

FINAL REPORT

Contract Title:

Mattawoman Creek Watershed: Nutrient and Sediment Dynamics

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EXECUTIVE SUMMARY

The Smithsonian Environmental Research Center (SERC) was contracted in July, 1997 by Charles County Government to conduct a research project to define nonpoint (diffuse) sources of nutrients and sediments. The project was designed to assess current conditions and to provide information for projections of future conditions under different development scenarios. SERC has conducted nonpoint source research in other nearby areas with similar objectives for a number of years.

The project was focused on the watershed of Mattawoman Creek, but for technical reasons, we felt that the project would be more successful, if we included selected other watershed areas within Charles County. These areas were selected to be the best examples of various land use categories, such as row cropping or housing. Three sampling strategies were used. The first looks at dissolved constituents in 37 streams during base-flow (non-storm conditions) to examine the chemistry of groundwater as it emerges from the aquifers. The second sampling strategy looks continuously at all discharges of groundwater and storm flows in 11 streams using automated stream gauging/sampling stations that continuously sample stream water at a rate proportional to stream flows so that storm events will be sampled representatively. The third sampling strategy looks at discharges from a selected urban storm sewer, including toxic materials to meet the EPA and MDE NPDES requirements. Sampling discharges from the storm sewer includes automatic collection of discrete samples during different stages of storm flows. To complement sampling of storms at the storm sewer, similar storm samples were collected from another highly developed watershed.

We began seasonal samplings of base-flow at 36 sites in March, 1997 and have now sampled each season for three years, ending in May, 2000. Ten automated stations were completed and began taking samples and data in mid-April, 1998. A site for the urban storm sewer monitoring was approved by MDE in March, 1998. The selected storm sewer drains storm water from part of Saint Charles. In the spring of 1999 we equipped this site with an automated storm water sampler to collect discrete samples at different flow stages during storm events. We delivered storm samples to the Charles County laboratory for analysis of toxic materials, and we analyzed the storm samples for sediments and nutrients. We also used an automated sampler to collect flow proportional composite sample at the storm sewer, as at the other 10 automated stream monitors.

The two years during which we continuously monitored watershed discharges represented low and high extremes in annual precipitation. Total annual water discharge increased linearly with the percentage of developed land in the watershed in both years we studied, but the effect was strongest in the year with the most precipitation. Increased runoff from developed land is probably due to presence of impervious surfaces such as roofs and pavement.

Comparing stream water draining watersheds with different land use compositions, we found that concentrations of total phosphate and various forms of N increased and concentrations of silicate decreased with increases in the percentage of developed land. Concentrations of nitrate and silicate increased and the concentration of total organic carbon decreased as the percentage of cropland increased.

The discharges of total organic C and all forms of N and P increased significantly with increasing proportions of developed land in both the wet and dry years. The effects

on discharges are partly due to the effects of developed land on water flow and partly due to effects on concentrations. Discharge of nitrate increased significantly with the proportion of cropland as well as with the proportion of developed land.

Concentrations of particulate materials tended to increase as the flow rate increased, due to the increase in turbulence and erosion associated with increasing water flow. In contrast, concentrations of dissolved materials (e.g., nitrate, silicate, chloride, conductivity) often decrease with increases in water flow, reflecting a dilution of emergent ground water with surface runoff. The predominance of dissolved forms differed among nutrients. Generally forms of N were mostly dissolved, while forms of P were mostly particulate.

Differences in the effects of water flow on concentration lead to differences in the temporal variability of discharge. Materials such as nitrate and silicate that decrease in concentration with increasing water flow will be discharged more evenly over time than materials such as particulate matter that increase in concentration with increases in water flow. Discharges of particulate materials such as forms of P occur very irregularly during short periods of high flow. The temporal variability of discharge of total P illustrates the importance of continuous automated sampling to capture unpredictable episodes of high discharge.

Our results suggest that conversion of forested land to developed land will increase the discharges of water, N, P, and organic C, while conversion of forested land to cropland will increase the discharges of nitrate. Our results also suggest that conversion of cropland to developed land will decrease the discharge of nitrate, while increasing the discharges of water, P, ammonium, and organic N and C. It is not clear from the present study how the discharge of total N would be altered by conversion of cropland to developed land, but previous studies suggest that developed land generally discharges less total N than does cropland.

Predicting discharges in future years may be complicated by inter-annual variation in rainfall. This is dramatically illustrated by comparing the results of the two years we studied, which coincidentally included dry and wet conditions representing extremes occurring over decades. Discharges of water and nutrients will generally fall between the extremes we observed in this study. Usually the discharge of water varies over a wider range than do the concentrations of nutrients. In this study, we found no significant systematic effect of year on the annual flow-weighted mean concentrations of any substance. Therefore, nutrient discharges could be estimated by multiplying the flow-weighted mean concentrations measured in one year by the water flow of another year. Nutrient discharges can also be estimated with models that relate nutrient concentrations to water flow rates. However, our studies of storm events suggest that estimates of concentrations based on water flow rates will be very imprecise.

Predicting the effects of developed land on watershed discharges presents particular problems. Unlike cropland, developed land includes a wide range of land uses; such as residential, commercial, and industrial; which may differ in nutrient discharge. The effects of discharges from developed land on estuarine receiving waters will be related to changes in the discharge of water as well as the discharge of nutrients.

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INTRODUCTION

When receiving waters such as Mattawoman Creek become “over enriched” with nutrients, adverse effects will result. These include excessive algal populations, low dissolved oxygen, fish kills, and the production of nuisance blooms of blue-green cyanophytes and dinoflagellates such as *Pfiesteria*. Anticipated further land development in Charles County could either reduce or greatly increase the inputs of nutrients and sediments from the watershed, depending upon the manner of development. The main focus of this research project is to define nonpoint source (diffuse) watershed discharge rates that result from various types of land development. For comparison to developed lands, we also measured discharge rates from other important land uses, primarily forest, croplands, and housing areas on other watersheds in Charles County.

Land discharges move via two major hydrologic pathways: overland flows during storm events and the percolation of groundwater to stream channels. Groundwater is recharged by rainwater that infiltrates through the soils to the water table. In the inner Coastal Plain region, which includes Charles County, both of these hydrologic pathways account for a significant portion of the total land discharge. Our sampling strategy was designed to address the adequate sampling of both of these pathways (see Methods).

The Mattawoman Creek watershed is located in the inner Coastal Plain physiographic province. This region characteristically has layers of sedimentary soils with impervious clay layers interspersed between more porous coarser-grained soil layers. Rainwater on a given watershed infiltrates only to the first clay layer then moves laterally to a stream and emerges as surface water. Thus, stream discharges of both overland storm flows and groundwater can be related rather directly back to source areas on subwatersheds.

METHODS

Discharges of Dissolved Nutrients in Groundwater

Each season, during times of base flow of emerging groundwater (i.e., several days after any significant rainfall event), we sampled all 16 of the accessible tributaries draining subwatersheds of tidal Mattawoman Creek and four stations along reaches of the mainstem of Mattawoman Creek. We also sampled 16 tributaries of other watersheds in Charles County, selected to give a better representation of important land uses, such as urban, suburban, agricultural, and forest.

Altogether we sampled 36 stations each season from spring of 1997 through spring of 2000 (see Tables 1 and 2 for descriptions and Figs. 1 and 2 for a maps of the watersheds and their land uses) and one additional station (the station 96 storm sewer) from spring of 1999 through spring 2000. The samples were analyzed for the following parameters (all dissolved): conductivity, pH, alkalinity, alkaline cations (Na^+ , K^+ , Ca^{++} , Mg^{++}), nitrate, sulfate, chloride, dissolved silicate, total organic carbon, phosphate, organic phosphorus, ammonium, and organic nitrogen. Samples were filtered through pre-rinsed Millipore HA (0.45 μm pore size) filters in the field and put on ice until analyzed in the laboratory.

Total Discharges of Water, Nutrients, and Sediments

We installed ten automated, continuous monitoring and sampling stations on selected stream sites in the spring of 1998 and an eleventh automated station at the storm sewer in spring of 1999 (see Tables 1 and 2, Figs. 1 and 2). The stations were run through July 2000. The automated stations monitored stream stage height, converted stage height to rate of water discharge, and sampled stream water at a frequency proportional to stream flow rates. Thus, they sampled both overland storm flows during storm events and groundwater discharges at rates representative of total flow in the stream. These samples were truly representative of total watershed discharges from all upstream areas. The automated stations consisted of a stilling well, usually attached to a highway bridge abutment, and an instrument enclosure. The enclosure contained a data logger/computer, batteries, pumps, valves, sample containers, etc. The stations were solar powered. Samples were withdrawn directly from the middle of the stream channel and sampling hoses were flushed prior to sampling. We determined rating curves by measuring stream discharges manually at these eleven sites with current meters at times when the streams are at various stage heights. Each automated station had a Campbell CR-10 data logger to monitor stream stage heights, calculate discharge based on rating curves, integrate discharge over time, and control the samplers. Stage heights were stored in the data logger and transferred to a computer for further analysis.

Two sets of flow-proportional samples were collected each week at each station for laboratory analyses, one set of samples with and one set without sulfuric acid added as a preservative. The samples without preservative were analyzed for total suspended solids and dissolved silicate. The samples with preservative were analyzed for total phosphorus, total phosphate, nitrate, total ammonium, total nitrogen, and total organic carbon. Because the acid preservative dissolves particulate phosphate and ammonium, we measured the sums of the dissolved and particulate fractions of these substances. Nitrate is essentially all dissolved.

Concentrations of Dissolved and Particulate Nutrients at Different Stream Stages

To characterize the nutrient content of suspended solids, we also took discrete samples at known stream stage heights at the automated sampling stations. These samples were collected by hand and brought to the laboratory for immediate analysis. Because no preservative was used, we were able to measure the dissolved fractions of nutrients in filtered portions of the samples as well as the totals of dissolved and particulate fractions in unfiltered portions. From these measurements we calculated concentrations of particulate fractions by subtraction.

Storm Discharges of Water, Sediments, Nutrients, and Toxic Materials

To help Charles County meet the requirements of NPDES, we met with officials of MDE and Charles County and selected an appropriate storm sewer to monitor. The sewer selected was Number 96 at Saint Charles Parkway. It collects storm water from part of Saint Charles City and delivers it to Jordan Swamp (a tributary of Zekiah Swamp), which we sampled with automated station number 162.5 (Table 1, Fig. 1) at

Highway 5. We installed a stream stage height staff at site 96 when the site was approved in the spring of 1998 and began taking grab samples of groundwater flow emerging in the storm sewer. In the spring of 1999 we installed automated storm samplers at site 96 and station 162.5. At different stages of storm flow events, the storm samplers pumped water into separate bottles without preservatives. The samples were retrieved immediately after storms and analyzed for dissolved and total nutrients. Portions of the storm samples were delivered to the Mattawoman Treatment Plant for analyses of trace metals. Monthly grab samples of base flow were delivered to the Mattawoman Treatment Plant for analysis of coliform bacteria. To complement our storm sampling at site 96, we installed an automated sampler that collected flow-proportional composite samples the same as the samplers at the other 10 monitored watersheds (including 162.5).

Sample and Data Analyses

Reduced nitrogen was determined as total Kjeldahl N (TKN) with a Tecator block digester, Tecator steam distillation of ammonia, and ammonium determination on a Dionex, model 500, Ion Chromatograph. Ammonium was also determined on undigested samples by oxidation to nitrite and colorimetric determination of nitrite. Organic N was calculated as TKN minus ammonium. Total P was determined by perchloric acid digestion and colorimetric determination of phosphate. Phosphate in undigested samples was also determined colorimetrically and organic-P is calculated as total P minus phosphate. Whole water samples and filtered water were analyzed separately and particulate nutrient fractions were calculated as whole water concentrations minus dissolved concentrations. Organic and inorganic Carbon were determined with a Shimadzu, model TOC-5050, carbon analyzer. Nitrate, chloride, and sulphate were determined on a Dionex, model 500, ion chromatograph. Alkaline cations (Na, K, Ca, Mg) were determined with a Perkin Elmer, Model 3000, ICP emission spectrometer. Silicate was determined colorimetrically on an API model 300 automated colorimeter system.

Geographic Analysis

We used the ArcInfo geographic information system (GIS) software to organize and analyze geographic data on the watersheds draining to our 37 stream sampling sites. The location of each station was digitized from the USGS 7.5 minute topographic maps used to place the sampling sites in the field (Fig. 1). Drainage boundaries were defined from contour lines on the same maps then digitized (Fig. 1). The drainage boundaries were intersected with a digital land cover database (Fig. 2) to derive land cover proportions for each watershed (Table 2). The EPA land cover data were derived from Landsat-TM satellite imagery and classified into 19 land cover categories (USEPA 1994). Some of the categories were not well resolved (USEPA 1994), so we aggregated the 19 categories to 7 (Table 2). We also calculated the proportion of total developed land (low intensity developed plus high intensity developed) and summed cropland and grassland to derive a category that we called cleared land.

To investigate the effects of land use on watershed discharges, we used regression

analysis to relate water flow and nutrient concentrations to the proportions of three land covers: cropland, total developed land, and cleared land. We analyzed the effects of both cropland and cleared land (cropland plus grassland) because the land cover data set does not always accurately resolve cropland from grassland (USEPA 1994, Liu et al in press). Together with forest, total developed and cleared lands dominate the study watersheds, yet vary significantly in relative importance. Among the study watersheds, developed land ranges from 0-91%, cropland from 0-35%, and cleared land from 0-59% (Table 2). We did not include the forest as an explanatory variable because total developed land, cleared land, and forest sum to more than 98% of total land area for each of the 37 watersheds. Thus, forest is essentially 100%-(cleared land + developed land), and the inclusion of forest would be redundant with the other land cover categories. The drainage areas for watersheds 156 and 157.5 (Table 2) are primarily forested or grass with only a few percent present as low density developed or cropland. Some of the areas classified as "grass" were recently logged forest areas. Watersheds 163, 167, and 169 had the most cropland, but that was not the predominant land use for those watersheds or for Charles County in general. Watersheds 147 and 162.5 were dominated by developed land, especially by suburban housing.

Some of our sampling sites were selected to study the watershed of the Chapman's Landing housing development. Watershed 154 was selected because it is the only significant stream draining into the area of Chapman's Landing. Its watershed also had a fairly high amount of suburban development (Table 2). Sampling station 153 is on the same stream as station 154, but at the point where it leaves Chapman's Landing. There was very little development within the Chapman's Landing part of the watershed 154. Station 155 was selected because it is also on a stream draining part of Chapman's Landing. This portion of Chapman's Landing was mostly composed of forest and grass, with only about 6.5% low density developed areas.

Watershed 140.5 was selected because it was the point furthest downstream on the main stem of Mattawoman Creek that was readily accessible for installing and operating a station and was not tidally influenced. Thus, station 140.5 gives the best picture of the discharge of materials from the overall Mattawoman Creek watershed. The drainage area for station 140.5 was 63% forest, 15% developed, 1.5% cropland and 20% grass.

RESULTS

Effects of Land Use on Water Discharge

As the percentage of developed land increased, the amount of water discharge and the variability of discharge rate increased, due to impervious surfaces such as roofs and pavement in developed land. In watersheds with mostly developed land, rain events triggered pulses in water discharge that were more intense and shorter in duration than in watersheds with mostly undeveloped land. This is evident from the much more rapid changes in stream depth during storm runoff in highly developed watersheds compared to less developed watersheds (Fig. 3).

Total annual water discharge increased linearly with the percentage of developed land in the watershed in both years we studied, but the effect was strongest in the year

with most precipitation (Fig. 4). The extra runoff from developed land is probably due to impervious surfaces. Using a regression of flow versus the percentage of developed land we predicted the amount of flow for watersheds with 0% and 100% developed land (Table 3). In both years undeveloped land discharged about one fourth of the water received from precipitation. In contrast, developed land discharged about 60% of 62.5 cm of precipitation in the dry year and about 80% of 127.1 cm of precipitation in the wet year (Table 3, Fig. 4). The two years represent extreme departures from the average precipitation of about 110 cm. Differences in water discharge that were not explained by the percentage of developed land (Fig. 4) may partly reflect the imprecision of measuring discharge using records of stream depths in open channels.

Effects of Land Use on Concentrations of Nutrients and Sediments

In some cases the concentrations of nutrients and sediments in stream water were correlated with the percentages of cropland or developed land in the watersheds. We examined the effects of land use for the continuously monitored watersheds by comparing annual flow-weighted mean concentrations from the dry and wet years separately. Flow-weighted means were calculated by multiplying the concentrations in weekly composite samples by the water flow during the week, adding these products, and dividing by the total flow. The flow-weighted means best represent the average concentrations of discharged materials.

As the percentage of cropland increased, the concentrations of nitrate and silicate increased significantly in both years (Table 4). In contrast, total organic carbon concentration decreased with increase in percentage of cropland during the second year (Table 4). To separately illustrate the effects of cropland and developed land, we plotted concentrations versus the percentage of cropland for watersheds with <10% developed land (Fig. 5) and versus the percentage of developed land for watersheds with <5% cropland (Figs. 6 and 7). Because EMAP land use classifications are sometimes inaccurate in distinguishing cropland from grassland, we also examined the effects of cleared land, which is the sum of cropland and grassland. Cleared land had effects similar to those of cropland (Table 4).

Concentrations of total phosphate and forms of N increased and concentrations of silicate decreased with increases in the percentage of developed land (Table 4, Figs. 6 and 7). Nitrate, total ammonium, and total N concentrations increased significantly with increases in developed land in both years, but total organic N increased significantly in the wet year only. Discharges from watershed 96, the most highly developed watershed we studied, had markedly elevated concentrations of total phosphate, total ammonium, and total N, compared to concentrations that would be predicted from the proportion of developed land (Figs. 6 and 7). These high concentrations associated with the highest proportion of developed land have a strong influence on the statistical relationship between developed land and concentration. Moreover, this influence is only represented in the second year of the study (the wet year), because watershed 96 was not monitored in the first year.

Besides comparing the 10-11 continuously monitored watersheds, we also examined the effects of land use on concentrations of dissolved nutrients in base flow from 37 watersheds. Concentrations in base flow reflect the composition of groundwater

that emerges in the streams. We averaged the data from three years of seasonal base flow sampling for comparisons among watersheds. Nitrate concentrations in base flow increased as the cropland and developed land increased in the watersheds (Table 5), as we also observed for the flow-weighted mean concentrations (Figs. 5 and 6). However, concentrations of nitrate in base flow were generally higher than flow-weighted mean concentrations when measured at the same site (Figs. 5 and 6). This difference reflects the tendency for nitrate concentrations to be highest at low flow (see section on effects of stream flow rate below). Silicate concentrations in base flow increased significantly with increasing cropland, as found for flow-weighted mean concentrations of silicate (Fig. 5, Table 5). However, unlike the flow weighted mean concentrations, base flow concentrations of silicate were not significantly correlated with developed land (Fig. 7). Dissolved ammonium concentrations in base flow increased with increases in developed land (Table 5), as did flow-weighted means of total ammonium concentration in weekly composite samples (Fig. 6, Table 4). Increases in developed land also correlated with increases in dissolved inorganic C, conductivity, and concentrations of major anions (chloride, fluoride, and sulfate) and cations (sodium, potassium, magnesium, and calcium) (Table 5). Increasing cropland also increased conductivity, sulfate, potassium, and magnesium (Table 5). High concentrations of sodium and chloride in winter discharges from developed land probably came from applications of road de-icing salt.

Effects of Land Use on Discharges of Nutrients and Sediments

The effects of land use on both the water flow and on the material concentrations are reflected in the discharge of materials from watersheds. We calculated annual discharges by multiplying the annual flow-weighted mean concentrations (Table 6) by annual water discharge estimated from regressions against the percentage of developed land (Fig. 4, Table 3). We used these regression estimates of water flow rather than the measurements for individual watersheds because of the imprecision of measuring flow based on depth in open stream channels. Errors in measuring water flow may obscure underlying effects of land use on material discharges, so the regression predictions provide the best estimate of average water discharges for watersheds with given proportions of developed land.

The discharges of total organic C and all forms of N and P increased significantly with increasing developed land in both the wet and dry years (Table 7, Figs. 8, 9, and 10). The effects on discharges are partly due to the effect of developed land on water flow and partly due to effects on concentrations. Interestingly, the decrease in silicate concentration with increase in developed land (Fig. 7) was counteracted by the related increase in water flow (Fig. 4) resulting in no significant effect of developed land on silicate discharge (Table 7). Discharges of several nutrients, especially total ammonium and total phosphate, were especially elevated for the most developed watershed (96), reflecting the pattern of nutrient concentrations. The extreme data from watershed 96 had a strong influence on statistical relationships of nutrient discharges to developed land during the wet year, the only year when this watershed was monitored.

Discharge of nitrate increased significantly with the proportion of cropland as well as with the proportion of developed land (Table 7). However, the proportion of cropland did not have a significant effect on the discharges of other forms of N, forms of

P, or total organic C. Silicate discharges increased with increases in cropland, but the effect was only significant ($p < 0.05$) in the dry year (Table 7).

We used linear regressions to estimate the amount of materials discharged from watersheds with 100% or 0% developed land. The regressions for nutrients other than nitrate use the percentage of developed land as the only independent variable, because for these nutrients only developed land was significantly related to discharge. For nitrate we used the percentages of both developed land and cropland as independent variables. Predicted discharges differed greatly between the wet and dry years because of the differences in water flow, which encompass extremes usually observed over decades (Table 8). For 100% developed land, predicted total P discharge ranged from 0.9-2.8 kg P/ha from the dry to the wet year, predicted total N discharge ranged from 6.5-19 kg N/ha, and predicted total organic C discharge ranged from 47-138 kg C/ha. Predicted nitrate discharge from 100% cropland was higher (5.9-14.0 kg N/ha) than predicted nitrate discharge from 100% developed land (2.1-5.3 kg N/ha). For mixtures of developed land, cropland, and other land types, predictions of discharge can be obtained by linear interpolation of the predictions for 0 and 100% of the relevant land use type.

Effects of Stream Flow Rate

Relationships between water flow rate and concentrations of materials were revealed by analysis of grab samples collected at various stages of flow at the continuously monitored streams. These grab samples were analyzed for dissolved and total nutrients, while the composite flow weighted samples were only analyzed for total nutrients. Thus, the grab samples provided data on the proportion of dissolved nutrients as well as on the effects of stream flow. After accounting for the effects of land use, concentrations of particulate materials tended to increase as the flow rate increased (Table 9), probably due to the increase in turbulence and erosion associated with increasing water flow. In contrast, concentrations of dissolved materials (e.g., nitrate, silicate, chloride, conductivity, Table 9) often decrease with increases in water flow, reflecting a dilution of emergent ground water with surface runoff. Alkalinity and pH also decreased with increasing water flow, suggesting that emergent ground water is more alkaline than surface runoff. Some dissolved materials increased in concentration with increasing flow (e.g., dissolved phosphate and dissolved organic P, N, and C). Dissolved organic substances may be more enriched in surface runoff than in emergent ground water because organic matter may become adsorbed in aquifers.

The predominance of dissolved forms differed among nutrients. The proportions of dissolved ammonium and dissolved phosphate were highly variable, but dissolved ammonium usually made up the majority of the total ammonium, while dissolved phosphate was usually the minority of the total phosphate (Fig. 12). The proportions of dissolved organic P, N, and C declined as the concentration of the total amounts of these nutrients increased, suggesting that particulate fractions increased disproportionately as the total concentrations increased (Fig. 13). However, dissolved organic N and C generally made up the majority of their total concentrations, while dissolved organic P was usually the minority of the total phosphate (Fig. 13). Nitrate was assumed to be essentially all dissolved. Thus, in general forms of N were mostly dissolved, while forms of P were mostly particulate.

Effects of Storms

Intensive sampling of discharges from watersheds 96 and 162.5 during storms showed effects of flow similar to the effects observed with the more extensive grab sampling at all the monitored sites. Concentrations of particulate materials increased with increases in water flow rate, while concentrations of many dissolved substances decreased (Fig. 14, Table 10). There were also significant differences among storms and significant differences related to whether the stream flow was rising or declining within a particular storm event. At moderate and high flows concentrations of particulate and dissolved materials were generally higher during the rising phase of the storm flow than during the declining phase. At low flows, concentrations of particulate matter were higher in the declining phase than in the rising phase, while concentrations of dissolved matter were higher in the rising phase. This suggests the following sequence during storm: As the storm flow begins, particulate matter is in low concentration because erosion and resuspension have not yet occurred; as flow later intensifies, erosion and resuspension elevate concentrations of suspended particles. As flow begins to subside, sources of readily suspended material have been depleted so concentrations are less than at similar flow rates early in the storm. Finally, at the end of the storm concentrations are somewhat enriched above levels at the beginning of the storm because suspended material has not had time to settle out. A different sequence is suggested for dissolved substances such as nitrate and silicate: At the beginning of the storm, there is an enrichment of these dissolved substances due to a flushing of soluble material from the watershed. Later in the storm, concentrations decrease as stores of soluble material are depleted. It is possible to produce a statistical model that predicts concentration from flow rate and the phase of the storm event. However, there is often an order of magnitude range in concentrations observed at particular flow rates and phases of the storm. The high variance suggests that predictions of concentrations based on flow and storm phase would be very imprecise.

Differences in the effects of water flow on concentration lead to differences in the temporal variability of discharge. Materials such as nitrate and silicate that decrease in concentration with increasing water flow will be discharged more evenly over time than will materials such as particulate matter that increase in concentration with increases in water flow. The temporal variability of discharges from watershed 157.5 provides a typical example. Weekly flow of water follows the typical seasonal pattern of water flow reflecting seasonal changes in evapotranspiration rates (Fig. 15). Water flow also reflects the drought from the summer of 1998 through the summer of 1999, and the high rainfall the subsequent year. Superimposed on these fluctuations are short-lived peaks in water flow caused by major storms, the largest peak coming from Tropical Storm Floyd in September 1999. The highest concentrations of total P generally occur during times of highest flow, because most P is associated with particulate matter. Because discharge is the product of flow and concentration, short-lived peaks in water flow are very important in the discharge of total P. Consequently much of the total discharge of total P occurred during only two weeks that included major flow events (Fig. 15). In contrast, the discharge of nitrate is spread out more evenly through time than the flow of water (Fig. 16), because nitrate concentrations decrease and water flow rate increases. The temporal

variability of discharge of total P illustrates the importance of continuous automated sampling to capture unpredictable episodes of high discharge.

DISCUSSION

Our results suggest that conversion of forested land to developed land will increase the discharges of water, N, P, and organic C, while conversion of forested land to cropland will increase the discharges of nitrate. Our results also suggest that conversion of cropland to developed land will decrease the discharge of nitrate, while increasing the discharges of water, P, ammonium, and organic N and C. It is not clear from the present study how the discharge of total N would be altered by conversion of cropland to developed land, but previous studies suggest that developed land generally discharges less total N than does cropland. The Charles County study watersheds provided better information on the effects of developed land than on the effects of cropland, because more watersheds included high percentages of developed land than included high percentages of cropland. Our previous studies, elsewhere in the coastal plain, were better designed to address the effects of cropland than was the Charles County study (e.g., Jordan et al. 1997a). These studies showed a significant increase in the discharge of all forms of N with increasing proportions of cropland (Jordan et al. 1997a). Extrapolating from a regression of discharge versus percentage of cropland suggested that a watershed with 100% cropland discharges 18 kg total N/ha during a year of average runoff (Jordan et al. 1997a). By comparison, the Charles County study results suggest that 100% cropland discharges 6-14 kg nitrate-N/ha annually (ranging from dry-wet years). These rates are consistent with the broad ranges of N discharges from agricultural land found in other studies (e.g., see reviews by Beaulac and Reckhow 1982; and Frink 1991). Although other studies have shown increases in P discharge with increases in agricultural land (e.g., Rekolainen 1990; Correll et al. 1992; Nearing et al. 1993), P discharge may be more strongly influenced by the erodibility and P content of soils in the watershed than by agriculture (Jordan et al. 1997a). Our Charles County study suggests that watersheds with 100% developed land annually discharge 0.9-2.8 kg P/ha, and 6.5-19 kg N/ha (dry-wet year ranges). By comparison, other studies suggest annual discharges from developed or urban land of 0.3-2.8 kg P/ha and 4-28 kg N/ha, based on quartiles of studies reviewed by Beaulac and Reckhow (1982) and medians reviewed by Frink (1991).

Several caveats apply to extrapolating our results to different times, places, and mixtures of land use. For example, land use effects may differ among physiographic regions. This has been noted for the effect of cropland, which appears to release twice as much N in the Piedmont as it does in the Coastal Plain (Jordan et al. 1997a, b, c). The findings of our Charles County study will be most applicable to the Coastal Plain region in and near Charles County.

Caution must also be used in interpreting extrapolations of regressions of discharge versus land use. When we use regressions to predict discharges from watersheds with 100% of a given land use, we are ignoring possible interactions among different land use types. In a watershed with a mixture of land types, some areas such as cropland and developed land may act as nutrient sources while others areas such as wetlands and riparian buffers may act as nutrient sinks (e.g., Correll et al. 1992; Jordan et

al. 1993; 1999). Thus, a watershed with only nutrient source areas would release more nutrients than might be projected from comparisons to watersheds that include both sources and sinks.

Predicting discharges in future years may be complicated by inter-annual variations in rainfall. This is dramatically illustrated by comparing the results of the two years we studied, which coincidentally included dry and wet conditions representing extremes occurring over decades. Discharges of water and nutrients will generally fall between the extremes we observed in this study. For watersheds in this region, the inter-annual variability of water discharge generally exceeds inter-annual variability of nutrient concentrations (e.g., see long term studies of Correll et al. 1999a, b, c). In this study, we found no significant consistent effect of year on the annual flow-weighted mean concentrations of any substance (e.g., Figs. 5, 6, and 7). Therefore, nutrient discharges could be roughly estimated by multiplying the flow-weighted mean concentrations measured in one year by the water flow of another year. Water flows can be estimated with models that relate runoff to rainfall such as TOP model (Beven and Kirkby 1979; Quinn et al. 1995) and others (Haan 1982). Nutrient concentrations can be estimated with models that relate concentrations to water flow rates (Cohn et al. 1989; Gilroy et al. 1990; Cohn et al. 1992). However, our studies of storm events suggest that estimates of concentrations based on water flow rates will be very imprecise.

Predicting the effects of developed land presents particular problems. Unlike cropland, developed land includes a wide range of land uses, such as residential, commercial, and industrial, which may differ in nutrient discharge. Nutrient loads to these land types may be highly variable, depending on the application of fertilizers and the presence and efficacy of septic and sewage systems. Water discharges vary with the proportion of impervious surfaces. Erosion rates vary with disturbance to the soil. Because developed lands may differ in many important ways, the discharges from developed watersheds may be highly idiosyncratic. Thus the large differences between the two most developed study watersheds, 96 and 162.5, are not surprising. A nutrient source peculiar to watershed 96 may account for the discharges of ammonium and phosphate being much higher than expected from the percentage of developed land (91% developed, Figs. 8 and 9). In contrast, nutrient trapping lands or unusually low nutrient loads in watershed 162.5 may account for discharges of nutrients that are lower than expected from the percentage of developed land (70% developed, Figs. 8, 9, and 10). Predictions of the effects of developed land should be improved by studies of particular types of development, because efforts to reduce nutrient discharges from developed land must begin by identifying the most important nutrient sources from the wide range of possibilities.

The impacts of discharges from developed land are linked to increased discharges of both water and nutrients. Unlike cropland, which increases nutrient discharge without much change in water discharge, developed land significantly increases water discharge as well as nutrient discharge. Increased discharges of water alone could decrease salinity in estuarine receiving waters, thereby affecting biota adapted to particular salinities. On the other hand, the affects of increased nutrient discharge may be somewhat mitigated by accompanying increases in water discharge, because the increased discharge of water dilutes the nutrients and because biota respond to nutrient concentration rather than to nutrient flux. However, this dilution effect may not work as well for particulate nutrients

because these may become concentrated by sedimentation. Subsequent releases of dissolved nutrients from deposited sediments could then increase nutrient concentrations in ambient water. Assessing the effects of local development on Mattawoman Creek will require knowledge of water circulation, exchanges with the Potomac River, and the present status of nutrients and biota within the estuary.

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FIGURE CAPTIONS

Fig. 1. Map of the study watersheds showing three categories of stream sampling stations and their drainage areas. The stream map is EPA's reach file 3 (USEPA 1994b), and the rectangular grid maps the boundaries of USGS 7.5' topographic quadrangles.

Fig. 2. Land cover of the study watersheds (black outlines) and surrounding region. Land cover data are from the EPA EMAP program (USEPA 1994a), and the rectangular grid maps the boundaries of USGS 7.5' topographic quadrangles.

Fig. 3. Stream depth (m) relative to an arbitrary reference versus time for 8 days showing the more rapid depth changes during storms at a stream draining a more developed watershed.

Fig. 4. Annual water flow (cm, 1 cm = 100 m³/ha) during the dry (unfilled circles) and wet (filled circles) years versus percentage of developed land in watersheds. Lines fit by linear regression.

Fig. 5. Annual flow weighted mean concentrations for the dry (unfilled circles) and wet (filled circles) years; and mean concentrations in base flow (crosses) versus percentage of cropland in the watersheds with <10% developed land. Lines fit by linear regression.

Fig. 6. Annual flow weighted mean concentrations for the dry (unfilled circles) and wet (filled circles) years; and mean concentrations in base flow (crosses) versus percentage of developed land in the watersheds with <5% cropland. Lines fit by linear regression.

Fig. 7. Annual flow weighted mean concentrations for the dry (unfilled circles) and wet (filled circles) years; and mean concentrations in base flow (crosses) versus percentage of developed land in the watersheds with <5% cropland. Lines fit by linear regression.

Fig. 8. Annual discharges (kg P/ha) during the dry (unfilled circles) and wet (filled circles) years versus percentage of developed land in all the continuously monitored watersheds. Lines fit by linear regression.

Fig. 9. Annual discharges (kg N/ha) during the dry (unfilled circles) and wet (filled circles) years versus percentage of developed land. Discharges of nitrate are only for watersheds with <5% cropland, other discharges shown for all the continuously monitored watersheds. Lines fit by linear regression.

Fig. 10. Annual discharges (kg N or C/ha) during the dry (unfilled circles) and wet (filled circles) years versus percentage of developed land in all the continuously monitored watersheds. Lines fit by linear regression.

Fig. 11. Annual discharges of nitrate (kg N/ha) during the dry (unfilled circles) and wet (filled circles) years versus percentage of cropland in watersheds with <10% developed land. Lines fit by linear regression.

Fig. 12. Percentage of dissolved substance in total versus the concentration of the total substance.

Fig. 13. Percentage of dissolved substance in total versus the concentration of the total substance.

Fig. 14. Log of concentrations of total suspended solids (mg TSS/L), nitrate (mg N/L), and silicate (mg Si/L) versus the log of the water flow rate (L/(sec ha)) during the rising (filled circles) and declining (unfilled circles) phases of storms at watershed 96.

Fig. 15. Weekly water flow (m³/ha, top panel), total P concentration (μg P/L, middle panel), and weekly total P discharge (g P/ha, bottom panel) versus time at watershed 157.5. Concentration data are from weekly flow-proportional composite samples.

Fig. 16. Weekly water flow (m³/ha, top panel), nitrate concentration (μg N/L, middle panel), and weekly nitrate discharge (g N/ha, bottom panel) versus time at watershed 157.5. Concentration data are from weekly flow-proportional composite samples.

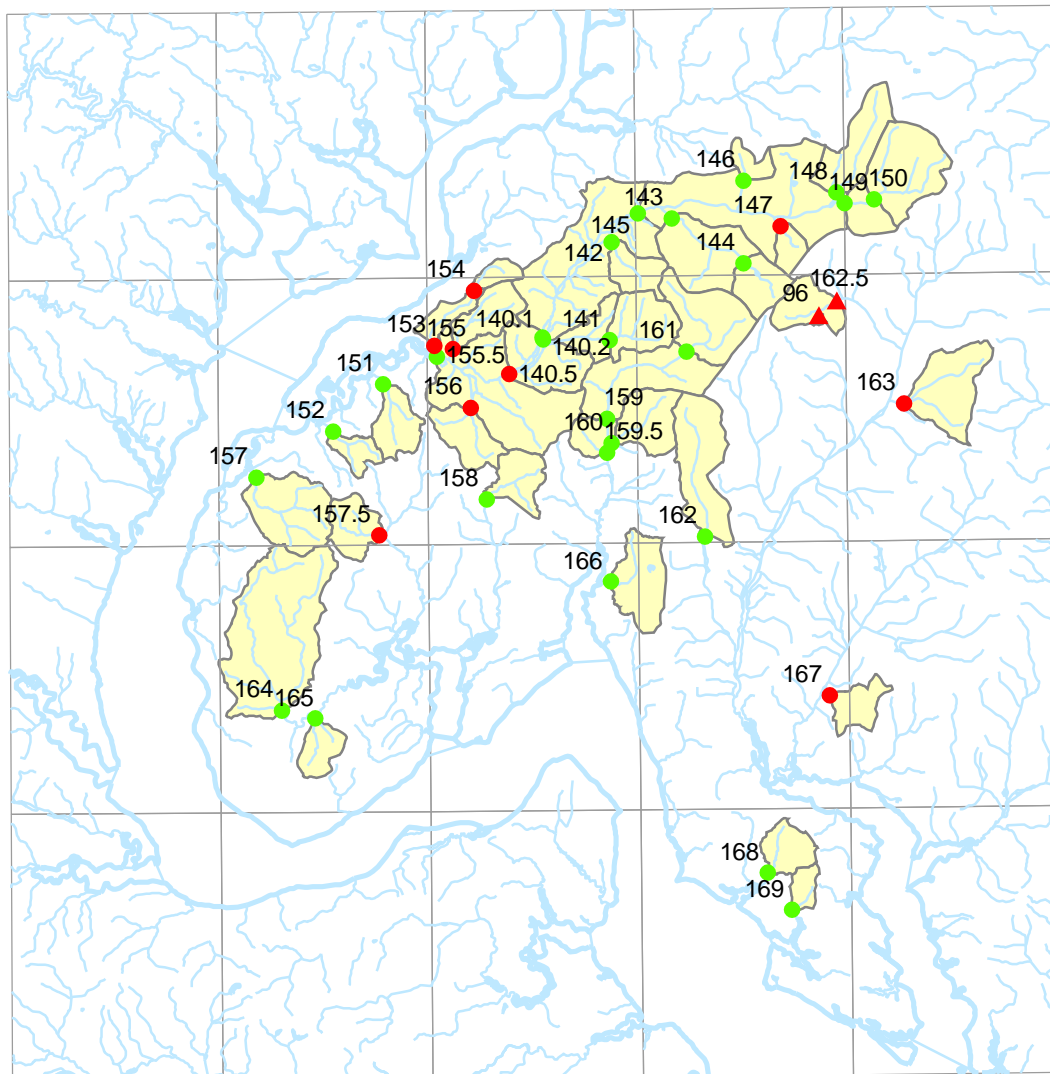


Figure 1. Map of the study watersheds showing three categories of stream sampling stations and their drainage areas. The stream map is EPA's reach file 3 (USEPA 1994b), and the rectangular grid maps the boundaries of USGS 7.5'

