strongest relationship for the Woods  
14 Creek watershed sites is the average distance to roads within the watershed, which is  
15 another indicator of the amount of development in the watershed ( $R= -0.944$ ; Figure 6A).  
16 For nitrate in Woods Creek, there is a strong relationship for distance to roads and nitrate  
17 with two points lying much higher than the line (Figure 6B). WC09 is the headwater site  
18 for Woods Creek and SR01 is above the confluence of Sarahs run and Woods Creek. For  
19 nitrate and % development there are three data points that are off the main trend; WC09  
20 and SR02 are headwater sites and SR01 is in a highly developed stream reach (Figure  
21 6C).

22 Stepwise multiple regression analysis was applied separately to median nitrate  
23 and chloride values for all of the land use and watershed characteristic values in order to



1 build an optimal linear model from the sets of regressors. Regressions were performed  
2 for all the sites, the tributaries, and Woods Creek separately.

3 For nitrate (in the Maury and tributaries) using all variables, regression analysis  
4 predicted 2 models; one included only agriculture ( $R^2=0.910$ ), and the second included  
5 agriculture and area ( $R^2=0.962$ ). If coefficients of the first model (agriculture only;  
6  $NO_3 = 0.0933(\% \text{Agriculture}) + 0.363$ ) are used to predict nitrate values, the values are all  
7 over-predicted for the Maury river mainstem sites (Figure 7A). If the area is included in  
8 the model ( $NO_3 = 0.848(\% \text{Agriculture}) - 4.09e-10(\text{Area}) + 0.926$ ), the nitrate is better  
9 predicted for these Maury sites (Figure 7B).

10 In order to investigate the influence of contributing watershed area to the water  
11 quality, the regression values for the tributaries were used to predict the values for the  
12 mainstem Maury. For the tributaries, 2 regression models were predicted; one with  
13 agriculture ( $R^2=0.977$ ) and one with agriculture and the average distance to roads in the  
14 100m buffer ( $R^2=0.995$ ). The coefficients from these models were used to predict values  
15 for nitrate in the mainstem Maury. For model 1: ( $NO_3 = 0.0817(\% \text{Agriculture}) + 0.976$ )  
16 the model overpredicted all of the Maury River sites (Figure 8A) and for model 2: ( $NO_3$   
17  $= 0.0702(\% \text{Agriculture}) - 0.00253(\text{Average distance to Roads in the 100m buffer}) +$   
18  $1.952$ ) had higher residuals for the Maury River sites (Figure 8B).

19 Similar regressions for median chloride concentrations were performed for all of  
20 the sites (excluding the Woods Creek tributary value as an outlier). For chloride, 2  
21 models were predicted; one included the % of urban land use ( $R^2=0.843$ ) and the other  
22 included %urban and the slope in the 100m buffer ( $R^2 = 0.942$ ). The models were used to  
23 predict chloride in the watershed (model 1:  $Cl = 2.575(\% \text{urban}) + 2.069$ ); Figure 9A) and

1 (model 2:  $Cl = 3.193(\%urban) - 0.453(\text{slope in the 100 m buffer}) + 5.862$ ; Figure 9B).

2 The distribution of the residuals for chloride are distinctly different than for nitrate  
3 indicating a different relationship to land use for these two constituents or a difference in  
4 loading or transfer processes.

5

## 6 **DISCUSSION**

7 Our data clearly confirms the control of water quality by land use practices. The  
8 major changes of water quality as represented by median nitrate correlated clearly with  
9 the major land use characteristics of the watershed. Baseflow water quality in the mid-  
10 Atlantic region of the U.S. is well correlated to land use (Herlihy et al., 1998), with  
11 chloride indicating any human activity while nitrate concentration is strongly correlated  
12 with agriculture. In this study, the best predictor of nitrate concentration from the  
13 multiple regression models is % agriculture, but the addition of road density improves the  
14 model measurably (Figure 8) for the tributary model. Road density is a surrogate for  
15 development and more completely characterizes the low-density development  
16 characteristic of former pasture areas than does the NLCD cell data. Moreover, nitrate  
17 concentration has a strong relationship to urban development on land use maps (Figure  
18 6B and 6C). Because we focus on a small, relatively densely developed watershed, we  
19 can infer that development will be an increasingly important contributor of nitrate to the  
20 overall load, even in a headwater area. Sprague et al. (2000) partition more than one  
21 third of the overall nitrogen load in the James River to developed sources including septic  
22 tanks. Their modeling of the upper James River shows the most concentrated load in the  
23 Maury River watershed comes from urbanized areas. Thus, agriculture is the dominant

1 control on nitrate concentration in the Maury River, but development may be an  
2 important contribution where low density development follows agricultural patterns. In  
3 fact, the Woods Creek data show that urban loading, given a high impervious cover, can  
4 be as high as agriculture (Figure 6C).

5         The attribution of nitrate source to agriculture is in some ways confounded by the  
6 nearly total correlation of multiple landscape characteristics. The median nitrate value is  
7 also highly correlated to carbonate bedrock, percent forest, and slope. Agricultural  
8 activity occurs primarily in the Great Valley carbonate sections of the watershed, with  
9 some pasture/hay in the shale valleys of the headwaters (Figure 1). Likewise, the inverse  
10 correlation of high slope and agriculture is logical. This covariation of predictor  
11 variables is unfortunate because Lowrance et al. (1995) suggest that both geology and  
12 slope should change the behavior of shallow groundwater flow paths, and hence the  
13 delivery of nitrate to streams. In shale and steep sandstone areas, water flow is  
14 concentrated in the rhizosphere and removes nitrate. In carbonates, deep water flow  
15 paths and seepage to the river at discrete discharge points limits the ability of vegetation,  
16 particularly riparian buffers to interact with water to remove nitrogen. In steep forested  
17 areas, high permeability soils transmit water as throughflow which has an opportunity to  
18 interact with saturated zones at the base of the slope. We cannot eliminate the effect of  
19 slope and rock type from our data because of the covarying landscape metrics, but we  
20 suspect it may be a combination of several effects. In a national dataset, Omernik (1977)  
21 found no relationship of water quality measures to geology when considering land use.

22         Lowrance et al. (1995) also predict that riparian buffers will be of little affect in  
23 treating nitrogen pollution in the Valley and Ridge due to limited floodplain area and

1 complex flow paths. In our models, road density is the only riparian buffer variable that  
2 appears as a predictor of water quality. The forest in riparian buffer areas is either  
3 ineffective, as suggested by Lowrance et al. (1995), or the forest buffer area is simply  
4 mirroring the conditions in the watershed uplands. The latter is borne out by the high  
5 correlation of the two variables (FOREST, FORBUF; Table 1). At the synoptic level of  
6 our data, we cannot determine the effect of forest buffers, because they apparently do not  
7 exist in great enough quantity in the agricultural areas to separate them out as a variable.

8         The behavior of chloride, which is the conservative tracer that is a “good  
9 surrogate indicator for general human disturbance in the watershed” when including  
10 agriculture (Herlihy et al., 1998), is more strongly predicted by developed sources  
11 (URBAN). However, when excluding the Woods Creek outlier, chloride concentration is  
12 not correlated with agricultural activity. The negative correlation for SLOPE in the  
13 multiple regression model is likely a reflection of the fact that steep slopes that don’t  
14 support agriculture or urban land uses, rather than a true relationship between slope and  
15 the transport or production of chloride.

16         Differences in loading or transport of chloride and nitrate concentration becomes  
17 evident by looking at the data from upstream to downstream (Figure 3). After leaving the  
18 headwaters region, the water quality deteriorates with increasing inputs from agricultural  
19 and urban sources. For just the Maury River mainstem sites, the peak of chloride  
20 coincides with the peak of urbanized land use percentage at MR06 (Figure 3) below the  
21 two towns and development paralleling two interstates (Figure 1). The large drop in  
22 chloride near the mouth of the stream shows the influx of Bufffalo Creek, which has little  
23 urbanization. On the other hand, nitrate concentration increases upon entering the

1 agricultural and developed valley, but it does not continue to rise. The percentage of  
2 forest decreases across the valley reaching its lowest value at the MR07. Thus the spatial  
3 trend of nitrate concentration does not follow the increasing percentage of roads, urban,  
4 and agricultural land use across the valley. The downstream Maury River sites (MR02-  
5 MR07) have less nitrate than is predicted by the trend of land use and by the expected  
6 trend from tributary loads (Figure 8). Even though the tributaries continue to supply high  
7 nitrate concentrations to the Maury, the concentration does not increase below Lexington  
8 (MR04). This under-prediction occurs despite steadily increasing values for both urban  
9 and agricultural land use within the lower reaches of the watershed. This change with  
10 increasing distance along the stream is further identified by the improvement of the  
11 multiple regression model with the addition of area (Figure 7).

12 The clear result that nitrate concentration in baseflow discharge for the downstream  
13 segment of the Maury River mainstem (Figure 3) signals either a change in the rate of  
14 delivery of nutrients to the stream or their uptake by biological processes. As the Maury  
15 River leaves the headwaters underlain by sandstone and shale in the Allegheny  
16 Mountains and enters the Great Valley underlain by carbonates, karst processes dominate  
17 the flow paths for groundwater. Baseflow per unit area is greater the downstream gauge  
18 (Figure 1), particularly in the summer and during the lowest discharge periods. The karst  
19 surficial characteristics and lower relief of the valley promote the increased baseflow and  
20 reduced stormflow per unit area of the watershed. Increased water retention will have the  
21 effect of diluting the nutrient concentration in groundwater, as suggested by Hill (1996)  
22 for riparian buffers. However, concentration of the conservative tracer chloride does not  
23 have the same decrease for the valley section of the river compared with the tributaries

1 and upstream segment of the mainstem (Figures 3 and 9). The mainstem Maury River  
2 sites are not different from the tributary sites when predicting chloride concentration with  
3 land use characteristics; thus, the conservative and non-conservative ions have different  
4 basin scaling behaviors.

5         If dilution is not reducing nitrate concentrations, then organic or inorganic  
6 processes are responsible for the uptake of nutrients along the flow path. Uptake by  
7 organic matter and denitrification by bacteria remove nitrogen as waters move along the  
8 flow path. In larger watersheds, more time allows a greater amount of nutrient spiraling  
9 (Allan, 1995). In a smaller watershed in upstate New York, Wall et al. (1998) observed  
10 nitrogen utilization by phytoplankton uptake in the low-slope segments of the main  
11 stream. This mechanism likely represents only a temporary removal of the nitrogen and  
12 storage in stream flora, because greater nutrient export generally occurs during flood  
13 flows (Allan, 1995) that is not represented in our sampling. More permanent uptake and  
14 denitrification also occurs in the hyporheic zone and in stagnant or dead zones associated  
15 with low water velocity (Duff and Triska, 2000). The opportunities for riparian buffer  
16 uptake and nitrate reduction increase in larger order streams with more stagnant stream-  
17 side channels. Hinkle et al. (2001) observed significant vegetative nitrate uptake and/or  
18 nitrate reduction by river water transport into the sediments adjacent to the channel. The  
19 main stem of the Maury River downstream of sampling point MR02 has nearly 100  
20 percent riparian forest buffer due to topographic constraints on agriculture. Moreover,  
21 the lower reaches of the Maury have a wider floodplain with an alluvial fill that supports  
22 the biotic uptake and subsurface transformation of nutrients. Thus the sidestream and

1 instream biota have the potential to lower the nitrate concentration relative to tributary  
2 predictions.

3 This transformation and/or storage of nitrate is clear for the Maury River mainstem,  
4 but the absolute size of the basin does not appear to be the sole factor for nitrate scaling.  
5 In Woods Creek (Figure 1 and 6C), nitrate concentration is high but decreases in the  
6 downstream direction through the edges of Lexington. Woods Creek and its major  
7 tributary, Sarahs Run - which is adjacent to a major US highway and flows Department  
8 of Transportation and agricultural chemical storage facility (sources of chlorides and  
9 nutrients) - enter with lower water quality associated with agricultural land use and  
10 generally improve flowing through the low and high density sewerred residential sections  
11 of Lexington. Water quality in Woods Creek again degrades passing through the  
12 commercial center of Lexington down to the confluence with the Maury River. The  
13 opportunity for storage or uptake improve the water even though the road and urban  
14 contributions should be increasing. This water quality improvement occurs below a golf  
15 course where water storage in a pond may provide the opportunity for nutrient uptake,  
16 much like in the higher-order Maury River

17

## 18 SUMMARY

19 In summary, our findings confirm the well-known relationship between land use  
20 and solute load. We can well predict nitrate and chloride concentration with agricultural  
21 and urban development. However, our results show that nitrate loads at downstream  
22 sampling stations are not as high as predicted based on land use. This finding is contrary  
23 to predictability of chloride concentration. Moreover, all of the major predictors of water

1 quality are inter-correlated, so we unable to separate the effect of land use, topography,  
2 and geology. While the data do largely confirm the control of water quality by land use  
3 practices, they further indicate that spatial changes of water quality depend on stream  
4 path opportunities for remediation or the geological control of preferential flow paths.  
5 These results for a spatially varied Valley and Ridge watershed in the Chesapeake Bay  
6 drainage basin both confirm previous findings and suggest additional research avenues.

7

8

#### 9 ACKNOWLEDGEMENTS

10 We would like to thank our MRA field volunteers, laboratory volunteers, and  
11 Board members. We are indebted to the Washington and Lee University Geology and  
12 Biology Departments for their support and contributions. We also acknowledge the City  
13 and County governments, the Virginia Military Institute and Environment Virginia, the  
14 NFWF/EPA for initial funding, and the NSF DUE (#9952519) for funding the ICP-OES  
15 equipment used in the laboratory. The views and conclusions contained in these  
16 documents are those of the authors and should not be interpreted as representing the  
17 opinions or policies of the U.S. Government. Mention of trade names or commercial  
18 products does not constitute their endorsement by the U.S. Government.

19

20



1 REFERENCES

2 Allan, D.J., D.L. Erickson, and J. Fay. 1997. The influence of catchment land use on  
3 stream integrity across multiple spatial scales. *Freshwater Biology*. 37: 149-161.

4

5 Dillon, P.J., and W.B. Kirchner, 1975. The effects of geology and land use on the export  
6 of phosphorus from watersheds. *Water Research*. 9:135-148.

7

8 Duff, J.H., and F.J. Triska. 2000. Nitrogen biogeochemistry and surface – subsurface  
9 exchange in streams. *In* J.B. Jones and P.J. Mulholland (eds.) *Streams and Groundwaters*.  
10 Academic press, New York. 197-217.

11

12 Herlihy, A.T., J.L. Stoddard, and C.B. Johnson. 1998. The relationship between stream  
13 chemistry and watershed land cover data in the mid-Atlantic region, U.S. *Water, Air and*  
14 *Soil Pollution*. 105: 377-386

15

16 Hession, W. C., M. McBride, and M. Bennett. 2000. Statewide non-point-source  
17 pollution assessment methodology, *Journal of Water Resources Planning and*  
18 *Management*.126:146-155.

19

20 Hill, A.R. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental*  
21 *Quality*. 25:743-755

22

1 Hinkle, S.R., J.H. Duff, F.J. Triska, A. Laenen, E.B. Gates, K.E. Bencala, D.A. Wentz,  
2 and S.R. Silva. 2001. Linking hyporheic flow and nitrogen cycling near the Wilamette  
3 River - a large river in Oregon, USA. *Journal of Hydrology*. 244:157-180.  
4

5 Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Relating nutrient discharges from  
6 watersheds to land use and streamflow variability. *Water Resources Research*. 33(11):  
7 2579-2590.  
8

9 Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver,  
10 D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield, K.W. Staver, W. Lucas, and  
11 A.H. Todd. 1995. *Water Quality Functions of Riparian Forest Buffer Systems in the*  
12 *Chesapeake Bay Watershed*. U.S. EPA Chesapeake Bay Program. EPA 903-R-95-004  
13 CBP/TRS 134/95. 67 p.  
14

15 Omernik, J.M. 1977. Nonpoint source -stream nutrient level relationships: A nationwide  
16 study. U. S. EPA/600/2-77/105. 151p.  
17

18 Sprague, Lori A., Michael J. Langland, Steven E. Yochum, Robert E. Edwards, Joel D.  
19 Blomquist, Scott W. Phillips, Gary W. Shenk, and Stephen D. Preston. 2000. *Factors*  
20 *Affecting Nutrient Trends in Major Rivers of the Chesapeake Bay Watershed*, *Water-*  
21 *Resources Investigations Report 00-4218*, U. S. Geological Survey.109 p.  
22

- 1 Virginia Department of Conservation and Recreation. 2000. Commonwealth of Virginia  
2 Tributary Strategy: Goals for nutrient and sediment reduction in the James River. Public  
3 Comment Draft. 41 p.  
4
- 5 Vogelmann, J.E., S.M. Howard, L. Yang, C.R. Larson, B.K. Wylie, N. Van Driel. 2001.  
6 Completion of the 1990s National Land Cover Data Set for the Conterminous United  
7 States from Landsat Thematic Mapper Data and Ancillary Data Sources,  
8 Photogrammetric Engineering and Remote Sensing. 67:650-652.  
9
- 10 Wall, G. R.; Phillips, P. J. Riva-Murray, K.1998. Journal of Environmental Quality.  
11 27(2): 381-389.

Figure 1  
 Knapp, Harbor, and Ginwalla  
 Defining basin water quality: Land use, tributary input, and downstream dynamics

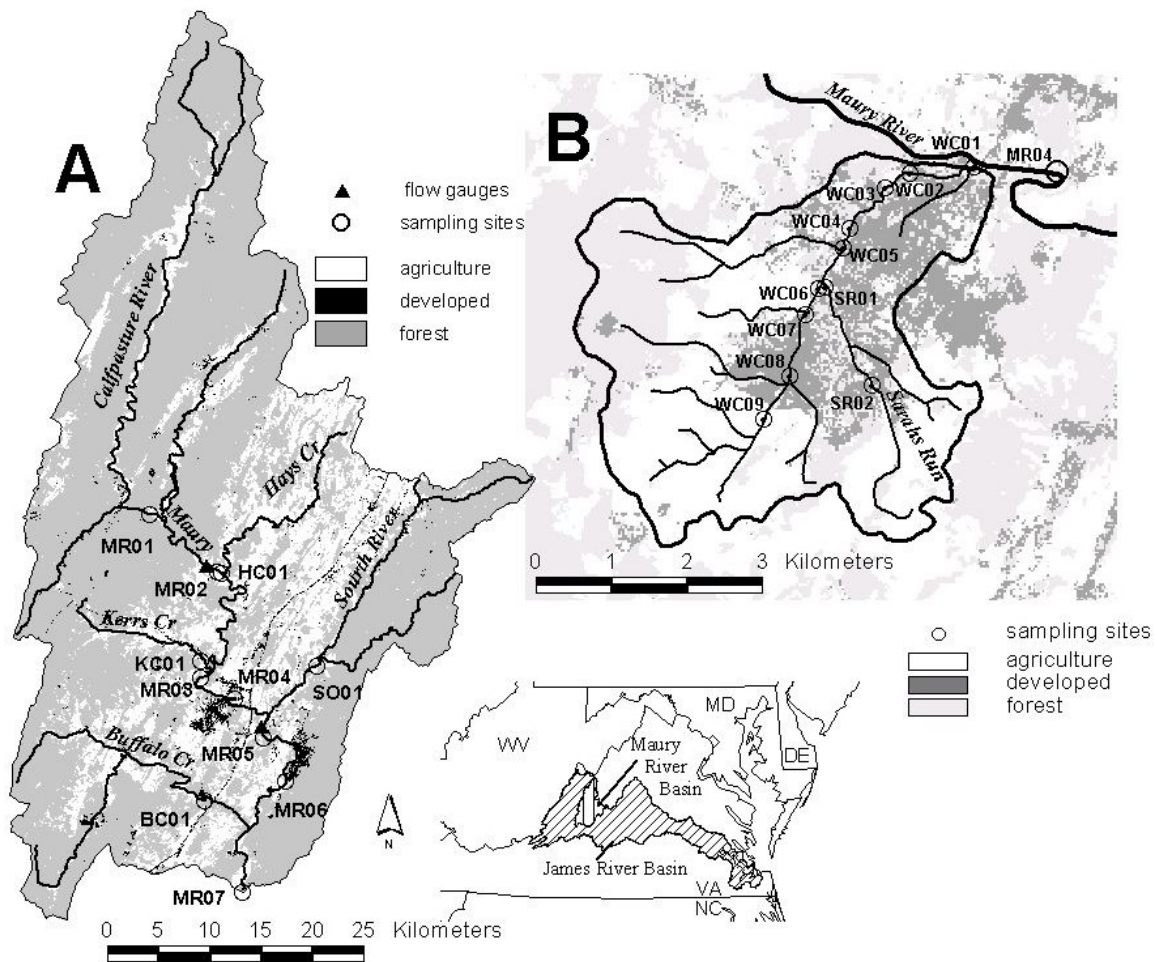


Figure 2  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

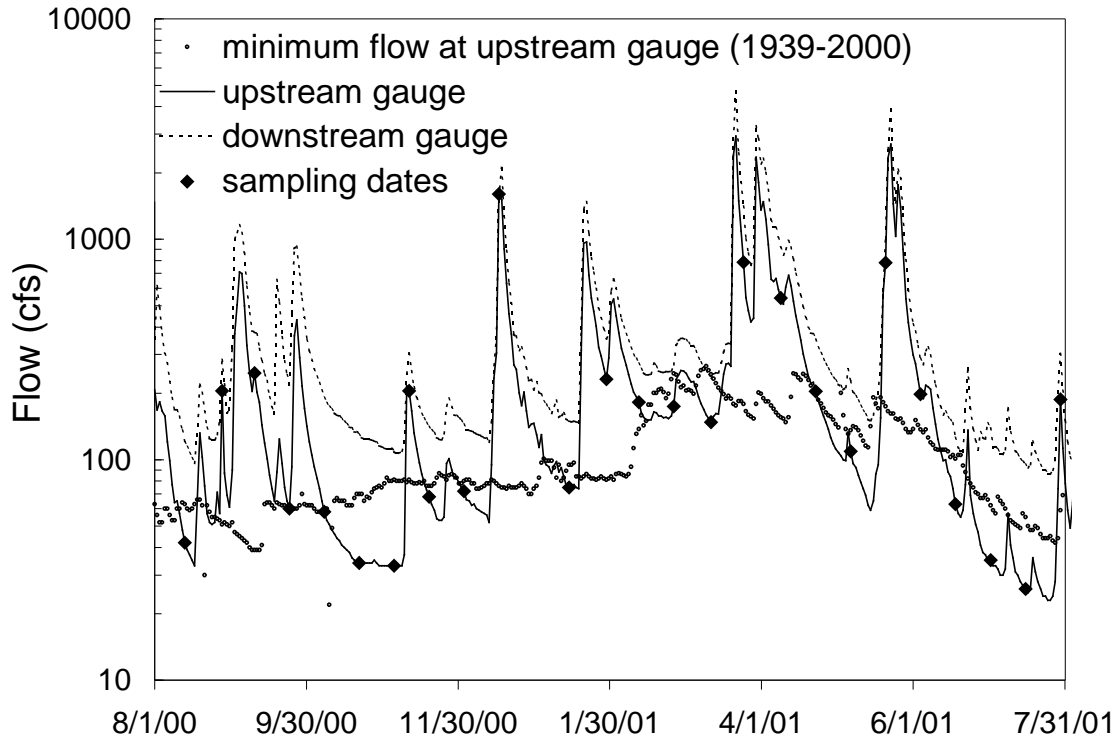


Figure 3  
 Knapp, Harbor, and Ginwalla  
 Defining basin water quality: Land use, tributary input, and downstream dynamics

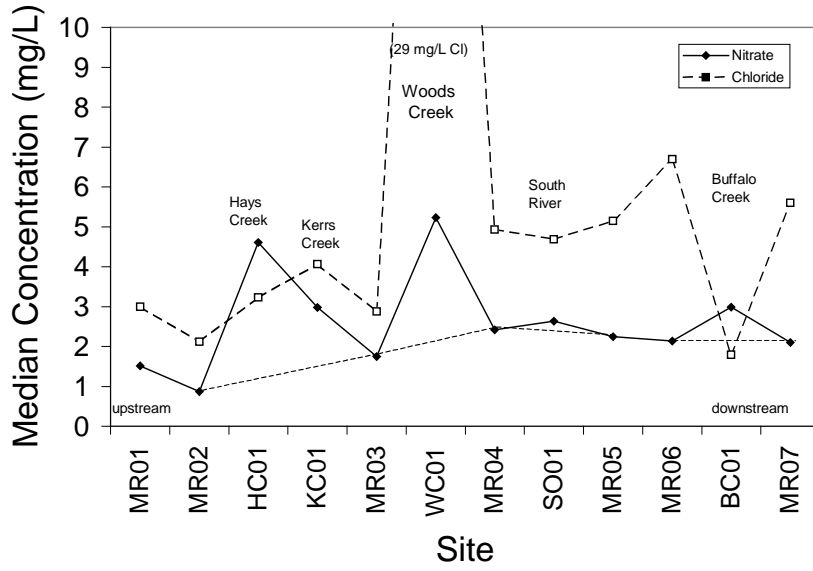


Figure 4  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

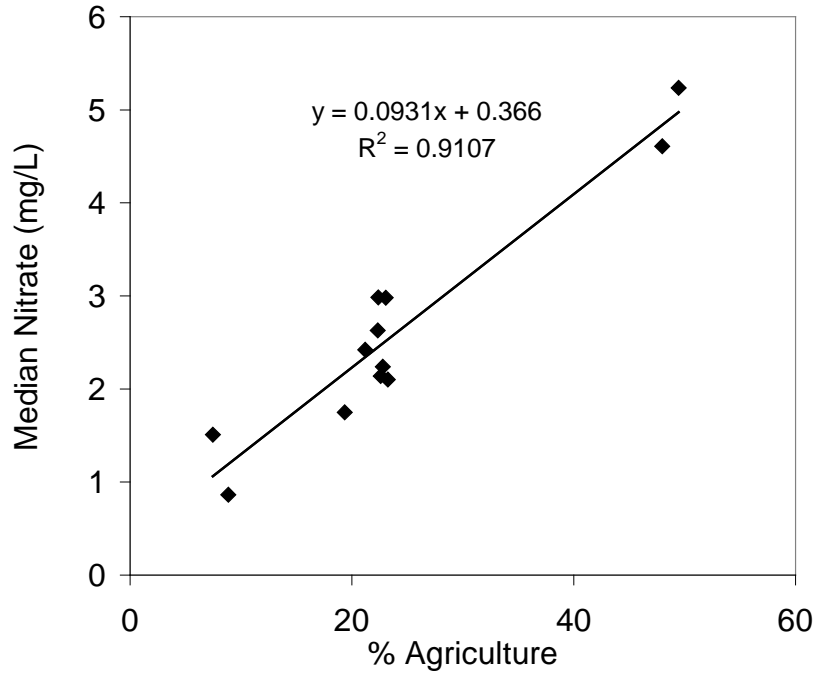
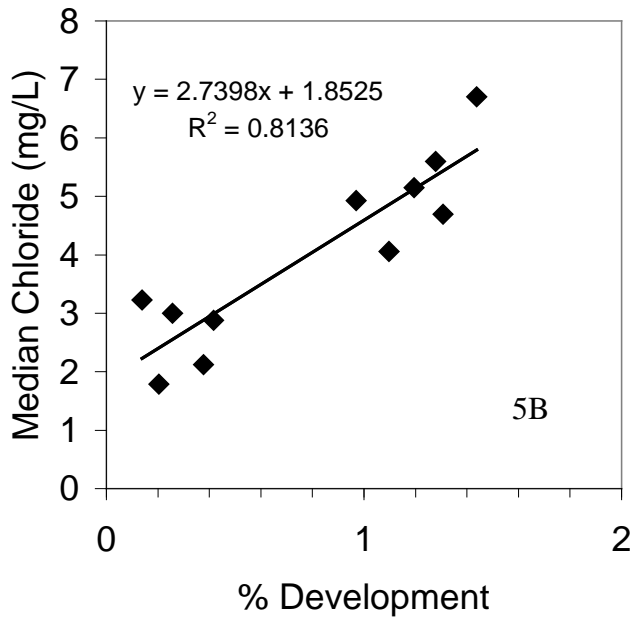
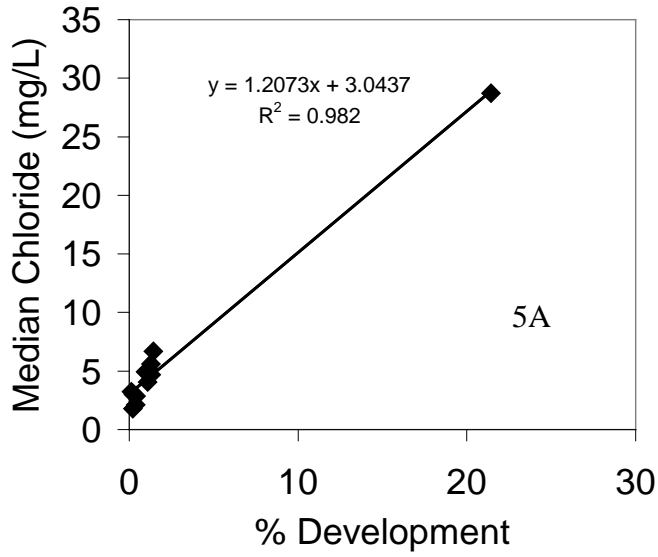


Figure 5  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

1





- 1 Figure 6
- 2 Knapp, Harbor, and Ginwalla
- 3 Defining basin water quality: Land use, tributary input, and downstream dynamics

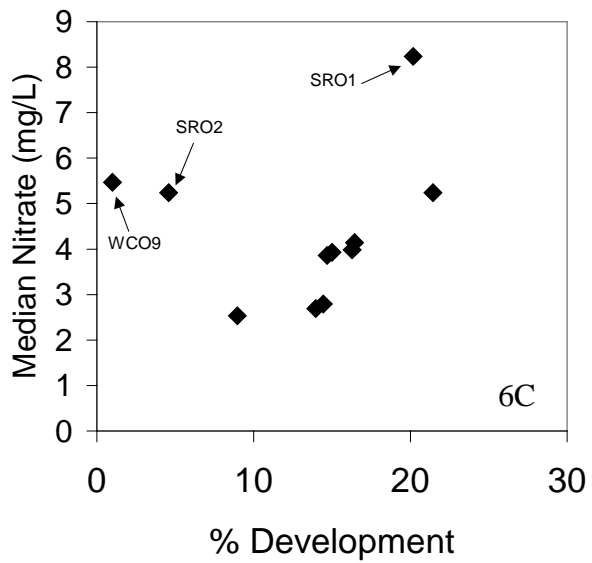
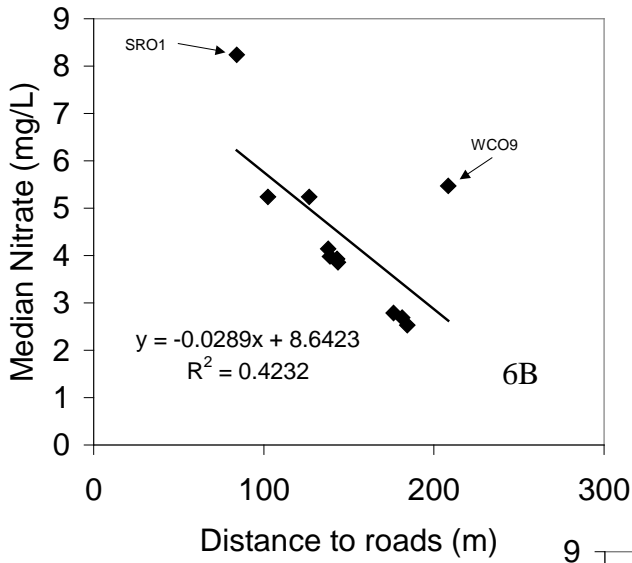
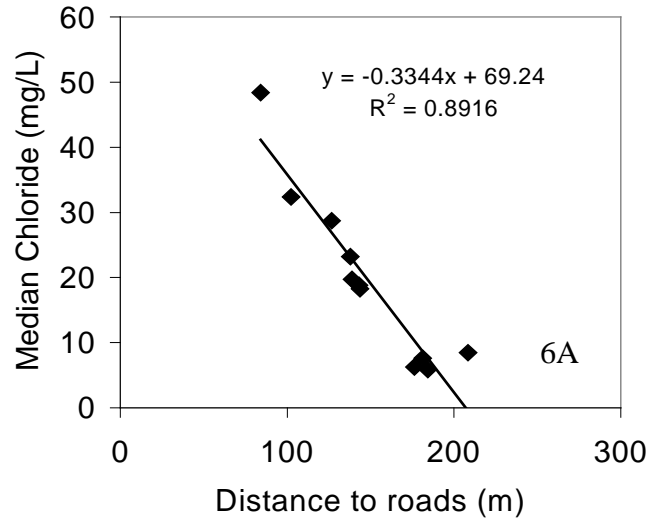


Figure 7  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

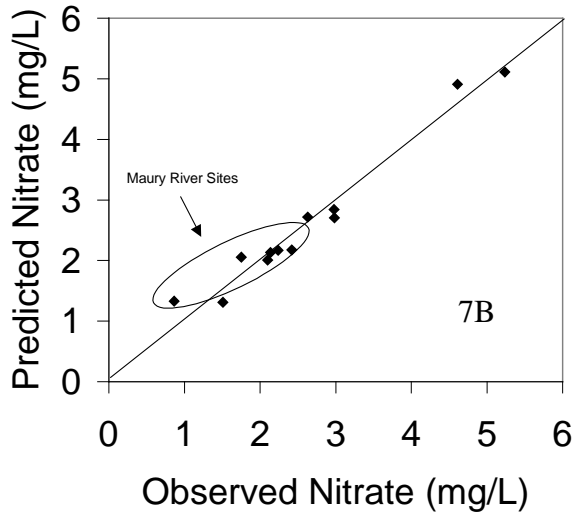
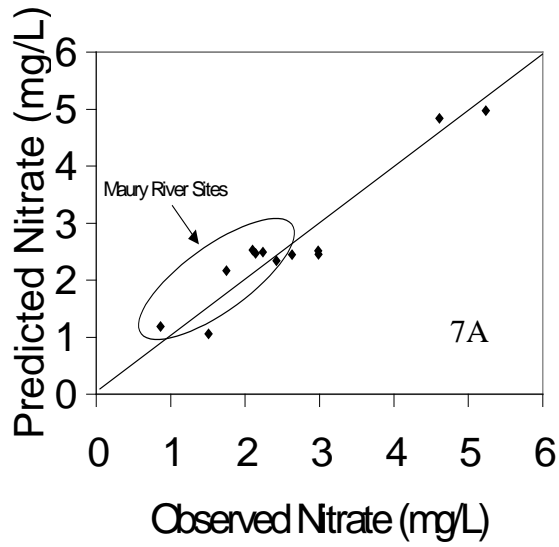


Figure 8  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

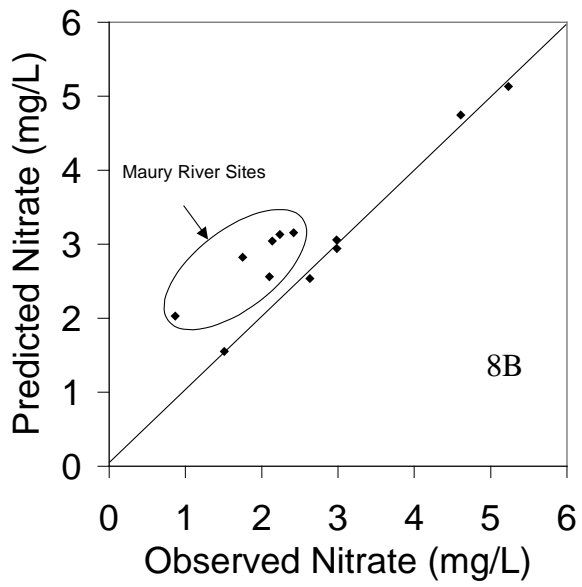
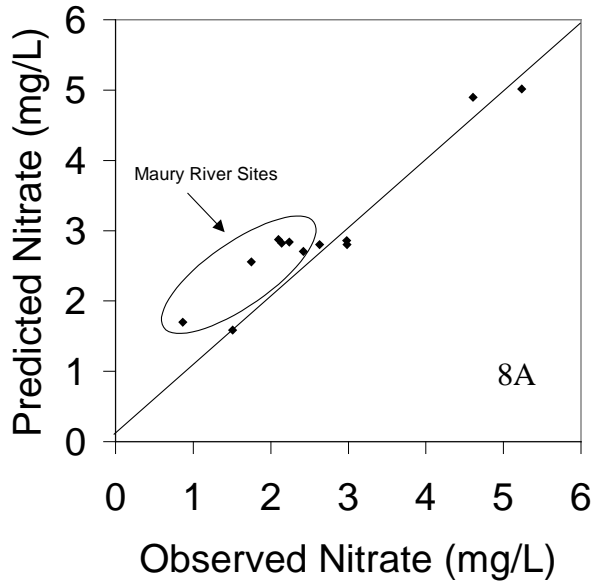
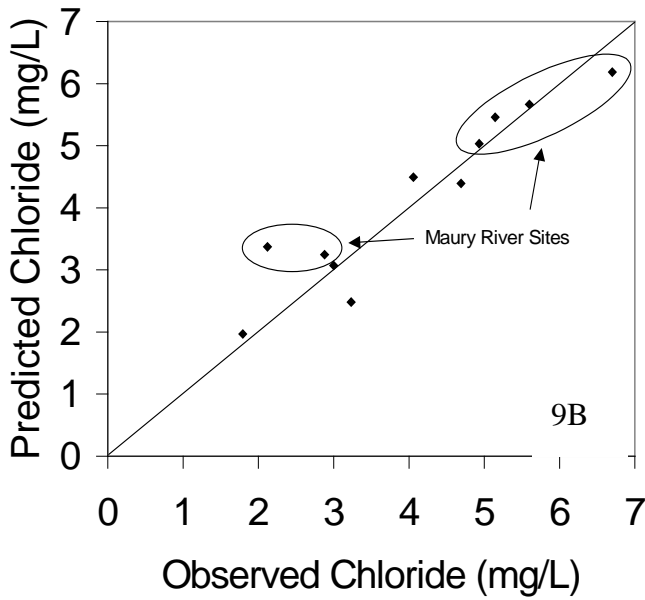
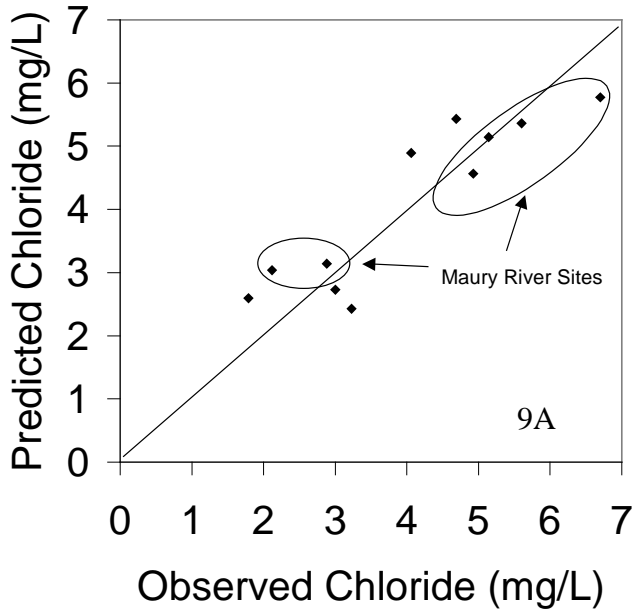


Figure 9  
Knapp, Harbor, and Ginwalla  
Defining basin water quality: Land use, tributary input, and downstream dynamics

1



1 Figure 1. Study sites and sampling locations. A. The Maury River watershed showing  
2 the locations of the flow gauges, and sampling sites overlying the land use map. B. The  
3 Woods Creek sub-basin with the locations of the sampling sites overlying the land use  
4 map.

5  
6  
7 Figure 2. Flow data for the year sampling period for both the upstream and downstream  
8 gauges (labeled on Figure 1). The minimum flow for a 41 year period and the dates of  
9 sampling in the Maury River are shown.

10  
11  
12 Figure 3. Median concentrations for both nitrate and chloride for each of the Maury  
13 River sites and tributaries. MRO1 –MRO7 are the upstream to downstream sampling  
14 sites for the Maury (as shown in Figure 1). HC01 is the Hays Creek tributary stream;  
15 KC01 is the Kerrs Creek tributary; WC01 is the Woods Creek tributary; SO01 is the  
16 South River tributary; and BC01 is the Buffalo Creek tributary.

17  
18  
19 Figure 4. % Agriculture versus median nitrate concentration for the Maury River and  
20 tributaries.

21  
22  
23 Figure 5. % Development versus median chloride concentration A., All sites including  
24 the Woods Creek tributary; and B., all sites excluding the Woods Creek outlier.

25  
26  
27 Figure 6. Relationships for the sites along the Woods Creek urban corridor. A., Distance  
28 to roads versus median chloride concentration; B., Distance to roads versus median  
29 nitrate concentration. WC09 and SR01 are the headwaters of the Woods Creek and its  
30 tributary, respectively; C., % Development versus median nitrate concentration. WC09  
31 and SR02 are both headwater sites in predominantly agricultural land.

32  
33  
34 Figure 7. Observed versus predicted nitrate for two models: A., including agriculture as a  
35 the single predictor; and B., including agriculture and area as predictors.

36  
37  
38 Figure 8. Observed versus predicted nitrate using the tributaries to predict the Maury  
39 sites: A., including agriculture as the single predictor; and B., including agriculture and  
40 distance to roads as predictors.

41  
42  
43 Figure 9. Observed versus predicted chloride for two models: A., using % urban as the  
44 single predictor; and B., using % urban and the slope and predictors.

Table 1: Correlation matrix for the Maury River sites and tributaries. AREA = contributing area (m) of land; AREABUF = area (m) in the 100m buffer; CO3= % of carbonate; CO3BUF = % of carbonate in the 100m buffer; AGR = % agriculture; FOREST = % of forested land cover; URBAN = % of developed land; AGRBUF = % agriculture in the 100m buffer; FORBUF= the % forest in the 100m buffer; URBBUF = % developed in the 100m buffer; SLOPE = the average slope of the land; SLOPE = the average slope in the 100m buffer; ROAD = the average distance to roads (m); ROADBUF = the average distance to roads (m) in the 100m buffer; MEDCL = the median chloride values (mg/L); MEDNO3 = median nitrate values (mg/L).

	AREA	AREABUF	CO3	CO3BUF	AGR	FOREST	URBAN	AGRBUF	FORBUF	URBBUF	SLOPE	SLOPEBU	ROAD	ROADBUF	MEDCL	MEDNO3
AREA	1.000	<b><u>0.992</u></b>	-0.461	-0.352	-0.355	0.375	-0.325	-0.250	0.314	-0.313	0.210	-0.044	-0.065	0.083	<b><u>0.624</u></b>	-0.552
AREABUF	<b><u>0.992</u></b>	1.000	-0.381	-0.271	-0.297	0.326	-0.309	-0.193	0.274	-0.299	0.192	0.022	-0.049	0.115	<b><u>0.670</u></b>	-0.489
CO3	-0.461	-0.381	1.000	<b><u>0.988</u></b>	<b><u>0.924</u></b>	<b><u>-0.883</u></b>	0.570	<b><u>0.891</u></b>	<b><u>-0.878</u></b>	0.556	<b><u>-0.776</u></b>	-0.119	-0.391	-0.340	<i>-0.020</i>	<b><u>0.953</u></b>
CO3BUF	-0.352	-0.271	<b><u>0.988</u></b>	1.000	<b><u>0.899</u></b>	<b><u>-0.845</u></b>	0.514	<b><u>0.909</u></b>	<b><u>-0.860</u></b>	0.501	<b><u>-0.768</u></b>	-0.121	-0.440	-0.387	<i>0.022</i>	<b><u>0.910</u></b>
AGR	-0.355	-0.297	<b><u>0.924</u></b>	<b><u>0.899</u></b>	1.000	<b><u>-0.960</u></b>	<b><u>0.630</u></b>	<b><u>0.907</u></b>	<b><u>-0.935</u></b>	<b><u>0.618</u></b>	<b><u>-0.864</u></b>	-0.253	-0.480	-0.346	<i>0.158</i>	<b><u>0.954</u></b>
FOREST	0.375	0.326	<b><u>-0.883</u></b>	<b><u>-0.845</u></b>	<b><u>-0.960</u></b>	1.000	<b><u>-0.822</u></b>	<b><u>-0.783</u></b>	<b><u>0.980</u></b>	<b><u>-0.814</u></b>	<b><u>0.919</u></b>	0.364	0.505	0.389	<i>-0.205</i>	<b><u>-0.937</u></b>
URBAN	-0.325	-0.309	0.570	0.514	<b><u>0.630</u></b>	<b><u>-0.822</u></b>	1.000	0.327	<b><u>-0.815</u></b>	<b><u>1.000</u></b>	<b><u>-0.788</u></b>	-0.490	-0.416	-0.369	<b><u>0.918</u></b>	<b><u>0.664</u></b>
AGRBUF	-0.250	-0.193	<b><u>0.891</u></b>	<b><u>0.909</u></b>	<b><u>0.907</u></b>	<b><u>-0.783</u></b>	0.327	1.000	<b><u>-0.811</u></b>	0.316	<b><u>-0.752</u></b>	-0.221	-0.505	-0.417	<i>0.047</i>	<b><u>0.845</u></b>
FORBUF	0.314	0.274	<b><u>-0.878</u></b>	<b><u>-0.860</u></b>	<b><u>-0.935</u></b>	<b><u>0.980</u></b>	<b><u>-0.815</u></b>	<b><u>-0.811</u></b>	1.000	<b><u>-0.810</u></b>	<b><u>0.961</u></b>	0.479	<b><u>0.590</u></b>	0.506	<i>-0.140</i>	<b><u>-0.906</u></b>
URBBUF	-0.313	-0.299	0.556	0.501	<b><u>0.618</u></b>	<b><u>-0.814</u></b>	<b><u>1.000</u></b>	0.316	<b><u>-0.810</u></b>	1.000	<b><u>-0.789</u></b>	-0.506	-0.424	-0.378	<b><u>0.911</u></b>	<b><u>0.649</u></b>
SLOPE	0.210	0.192	<b><u>-0.776</u></b>	<b><u>-0.768</u></b>	<b><u>-0.864</u></b>	<b><u>0.919</u></b>	<b><u>-0.788</u></b>	<b><u>-0.752</u></b>	<b><u>0.961</u></b>	<b><u>-0.789</u></b>	1.000	<b><u>0.667</u></b>	0.568	0.511	<i>0.006</i>	<b><u>-0.807</u></b>
SLOPEBUF	-0.044	0.022	-0.119	-0.121	-0.253	0.364	-0.490	-0.221	0.479	-0.506	<b><u>0.667</u></b>	1.000	0.365	0.450	<i>0.268</i>	-0.190
ROAD	-0.065	-0.049	-0.391	-0.440	-0.480	0.505	-0.416	-0.505	<b><u>0.590</u></b>	-0.424	0.568	0.365	1.000	<b><u>0.928</u></b>	<i>-0.218</i>	-0.375
ROADBUF	0.083	0.115	-0.340	-0.387	-0.346	0.389	-0.369	-0.417	0.506	-0.378	0.511	0.450	0.928	1.000	<i>0.034</i>	-0.322
MEDCL	-0.240	-0.221	0.556	0.506	<b><u>0.640</u></b>	<b><u>-0.826</u></b>	<b><u>0.992</u></b>	0.335	<b><u>-0.817</u></b>	<b><u>0.991</u></b>	<b><u>-0.787</u></b>	-0.478	-0.439	-0.364	1.000	<b><u>0.656</u></b>
MEDNO3	-0.552	-0.489	<b><u>0.953</u></b>	<b><u>0.910</u></b>	<b><u>0.954</u></b>	<b><u>-0.937</u></b>	<b><u>0.664</u></b>	<b><u>0.845</u></b>	<b><u>-0.906</u></b>	<b><u>0.649</u></b>	<b><u>-0.807</u></b>	-0.190	-0.375	-0.322	<i>0.023</i>	1.000

**Bold and underlined values** correlation is significant at the 0.01 level (2-tailed).

**Bold values** correlation is significant at the 0.05 level (2-tailed).

Italicized column with *MEDCL* (Median Chloride) is for the values excluding Woods Creek