Dissolved Silica in the Tidal Potomac River and Estuary, 1979–81 Water Years

A Water-Quality Study of the Tidal Potomac River and Estuary

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Dissolved Silica in the Tidal Potomac River and Estuary, 1979–81 Water Years

A Water-Quality Study of the Tidal Potomac River and Estuary

By S. F. Blanchard

U.S. GEOLOGICAL SURVEY WATER-SUPPLY PAPER 2234–H
Any use of trade names and trade marks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.
Tidal rivers and estuaries are very important features of the Coastal Zone because of their immense biological productivity and their proximity to centers of commerce and population. Most of the shellfish and much of the local finfish consumed by man are harvested from estuaries and tidal rivers. Many of the world’s largest shipping ports are located within estuaries. Many estuaries originate as river valleys drowned by rising sea level and are geologically ephemeral features, destined eventually to fill with sediments. Nutrients, heavy metals, and organic chemicals are often associated with the sediments trapped in estuaries. Part of the trapped nutrients may be recycled to the water column, exacerbating nutrient-enrichment problems caused by local sewage treatment plants, and promoting undesirable algae growth. The metals and organics may be concentrated in the food chain, further upsetting the ecology and threatening the shell and finfish harvests. Our knowledge of the processes governing these phenomena is limited and the measurements needed to improve our understanding are scarce.

In response to an increasing awareness of the importance and delicate ecological balance of tidal rivers and estuaries, the U.S. Geological Survey began a 5-year interdisciplinary study of the tidal Potomac River and Estuary in October of 1977. The study encompassed elements of both the Water Resources Division’s ongoing Research and River Quality Assessment Programs. The Division has been conducting research on various elements of the hydrologic cycle since 1894 and began intense investigation of estuarine processes in San Francisco Bay in 1968. The River Quality Assessment program began in 1973 at the suggestion of the Advisory Committee on Water Data for Public Use which saw a special need to develop suitable information for river-basin planning and water-quality management. The Potomac assessment was the first to focus on a tidal river and estuary. In addition to conducting research into the processes governing water-quality conditions in tidal rivers and estuaries, the ultimate goals of the Potomac Estuary Study were to aid water-quality management decision-making for the Potomac, and to provide other groups with a rational and well-documented general approach for the study of tidal rivers and estuaries.

This interdisciplinary effort emphasized studies of the transport of the major nutrient species and of suspended sediment. The movement of these substances through five major reaches or control volumes of the tidal Potomac River and Estuary was determined during 1980 and 1981. This effort provided a framework on which to assemble a variety of investigations:

1. The generation and deposition of sediments, nutrients, and trace metals from the Holocene to the present was determined by sampling surficial bottom sediments and analyzing their characteristics and distributions.
2. Bottom-sediment geochemistry was studied and the effects of benthic exchange processes on water-column nutrient concentrations ascertained.
3. Current-velocity and water-surface-elevation data were collected to calibrate and verify a series of one- and two-dimensional hydrodynamic flow and transport models.
4. Measurements from typical urban and rural watersheds were extrapolated to provide estimates of the nonpoint sources of sediments, nutrients, and biochemical oxygen demand during 1980 and 1981.
5. Intensive summertime studies were conducted to determine the effects of local sewage-treatment-plant effluents on dissolved-oxygen levels in the tidal Potomac River.
6. Species, numbers, and net productivity of phytoplankton were determined to evaluate their effect on nutrients and dissolved oxygen.
7. Wetland studies were conducted to determine the present-day distribution and abundance of submerged aquatic vegetation, and to ascertain the important water-quality and sediment parameters influencing this distribution.
8. Repetitive samples were collected to document the distribution and abundance of the macrobenthic infaunal species of the tidal river and estuary and to determine the effects of changes in environmental conditions on this distribution and abundance.

The reports in this Water-Supply Paper series document the technical aspects of the above investigations. The series also contains an overall introduction to the study, an integrated technical summary of the results, and an executive summary which links the results with aspects of concern to water-quality managers.

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A WATER-QUALITY STUDY OF THE TIDAL POTOMAC RIVER AND ESTUARY

Dissolved Silica in the Tidal Potomac River and Estuary, 1979–81 Water Years

By S.F. Blanchard

Abstract
The Potomac River at Chain Bridge is the major riverine source of dissolved silica (DSi) to the tidal Potomac River and Estuary. DSi concentrations at Chain Bridge are positively correlated with river discharge; river discharge is an important factor controlling rates of supply, dilution, and residence time. When river flow is high, the longitudinal DSi distribution is conservative. When river flow is low, other processes, such as phytoplankton uptake, benthic flux, resuspension, ground-water discharge, and water-column dissolution of diatoms, tend to be more influential than the river. Elevated concentrations of DSi in sewage-treatment-plant effluent in the Washington, D.C., area raise the DSi concentration of receiving Potomac River water. The tidal river zone serves as a net sink for DSi as a result of phytoplankton uptake. Ultimately, the biogenic silica from the tidal river is transported to the transition zone, where it is mineralized. As a result, the DSi concentration in the transition zone increases during summer. The DSi concentrations in the estuarine zone are largely controlled by dilution by Chesapeake Bay water and by phytoplankton uptake.

INTRODUCTION

Background of Study
In response to public concern about the importance and delicate ecological balance of tidal rivers and estuaries, the U.S. Geological Survey began a 5-year interdisciplinary Potomac Estuary Study in October 1977. The study focused on important water-quality considerations. Because the majority of the 3 million people who live in the Potomac River basin are concentrated in the Washington metropolitan area, and because the primary business in the basin is government, the Potomac River is relatively free from the pollution problems associated with manufacturing and chemical industries. The effects of such processes as sedimentation and nutrient enrichment can be studied in the tidal Potomac River and Estuary relatively independently of complications from other types of pollutants.

The general objectives of the Potomac Estuary Study (Callendar and others, 1984) are to (1) provide a better understanding of basic physical, chemical, and biological mechanisms governing life cycles of phytoplankton, submersed vegetation, and bottom-dwelling animals in the tidal Potomac River and Estuary, (2) develop, calibrate, and verify the mathematical flow and transport models necessary for predicting the movement and fate of nutrients and algae, and (3) develop, refine, and standardize efficient techniques for studying the water quality of the Potomac and other tidal rivers and estuaries so that other investigators can conduct their studies more efficiently.

Purpose and Scope
This paper describes dissolved silica, a plant nutrient, in the tidal Potomac River and Estuary for the 1979–81 water years. Processes such as the rate of river discharge, saltwater dilution, phytoplankton uptake, estuarine circulation, sewage-treatment-plant discharge, and benthic flux are described and related to spatial and temporal variations in the distribution of dissolved silica (DSi).

The Tidal Potomac River and Estuary
The tidal Potomac River and Estuary is defined as the lower 187 km (kilometers) of the main stem of the Potomac River extending from Chain Bridge, Washington, D.C.—the furthest extent of tides—to Point Lookout, Md. The tidal Potomac River and Estuary is the second largest tributary to the Chesapeake Bay estuarine system and has a surface area of 1,251 km² (square

Dissolved Silica in the Tidal Potomac River and Estuary, 1979–81 Water Years
kilometers) (Cronin, 1971). The width of the tidal Potomac varies from less than 1 km at Washington, D.C., to 9.7 km at the mouth of the estuary. The average depth is 5.8 m (meters), and the maximum depth is 36.5 m, at Mathias Point, Va. Major locational features of the tidal river and estuary are shown in figure 1.

The Potomac River supplies approximately 80 percent of the freshwater flow entering the tidal river and estuary and is the major source of riverborne dissolved and suspended material. River inflow affects the DSI distribution through altering rates of supply, dilution, and removal. Freshwater inflow from the Potomac River to

Figure 1. Tidal Potomac River and Estuary.
the tidal river and estuary is measured at Little Falls Dam, 1.9 km upstream from Chain Bridge. The drainage area upstream from the gaging station is 29,940 km². For the 51-year period of record 1931–81 (U.S. Geological Survey, 1982), the maximum discharge was 13,700 m³/s (cubic meters per second) in March 1936, the minimum discharge was 3.43 m³/s in September 1966, and the average annual discharge was 327.8 m³/s. Streamflow fluctuates seasonally, with the highest flow occurring during late winter and early spring and the lowest flow occurring during late summer.

The tidal Potomac River and Estuary can be divided into three distinctly different hydrodynamic zones (fig. 1). These zones are shown in detail in figures 2, 3, and 4. The tidal river zone contains freshwater and is strongly influenced by riverflow but also experiences tides and their associated cyclical reversals of flow. This reach is characterized by riverine water chemistry and is affected by major municipal wastewater discharges. The transition zone represents the zone of mixing between the freshwater of the Potomac River and the saltwater of Chesapeake Bay. This reach is characterized by high turbidity and biological diversity. The estuarine zone is strongly influenced by Chesapeake Bay and tidal flow. Freshwater inflow of the Potomac River is the major factor affecting nontidal circulation and significantly affects tidal circulation. Salinity in the tidal river and estuary varies in relation to river discharge, as illustrated in figure 5. When freshwater inflow is high, salinities are depressed and the top-to-bottom salinity differences become large. When freshwater inflow is low, salinity values in the estuarine zone approach those of Chesapeake Bay. The normal extent of saltwater is from Quantico, during summer low-flow periods, to Morgantown, during late winter and early spring high-flow periods. During extreme flow events, the saltwater-freshwater interface is usually located outside the transition zone. Webb and Heidel (1970) reported saltwater as far upstream as Hatton Point, Md. (fig. 2), during 1966, and Blanchard and Hahl (1981) reported salinities as low as 0.5 ppt (parts per thousand) at the U.S. Route 301 bridge (fig. 4) during 1979.

Data Sources

The main data base used for this report is presented by Blanchard and Hahl (1981), Blanchard and others (1982), and Blanchard and Coupe (1982). Data from several longitudinal sampling cruises conducted in 1977 and 1978 are used to further substantiate conclusions based on the 1979–81 water years data. The longitudinal data are reported by Smith and Herndon (1979, 1980a, 1980b, 1980c). In addition to the above data, interstitial-water data reported by Goodwin and others (1984) and phytoplankton-abundance and generic-composition data reported by Cohen and others (1985) are used.

Results from a nutrient transport box model (Bennett, 1983) for the tidal river and estuary, for the 1979–81 water years, are used in this report as a tool to aid in data interpretation. The transport model is an unsteady-state version of the model discussed by Officer (1980).

METHODS

Water-quality samples were collected at five major stations located in the tidal river and estuary at least weekly during the 1979–81 water years. The stations are shown as lines in figures 2, 3, and 4 to indicate the cross section of the river used as the sampling station. These samples were collected during various predicted tidal conditions such as during periods of maximum flood velocity, maximum ebb velocity, high slack water, and low slack water. During periods of greatly increased river discharge, the tidal sequence of sampling was discontinued and samples were collected several times a day to document the increased transport of dissolved and suspended material.

In addition to the weekly sampling, a 2- to 3-day longitudinal river-sampling cruise was made each month between Washington, D.C., and Chesapeake Bay. Samples were collected at the five major stations, at two Chesapeake Bay stations, and at several intervening stations. The Chesapeake Bay stations were located east of Point Lookout, Md. (latitude 38°02'00", longitude 76°12'41") and east of Smith Point, Va. (latitude 37°52'48", longitude 76°09'42"). The intervening stations were located (figs. 2–4) between the major stations to document longitudinal variations in water quality more accurately.

Dissolved-silica concentrations were determined at the Atlanta Central Water Quality Laboratory of the U.S. Geological Survey. Silica concentrations were determined using the molybdate blue colorimetric method as described by Skougstad and others (1979) and the American Public Health Association and others (1975). The applicable range of this method is 0.1 mg/L (milligram per liter) to 60 mg/L, and the estimated precision, according to Friedman and Beetam (1979), is 5 percent. In this paper dissolved silica generally is reported as milligrams of SiO₂ per liter.

For a more complete and detailed description of the methods of sample collection and analyses, refer to the annual hydrologic data reports by Blanchard and Hahl (1981), Blanchard and others (1982), and Blanchard and Coupe (1982).
Figure 2. Tidal river zone showing major water-quality sampling stations and intervening sampling stations.

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Figure 3. Transition zone showing major water-quality sampling stations and intervening sampling stations.
DISSOLVED SILICA IN THE TIDAL POTOMAC RIVER AND ESTUARY

Dissolved Silica in Natural Waters

Dissolved silica observed in natural waters results primarily from the chemical breakdown of silicate minerals, such as kaolinite and montmorillonite, in the processes of weathering. The rate at which DSi is supplied from these minerals varies with the climate, the topography, the vegetation, and the nature of the original mineral. Another natural source of DSi is the dissolution of siliceous organisms.

The solubility of these solid silica-source materials is a major factor in determining the content of DSi in natural waters (Polzer, 1967). Quartz is the mineral with the lowest solubility. Morey and others (1962) reported a solubility of 6 mg/L at 25 °C. Siever (1957) also investigated the solubility of quartz and suggested a range of between 7 and 14 mg/L. Amorphous silica has the highest solubility, approximately 120 mg/L; Krauskopf (1956) reported a solubility range of 100 to 140 mg/L, Siever (1962) a range of 120 to 140 mg/L, and Morey and others (1962) a solubility of 115 mg/L. Waters in equilibrium with other siliceous solids, such as feldspars, clay minerals, mica, and volcanic rocks, contain intermediate amounts of DSi.

According to laboratory test results, the solubility of siliceous solids is affected by temperature and pH. Okamota and others (1957), Morey and others (1962), and Iler (1979) all demonstrated that as temperature increases, the solubility of amorphous silica also increases. Iler (1979) reported a possible solubility...
minimum at pH 7 to pH 8. In more acidic waters the solubility increases slightly, and in more basic waters the solubility increases sharply, particularly from pH 9 to pH 11.

The world mean concentration of DSI in streams is reported by Livingstone (1963), Davis (1964), and Bricker and Garrels (1967) to be 13 mg/L. The mean concentration for North America reported by Aston (1983) is 9.0 mg/L. The concentration of DSI in most oceans is much less; Siever (1962) states that the average concentration is usually less than 1 mg/L. DSI in natural water is generally accepted as being in the form of monomolecular silicic acid, $H_4SiO_4$ (Krauskopf, 1956; Siever, 1962; Hem, 1970; Iler, 1979). This form results from the reaction $2H_2O + SiO_2 = H_4SiO_4$. Krauskopf (1956), Iler (1979), and Stumm and Morgan (1981) reported that when water has a pH between 9.0 and 10.7, silicate ions, most likely $(HO)_3SiO^-$ and $(HO)_2SiO_2^-$, also form and solubility increases rapidly.

Dissolved silica is an important nutrient used by planktonic diatoms for cell division and growth. According to Paasche (1973), the greatest uptake of DSI by diatoms occurs at the time of cell division. This uptake can reduce DSI concentrations to near-zero levels. Kilham (1971) suggests that the ambient DSI concentrations may determine which diatom species becomes dominant. Kilham (1971), Schelske and Stoermer (1972), Officer and Ryther (1980), and Paasche (1980) go even further to suggest that continued depletion of DSI may result in the replacement of a dominant diatom population by a less favorable population of blue-green and green algae. Thus, the ambient DSI concentration may be an important factor in determining the dominant diatom species and also the dominant type of phytoplankton.

The part of the silica cycle that is pertinent to this paper is presented in figure 6. This diagram of the silica cycle was compiled from Siever (1957), Davis (1964), Bricker and others (1968), Kennedy (1971), and Paasche (1980).
longitudinal profile typical of the summer season. There is a source of DSi at Alexandria, the effluent of the Blue Plains Sewage-Treatment Plant (fig. 2), a sink at Quantico, probably attributable to phytoplankton uptake, and another source at Morgantown, possibly attributable to benthic inputs or the dissolution of diatom frustules. Figure 10 is similar to figure 8B. Although the DSi source at Alexandria, effluent from the Blue Plains plant, is a point source, it does not appear as a spike, but rather as a hump because of the effects of tidal movement and mixing. This distribution is typical of high-flow conditions and is generally observed during winter and spring.

There are, however, several consistent features of the longitudinal distributions that should be noted. First, DSi concentrations at Alexandria are generally higher than DSi concentrations in the water entering the tidal river at Chain Bridge. This effect is most pronounced during low-flow periods. Second, DSi concentrations are usually higher throughout the tidal river and estuary during high-flow periods than during low-flow periods. Third, in most cases, there is an inverse relation between DSi concentration and salinity. Finally, there is a consistent late summer-early fall DSi distribution that consists of a minimum concentration in the vicinity of Quantico.
and a concentration increase in the vicinity of Morgantown.

**Point Sources of Dissolved Silica**

**River Discharge and Supply**

The river input of DSI and freshwater past Chain Bridge is the most dominant factor affecting the distribution of DSI in the tidal river and estuary. Riverine input directly affects the supply, dilution, and removal of DSI and indirectly affects all other processes. For example, river discharge affects the uptake of DSI by phytoplankton through variations in the water residence time. Therefore, understanding the role of river supply and discharge is essential to understanding the processes that control the distribution of DSI. The influence of river input on these other processes is discussed later.

The Potomac River at Chain Bridge is the major point source of dissolved silica entering the tidal river and estuary. According to Blanchard and Hahl (1987), the amount of DSI passing Chain Bridge was 77,000 Mg (megagrams) in 1979, 85,000 Mg in 1980, and 26,000 Mg in 1981. The discharge-weighted mean DSI concentration for the 1979–81 water years was 5.6 mg/L; this is below the North American mean river concentration of 9.0 mg/L. The DSI represents approximately 4 percent of the total dissolved solids passing Chain Bridge. The low DSI concentration is probably a result of the abundance of rock types in the river basin that have either a high quartz content (low silica solubility) or a high calcium content (low silica content).

DSI is significantly correlated (at the 99-percent confidence level) with river discharge. The positive correlation explains little of the variation in daily DSI concentrations, but it does explain approximately half the variation in monthly mean concentrations. This relation is contrary to the findings of Edwards (1973), Kennedy (1971), and Davis (1964), who found no significant correlation between DSI and river discharge.

The DSI-river discharge correlation does not adequately describe the relation because of the additional variations caused by the uptake of DSI by phytoplankton, the freshwater dilution of DSI during extreme flood events, and, particularly, the hysteretic response of DSI to increases in river discharge. The uptake of DSI by phytoplankton is demonstrated in figures 11, 12, and 13, which show DSI, river discharge, and chlorophyll $a$ for the 1979–81 water years. DSI concentrations decreased owing to biological removal during July and August 1981, as shown by figure 13. The biological removal is indicated by the corresponding increase in chlorophyll $a$ concentrations and the decrease in DSI concentrations. Chlorophyll $a$ is used here as an indicator of phytoplankton biomass. Chlorophyll $a$ concentrations are significantly correlated (at the 99-percent confidence level) with DSI concentrations. A three-variable model for mean monthly concentrations of DSI shows the importance of phytoplankton uptake in determining DSI concentration. The variables for dissolved oxygen and chlorophyll $a$ are related to phytoplankton.

$$DSI = 0.04263CHL + 0.00018DIS - 0.46322 \text{DO} + 7.957$$

$\rho^2 = 0.76$ (1)

where

- $DSI =$ estimated mean monthly DSI concentration, in milligrams per liter;
- $CHL =$ mean monthly chlorophyll $a$ concentration, in micrograms per liter;
- $DIS =$ mean monthly discharge, in cubic meters per second;
- $DO =$ mean monthly dissolved oxygen concentration, in milligrams per liter; and
- $\rho^2 =$ regression coefficient, proportion of total variation explained by the regression.

DSI demonstrates a hysteretic cyclical response to changes in discharge. Figure 14 shows this effect for a runoff event from January 8 to February 19, 1980. The DSI concentration increases during the rising limb of the hydrograph and continues to increase until it reaches peak concentration during the falling limb. This hysteretic cyclical response can be explained by examining the pathway of the water between the input of the precipitation to the soil and the output of the river at Chain Bridge.
Figure 8. Idealized longitudinal distribution of dissolved silica resulting from the mixing of silica-rich river water with silica-poor Chesapeake Bay water. (Modified from Peterson and others, 1975, fig. 4, p. 159.)
wave. This lag effect has been documented for suspended sediment by Heidel (1966) and for dissolved chemical species by Glover and Johnson (1974) and Walling and Foster (1975). The result of this lag effect is that the rise in discharge occurs before the rise in DSi concentration. Figure 15 shows a consistent time delay between the peak discharge and the peak DSi concentration. Therefore, the consistently observed hysteretic response of DSi to increases in river flow is due to the delay of the high-DSi-concentration water from the soil reaching the river and the further delay of the maximum DSi concentration traveling downstream at a slower velocity than the flood wave.

The two highest peak discharges of the study period occurred in January and February 1979. Figure 11 shows that for each of the storm runoff events there was a decrease in the DSi concentration corresponding to the peak discharge. In both cases, the initial runoff was from snowmelt, which would dilute the river DSi concentration. These two instances are the only times during the study period when there was a significant decrease in DSi as a result of an increase in river discharge.

As described by Kennedy (1971), rainfall, containing essentially no DSi, infiltrates the soil and dissolves readily soluble substrate minerals. As the precipitation continues, the water percolates deeper into the soil, increasing the time of contact, and dissolves some of the less soluble silicate minerals. If the rainfall is of sufficient intensity or duration, overland flow and subsurface flow begin. When this flow reaches the river, it increases the DSi concentration. As the precipitation and overland flow cease, subsurface flow continues to contribute to the DSi concentration in the river for several days. The maximum DSi content of the water reaching the river occurs when the combined DSi concentration of overland flow and subsurface flow reaches a maximum. According to Davis (1964), Bricker and others (1968), and Kennedy (1971), DSi is acquired by the runoff in a short time period of between a few hours and a few days. Although the release of silica is rapid, there is a delay between when the precipitation starts and when the maximum DSi concentration in the river is reached.

Once in the river, DSi is carried along at the mean water velocity, which is less than the velocity of the flood wave. This lag effect has been documented for suspended sediment by Heidel (1966) and for dissolved chemical species by Glover and Johnson (1974) and Walling and Foster (1975). The result of this lag effect is that the rise in discharge occurs before the rise in DSi concentration. Figure 15 shows a consistent time delay between the peak discharge and the peak DSi concentration. Therefore, the consistently observed hysteretic response of DSi to increases in river flow is due to the delay of the high-DSi-concentration water from the soil reaching the river and the further delay of the maximum DSi concentration traveling downstream at a slower velocity than the flood wave.

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Figure 11. Dissolved-silica and chlorophyll $a$ concentrations and discharge at Chain Bridge, 1979 water year.

Sewage-Treatment-Plant Discharge and Supply

Sewage-treatment-plant effluent is often a major source of nutrients in estuaries. Usually, the nutrients of most concern are nitrogen and phosphorus. However, as Garside and others (1976) and Simpson and others (1975) have demonstrated for the Hudson River Estuary, N.Y., DSI concentration can increase significantly as a result of sewage-treatment-plant discharges. According to Garside and others (1976), the mean DSI concentration of secondary effluent is 40 mg/L. According to Horne (1978), it is 50 mg/L, of which 15 mg/L is from domestic use and treatment. Metcalf and Eddy, Inc. (1979), reports a lower increase in DSI concentrations, 2 to 10 mg/L, due to domestic water use. Therefore, DSI concentrations in sewage-treatment-plant discharges should be greater than those entering the tidal river at Chain Bridge.

The tidal Potomac River and Estuary has several sewage-treatment plants located in the tidal river zone. The Blue Plains plant (fig. 2) is the largest; it had a mean monthly discharge of 14 m$^3$/s (cubic meters per second) and an estimated mean DSI concentration of 9.7 mg/L for the 1979–81 water years (Coupe and Webb, 1983). This is 4.1 mg/L higher than the mean DSI concentration of 5.6 mg/L at Chain Bridge. The Blue Plains plant supplies approximately 75 percent of the combined DSI load from all the sewage-treatment plants in the Washington, D.C., metropolitan area.
Most of the discharge from the Blue Plains plant is derived from drinking-water supply for the city of Washington, D.C. Therefore, the monthly mean DSi concentration and loads presented for the plant in table 1 are based on the sum of (1) the average of the monthly DSi concentrations from the two Metropolitan Washington drinking-water-treatment plants (Dalecarlia and McMillan) and (2) the average annual increase (4.0 mg/L) in DSi concentrations due to domestic water use. The sewage-treatment plants in the tidal river zone supplied only 7 percent of the combined Chain Bridge-sewage treatment plant DSi load for the 1979–81 water years. However, as figure 16 shows, during periods of low flow, the Blue Plains plant can supply more DSi to the tidal river than the riverine input at Chain Bridge. Data in figure 17 from a longitudinal river-sampling trip on March 3, 1981, show an increase in the DSi concentration at Alexandria due to discharge from the Blue Plains plant. The increase in DSi concentration at Alexandria depends on the discharges and concentrations of both Chain Bridge and the Blue Plains sewage-treatment plant and can be estimated by the following equation:

$$\overline{\text{DSi}_{\text{ALEX}}} = \frac{[\text{DSi}_{\text{CB}} \times \text{DIS}_{\text{CB}}] + [\text{DSi}_{\text{BPSTP}} \times \text{DIS}_{\text{BPSTP}}]}{\text{DIS}_{\text{CB}} + \text{DIS}_{\text{BPSTP}}}$$  \hspace{1cm} (2)
Figure 13. Dissolved-silica and chlorophyll a concentrations and discharge at Chain Bridge, 1981 water year.

where

- $\text{DS}_{\text{ALEX}} =$ estimated DSi concentration at Alexandria, in milligrams per liter;
- $\text{DIS}_{\text{CB}} =$ discharge at Chain Bridge, in cubic meters per second;
- $\text{DSi}_{\text{CB}} =$ DSi concentration at Chain Bridge, in milligrams per liter;
- $\text{DSi}_{\text{BPSTP}} =$ DSi concentration at Blue Plains Sewage-Treatment Plant, in milligrams per liter;
- $\text{DIS}_{\text{BPSTP}} =$ discharge of Blue Plains Sewage-Treatment Plant, in cubic meters per second.

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Figure 18 shows measured Alexandria DSi concentrations overlain by the estimated DSi concentrations, \( \text{DSi}_{\text{ALEX}} \), computed from equation 2. Alexandria DSi concentrations regressed against those estimated from equation 2 yield the following linear-regression model \((r^2 = 0.78)\):

\[
\text{DSi}_{\text{ALEX}} = 0.069 + 0.924 \text{DSi}_{\text{ALEX}}
\]

The regression shows that 78 percent of all the variation in the DSi concentration at Alexandria can be explained by adding the DSi load from the Blue Plains plant to the Chain Bridge DSi load.

## Factors Affecting Distribution of Dissolved Silica

### Estuarine Circulation

Estuarine circulation patterns are primarily the result of the combination of four flow components: river, tide, density, and wind. The river flow component varies...
Table 1. Monthly mean dissolved-silica concentrations and loads for the Blue Plains Sewage-Treatment Plant, 1979–81 water years
[Discharge in cubic meters per second; average concentration in milligrams per liter of SiO$_2$; total load in megagrams per day]

<table>
<thead>
<tr>
<th>Month</th>
<th>1979 water year</th>
<th></th>
<th></th>
<th>1980 water year</th>
<th></th>
<th>1981 water year</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Discharge</td>
<td>Average concentration</td>
<td>Total load</td>
<td>Daily load</td>
<td>Discharge</td>
<td>Average concentration</td>
<td>Total load</td>
</tr>
<tr>
<td>October</td>
<td>12</td>
<td>6.0</td>
<td>192.4</td>
<td>6.2</td>
<td>16</td>
<td>14.4</td>
<td>623.0</td>
</tr>
<tr>
<td>November</td>
<td>13</td>
<td>6.3</td>
<td>213.6</td>
<td>7.1</td>
<td>14</td>
<td>12.9</td>
<td>472.8</td>
</tr>
<tr>
<td>December</td>
<td>13</td>
<td>10.6</td>
<td>371.3</td>
<td>12.0</td>
<td>14</td>
<td>10.2</td>
<td>384.8</td>
</tr>
<tr>
<td>January</td>
<td>13</td>
<td>10.8</td>
<td>376.6</td>
<td>12.1</td>
<td>15</td>
<td>10.7</td>
<td>432.5</td>
</tr>
<tr>
<td>February</td>
<td>13</td>
<td>12.0</td>
<td>381.3</td>
<td>13.6</td>
<td>14</td>
<td>8.5</td>
<td>301.8</td>
</tr>
<tr>
<td>March</td>
<td>13</td>
<td>11.8</td>
<td>411.6</td>
<td>13.3</td>
<td>16</td>
<td>10.1</td>
<td>435.5</td>
</tr>
<tr>
<td>April</td>
<td>13</td>
<td>11.1</td>
<td>376.3</td>
<td>12.5</td>
<td>17</td>
<td>5.6</td>
<td>248.3</td>
</tr>
<tr>
<td>May</td>
<td>13</td>
<td>7.8</td>
<td>273.3</td>
<td>8.8</td>
<td>17</td>
<td>12.8</td>
<td>586.4</td>
</tr>
<tr>
<td>June</td>
<td>14</td>
<td>16.8</td>
<td>611.5</td>
<td>20.4</td>
<td>16</td>
<td>14.1</td>
<td>590.4</td>
</tr>
<tr>
<td>July</td>
<td>13</td>
<td>7.9</td>
<td>276.8</td>
<td>8.9</td>
<td>16</td>
<td>14.9</td>
<td>640.3</td>
</tr>
<tr>
<td>August</td>
<td>14</td>
<td>12.8</td>
<td>481.0</td>
<td>15.5</td>
<td>16</td>
<td>10.9</td>
<td>470.0</td>
</tr>
<tr>
<td>September</td>
<td>15</td>
<td>11.8</td>
<td>463.5</td>
<td>15.5</td>
<td>16</td>
<td>10.6</td>
<td>442.3</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>192.4</td>
<td>11.700</td>
<td>5,628</td>
</tr>
</tbody>
</table>

considerably, and with it the circulation and salinity patterns in the estuary. The higher the flow, the more riverine the system and the more conservative the DSi profile. Higher inflow rates also increase flushing rates and lower constituent residence times, allowing less time for other processes to act. For example, table 2 shows the riverine input of DSi and freshwater at Chain Bridge for May and June 1980. In May, the estuary had roughly six times the DSi load and three times the freshwater input as it had in June. The residence time for May was therefore three times that for June. Thus, processes acting upon DSi during this 2-mo (month) period had approximately 18 times more time available per unit of silica in June than in May. This illustration shows the dominant role the rate of supply can have in affecting other processes. Figure 19 shows residence times for various flow conditions at Chain Bridge. Residence time is defined as

$$RT = \frac{V}{R}$$  \hspace{1cm} (4)

where

- $RT =$ flushing time, in seconds;
- $V =$ total volume in a given reach of the estuary, in cubic meters; and
- $R =$ rate of influx of freshwater, in cubic meters per second.

This assumes that the freshwater in the estuary is being displaced at the same rate as it is being added by river discharge at Chain Bridge. Table 3 shows residence times for two extreme flow periods—one with high flow (a

Table 2. Advective residence times for the tidal river and transiton zones, May and June 1980

<table>
<thead>
<tr>
<th>Month</th>
<th>Freshwater Input at Chain Bridge, in cubic meters per second</th>
<th>Dissolved silica load at Chain Bridge, in megagrams per day</th>
<th>Advective residence time for each reach, in days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chain Bridge to Quantico</td>
<td>Quantico to Morgantown</td>
<td>Chain Bridge to Morgantown</td>
</tr>
<tr>
<td>May</td>
<td>716</td>
<td>11,700</td>
<td>8.8</td>
</tr>
<tr>
<td>June</td>
<td>224</td>
<td>1,860</td>
<td>23.0</td>
</tr>
</tbody>
</table>

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mean daily discharge of 1,700 m$^3$/s) and the other with low flow (a mean daily discharge of 62 m$^3$/s). The residence time for the 328 m$^3$/s mean discharge at Chain Bridge for the period of record is also included in table 3. The two extreme flow periods serve as the upper and lower range limits for monthly residence times during the 1979–81 water years.

The tidal flow component is a back-and-forth flow that affects the DSi distribution primarily by locally mixing the water. The tidal excursion for the tidal river zone can be estimated from a one-dimensional unsteady-flow model that Schaffranek (1985) has applied to the Potomac. Tidal excursion is defined (McDowell and O’Conner, 1977) as the distance traveled by a water particle moving with the mean cross-sectional velocity for the period of the flood or ebb tide. Results from two model runs are presented in table 4; they show the variation of the tidal excursion with changes in flow and longitudinal position. Applying the estimated September 22, 1981, Alexandria tidal excursion to the Blue Plains Sewage-Treatment Plant effluent suggests that the effects of the high DSi effluent concentrations can be observed 3.75 km above the treatment-plant outfall.

The density flow component is caused by the difference in density between river water and seawater. The result is a net bottom upriver flow of dense seawater in opposition to the seaward flow of less dense river water. These opposing flows can result in vertical advection, which contributes to vertical mixing. The dense seawater is usually very low in DSi, resulting in dilution of the river water higher in DSi. During summer and early fall, when freshwater inflow is at a minimum, the bottom upriver tidal flow of dense seawater can have velocities capable of resuspending bottom sediment.
Schubel (1968) states that velocities greater than 35 to 50 cm/s (centimeters per second) usually result in resuspension. This resuspension provides additional particulate silica to the water column where in situ dissolution to DSi is possible. During August 1983, flood velocities greater than 60 cm/s were measured in the transition zone, an area where resuspension of the bottom sediments has repeatedly been observed.

Phytoplankton

The primary biological factor affecting DSi concentration is probably phytoplankton production. Other factors, such as zooplankton grazing and the uptake and release of DSi by submersed aquatic vegetation, could be important, but few data are available to describe their role in affecting the behavior of DSi. Therefore, only the role of phytoplankton is discussed.

The three hydrodynamic zones of the Potomac can be generally described as having typical phytoplankton characteristics and trends. The tidal river zone repeatedly experiences summer phytoplankton blooms and high chlorophyll \( a \) concentrations. This zone consistently has the highest summer biomass of phytoplankton (Lippson and others, 1979). The summer biomass in the tidal river zone is usually at least twice the biomass in either of the other two zones. Cell numbers are generally highest from July through September and lowest from December through February (Pollock, 1985). Discharge is an important factor influencing phytoplankton distribution in the tidal river. According to Pollock (1985), high discharges at Chain Bridge caused distributions of algae in the tidal river to be uniform. However, when discharges were low, diatoms and green algae were most abundant in the upper tidal river and blue-green algae was most abundant in the lower tidal river. Using a phytoplankton growth index, Bennett and others (1986) showed that hydraulic conditions in the tidal river were favorable for the development of chlorophyll \( a \) concen-

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**Table 3.** Residence times through the tidal river and transition zones for three periods with different flows

<table>
<thead>
<tr>
<th>Date</th>
<th>Residence time, in days</th>
<th>Mean discharge at Chain Bridge, in cubic meters per second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chain Bridge to Quantico</td>
<td>Quantico to Morgantown</td>
</tr>
<tr>
<td>2-21-79 to</td>
<td>3.7</td>
<td>6.5</td>
</tr>
<tr>
<td>3-17-79</td>
<td></td>
<td>1,700</td>
</tr>
<tr>
<td>8-21-81 to</td>
<td>85.0</td>
<td>150.0</td>
</tr>
<tr>
<td>9-17-81</td>
<td></td>
<td>62</td>
</tr>
<tr>
<td>51-year period of record</td>
<td>24.0</td>
<td>328</td>
</tr>
</tbody>
</table>
trations greater than 100 μg/L (micrograms per liter) during at least half of the 54 yr (years) of flow records at Chain Bridge. Peterson (1980) points out that nutrients in the tidal river do not often limit phytoplankton production and play a role secondary to river discharge in the seasonal timing of maximum phytoplankton development. Table 5 shows DSI and chlorophyll a mass-balance calculations for five reaches of the tidal river and estuary for the 1980 water year. The masses have been normalized by dividing by the appropriate volume for each reach; the resultant units are in megagrams per $1 \times 10^8$ cubic meters. This normalization allows for direct comparison of values between reaches. Examination of table 5 shows the tidal river reach between Alexandria and Quantico to be very productive with respect to chlorophyll a. There was a gain in chlorophyll a mass in this reach for each month of the 1980 water year regardless of flow conditions. Table 5 also shows a decrease in DSI mass in this reach for all but 2 mo during the 1980 water year. This reach is consistently a sink for DSI as a result of phytoplankton uptake, particularly in the summer, when DSI concentrations are often reduced to near zero, as shown by figure 20.

At Quantico, the boundary between the tidal river zone and the transition zone, DSI concentrations are inversely related to chlorophyll a concentrations. Figure 20 shows that the major peaks in chlorophyll a concentrations correspond to the minimum DSI concentrations. Regression analysis of one, two, and three variables against mean monthly DSI at Quantico produced the following results (eq. 5 represents the linear model that explained the most variation in the mean monthly DSI concentration):

$$\begin{align*}
\text{DSI}_0 &= 1.38 + 0.00426\text{CBMINQ} \\
\text{DSI}_0 &= 1.195 + 0.0000435\text{CBMAXQ} + 0.00008525\text{CBMNQ} \\
\text{DSI}_0 &= 1.8429 + 0.0000789\text{CBMNQ} - 0.0004854\text{NUMDI} + 0.0000479\text{CBMAXQ}
\end{align*}$$

where

- $\text{DSI}_0$ = estimated mean monthly dissolved-silica concentration at Quantico, in milligrams per liter;
- $\text{CBMINQ}$ = minimum discharge for a given month at Chain Bridge, in cubic meters per second;
- $\text{CBMAXQ}$ = maximum discharge for a given month at Chain Bridge, in cubic meters per second;
- $\text{CBMNQ}$ = monthly mean discharge for a given month at Chain Bridge, in cubic meters per second;
- $\text{NUMDI}$ = monthly mean number of diatoms at Quantico, Va., in cells per milliliter; and
- $r^2$ = regression coefficient.

The two-variable model (eq. 6) also involves DSI and two discharge terms for Chain Bridge. This model explains 60 percent of the variation in mean monthly DSI concentrations at Quantico. Both the one- and the two-variable models point again to the overall importance of discharge in controlling DSI concentrations through the alteration of the rates of supply and demand and the residence time. The three-variable model (eq. 7) includes a term for the monthly mean number of diatom cells at Quantico. This model explains 65 percent of the variation and suggests that the second most important factor controlling the variability of DSI concentration at Quantico, after discharge, is phytoplankton growth and biomass, particularly diatom biomass.

The transition zone generally has the lowest phytoplankton biomass of the estuarine system. The moderate salinities are apparently too high for the freshwater species of the tidal river to thrive and too low for the estuarine species. The low biomass in the transition zone can also be attributed to the high turbidity, which reduces the amount of available light in the water column, and to the increased average cross-sectional water depth (Peterson, 1980). Chlorophyll a concentrations generally

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Table 4. Tidal excursions at Alexandria and Hallowing Point, Va., for two periods during the 1981 water year

<table>
<thead>
<tr>
<th>Station</th>
<th>Date</th>
<th>Flow at Chain Bridge, in cubic meters per second</th>
<th>Tidal excursion, in kilometers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alexandria, Virginia</td>
<td>2-23-81</td>
<td>1,000</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>9-22-81</td>
<td>58</td>
<td>3.8</td>
</tr>
<tr>
<td>Hallowing Point, Virginia</td>
<td>2-23-81</td>
<td>1,000</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>9-22-81</td>
<td>58</td>
<td>5.6</td>
</tr>
</tbody>
</table>
reach their maximum in winter owing to dinoflagellates and in spring owing to diatoms. Chlorophyll \(a\) concentrations are at their minimum between July and September, when estuarine water with higher salinities migrates farthest upstream. According to Bennett and others (1986), moderately high Chain Bridge discharges have little adverse effect on the seasonal development of the chlorophyll \(a\) maxima and minima. The transition zone also can be characterized as a phytoplankton “die off” zone, especially in summer and early fall. Tidal river zone phytoplankton blooms typically are transported into the transition zone where saltwater-induced osmotic stress causes the phytoplankton to die. Figure 21 presents three longitudinal profiles of cell counts, which show cell count minima in the transition zone that confirm this “die off” of phytoplankton. The overall effect of this process is to lessen the use of DSi by phytoplankton in the transition zone and to contribute DSi to this reach in the form of diatom frustules for benthic or in situ water-column dissolution.

The esturine zone phytoplankton population is similar to that of Chesapeake Bay in that it is composed...
Table 5. Mass-balance calculations of dissolved silica (DSi) and chlorophyll \( a \) (Chl) for several reaches of the tidal Potomac River and Estuary, 1980 water year

<table>
<thead>
<tr>
<th>Month</th>
<th>Chain Bridge discharge</th>
<th>Chain Bridge to Alexandria</th>
<th>Alexandria to Quantico</th>
<th>Quantico to Morgantown</th>
<th>Morgantown to Piney Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DSi (mg/L)</td>
<td>Chl (mg/L)</td>
<td>DSi (mg/L)</td>
<td>Chl (mg/L)</td>
<td>DSi (mg/L)</td>
</tr>
<tr>
<td>October</td>
<td>950</td>
<td>1,500 (1.9)</td>
<td>630 (6.6)</td>
<td>150 (1.6)</td>
<td>420 (4.6)</td>
</tr>
<tr>
<td>November</td>
<td>510</td>
<td>250 (8.1)</td>
<td>(440) (11)</td>
<td>(390) 2.8</td>
<td>80 1.7</td>
</tr>
<tr>
<td>December</td>
<td>370</td>
<td>150 (15)</td>
<td>(620) (6.9)</td>
<td>(64) 4.0</td>
<td>(34) (3.8)</td>
</tr>
<tr>
<td>January</td>
<td>520</td>
<td>650 (18)</td>
<td>(880) (18)</td>
<td>(14) (9.5)</td>
<td>(29) (2.9)</td>
</tr>
<tr>
<td>February</td>
<td>230</td>
<td>(290) 3.6</td>
<td>(24) (6.3)</td>
<td>(140) (2.8)</td>
<td>(23) 0.8</td>
</tr>
<tr>
<td>March</td>
<td>660</td>
<td>150 (1.8)</td>
<td>1,440 (15)</td>
<td>390 (5.4)</td>
<td>(42) 18</td>
</tr>
<tr>
<td>April</td>
<td>870</td>
<td>(760) (4.8)</td>
<td>590 (14)</td>
<td>330 (5.5)</td>
<td>350 0.8</td>
</tr>
<tr>
<td>May</td>
<td>710</td>
<td>(325) (29)</td>
<td>940 (16)</td>
<td>170 7.1</td>
<td>220 (9.2)</td>
</tr>
<tr>
<td>June</td>
<td>220</td>
<td>(140) (12)</td>
<td>340 (2.9)</td>
<td>(150) 2.4</td>
<td>(35) (5.0)</td>
</tr>
<tr>
<td>July</td>
<td>120</td>
<td>810 (2.0)</td>
<td>660 (4.1)</td>
<td>(150) 0.4</td>
<td>(46) (1.1)</td>
</tr>
<tr>
<td>August</td>
<td>96</td>
<td>230 (10)</td>
<td>720 (0.5)</td>
<td>(210) (18)</td>
<td>(73) 3.5</td>
</tr>
<tr>
<td>September</td>
<td>47</td>
<td>150 (49)</td>
<td>440 (3.1)</td>
<td>(380) 1.1</td>
<td>(120) (1.0)</td>
</tr>
</tbody>
</table>

| Annual total | 2,700 (60) | 6,200 (100) | (450) (22) | 780 3.1 |

of brackish-water and marine species. During winter and spring the water column is well mixed, and there is usually a spring diatom bloom. Figure 22 presents the 1980 and 1981 water year chlorophyll \( a \) concentrations at Piney Point, Md., showing the characteristic spring bloom. During the summer, the water column becomes stratified and the phytoplankton are confined to the upper few meters. DSi concentrations in this reach are primarily affected by the influence of Chesapeake Bay waters and by phytoplankton uptake. During extreme high-flow events, DSi concentrations are also affected by riverine discharge at Chain Bridge.

**Benthic Inputs**

**Benthic Flux**

The concentration of DSi in the pore water of cores from the tidal Potomac River and Estuary is substantially higher than the DSi concentrations in the overlying water. This is consistent with the findings of others (Siever and others, 1965; Hurd, 1973; Schink and others, 1974), who have shown that there is almost always a higher concentration of DSi in the pore water than in the overlying water. In the Potomac, interstitial pore-water DSi concentrations ranged from 5.5 to 50 mg/L (Goodwin and others, 1984) in the top 2 cm (centimeters) of sediment. Figure 23 shows the vertical DSi concentration distribution in the interstitial waters for several sediment cores. These distributions show a steep gradient in the top 10 cm of the core, indicating a flux of DSi into the overlying water.

The formulation

\[
j = \phi_0 D_{i,0}^{sed} \frac{dC_i}{dx} \bigg|_{x=0}
\]

where

\[
\phi_0 = \text{sediment porosity in top 2 cm};
\]

\[
D_{i,0}^{sed} = \text{whole-sediment diffusion coefficient (Lerman, 1979)}; \quad \text{and}
\]

\[
\frac{dC_i}{dx} \bigg|_{x=0} = \text{concentration gradient, straight-line fit in the top 2 cm of core samples, discussed by Callender and Hammond (1982) for calculating diffusive fluxes was used with the interstitial pore-water data reported by Goodwin and others (1984) to calculate diffusive DSi fluxes for the tidal river and estuary. A straight-line concentration gradient in the top 2 cm of the sediment was used to calculate the diffusive fluxes. The tidal river and estuary was divided into nine segments on the basis of calculated diffusive fluxes. The fluxes were averaged monthly for each station and then areally for each segment to obtain a mean monthly diffusive flux for each segment. For months when no diffusive flux could be calculated for a segment because of lack of interstitial pore-water data, the diffusive flux and water temperature for the closest month was used in the following relation to estimate a diffusive flux. This relation,}

\[
Dissolved Silica in the Tidal Potomac River and Estuary, 1979–81 Water Years H21
The process of calculating diffusive flux outlined above resulted in 12 monthly mean diffusive fluxes with corresponding water-column temperatures for the month and year in which the cores were collected. This set of 12 “standard” monthly diffusive fluxes was used to estimate monthly diffusive fluxes for the 1979–81 water years by either (1) using the “standard” diffusive flux when it corresponded to the month and year of interest or (2) adjusting the “standard,” using equation 9, to the temperature of the water for the month and year of interest.

The diffusive fluxes were used to calculate monthly loads of DSi from the sediment for each of the three hydrodynamic zones. These loads are reported as megagrams of SiO₂ in table 6. Examination of table 6 shows little variation in the yearly input of DSi from the bottom sediments for each of the hydrodynamic zones. This is primarily a result of the method of calculation. Because most of the cores were taken in 1978 and 1979, the variation in loading is due to variations in temperature which were used with equation 9 to adjust the 1978 and 1979 core data for 1980 and 1981. Callender and Hammond (1982) compared average diffusive and in situ fluxes of DSi for the three hydrodynamic zones. The ratio of the in situ flux to the diffusive flux from this comparison (table 7) can be multiplied by the loads from diffusive fluxes to estimate loads for in situ fluxes. The annual loads from diffusive and in situ fluxes for each of the three hydrodynamic zones are reported in table 8.

The most important factors affecting the benthic flux of DSi for a given sediment composition are temperature, salinity, macrofaunal irrigation, and input of biogenous particulate silica. Increases in temperature increase the solubility of biogenic silica (Iler, 1979), the porosity and concentration gradient of the adjacent month is the same as the month to be estimated.

Table 6. Monthly benthic loads of dissolved silica based on diffusive flux, 1979–81 water years
[Loads in megagrams of SiO₂]

<table>
<thead>
<tr>
<th></th>
<th>1979</th>
<th>1980</th>
<th>1981</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tidal river</td>
<td>Transition</td>
<td>Estuarine</td>
</tr>
<tr>
<td>Month</td>
<td>zone zone</td>
<td>zone zone</td>
<td>zone zone</td>
</tr>
<tr>
<td>October</td>
<td>220</td>
<td>200</td>
<td>2,200</td>
</tr>
<tr>
<td>November</td>
<td>190</td>
<td>170</td>
<td>1,700</td>
</tr>
<tr>
<td>December</td>
<td>150</td>
<td>140</td>
<td>1,500</td>
</tr>
<tr>
<td>January</td>
<td>71</td>
<td>130</td>
<td>1,300</td>
</tr>
<tr>
<td>December</td>
<td>63</td>
<td>120</td>
<td>1,200</td>
</tr>
<tr>
<td>February</td>
<td>79</td>
<td>140</td>
<td>1,500</td>
</tr>
<tr>
<td>March</td>
<td>180</td>
<td>170</td>
<td>1,700</td>
</tr>
<tr>
<td>April</td>
<td>230</td>
<td>210</td>
<td>2,100</td>
</tr>
<tr>
<td>May</td>
<td>270</td>
<td>250</td>
<td>2,400</td>
</tr>
<tr>
<td>June</td>
<td>260</td>
<td>270</td>
<td>2,700</td>
</tr>
<tr>
<td>July</td>
<td>250</td>
<td>280</td>
<td>2,800</td>
</tr>
<tr>
<td>August</td>
<td>270</td>
<td>260</td>
<td>3,000</td>
</tr>
<tr>
<td>September</td>
<td>2,200</td>
<td>2,300</td>
<td>24,000</td>
</tr>
</tbody>
</table>

Figure 19. Residence times through the tidal river and transition zones for various flow conditions at Chain Bridge.

\[
\left( \frac{j_i}{T} \right)_{t_1} = \left( \frac{j_i}{T} \right)_{t_2}
\]

where

- \( j_i \) = diffusive flux,
- \( \eta \) = viscosity of water, and
- \( T \) = absolute temperature,

is based on the Stokes-Einstein relation discussed by Li and Gregory (1974) to estimate the self-diffusion coefficient of water. The use of equation 9 assumes that the
Figure 20. Monthly mean dissolved-silica and chlorophyll a concentrations for the Potomac River at Quantico, Va., 1979-81 water years.

Diffusion rate (Li and Gregory, 1974), and the overall flux of DSi from the sediments (Rippey, 1983). The temperature effect is fairly uniform throughout the tidal river and estuary. Increases in salinity also cause an increase in the DSi flux. Yamada and D’Elia (1984) showed an increase in the release of DSi from sediments as salinity increased between 10 and 20 ppt. Spatially, the tidal river and estuarine zones have fairly stable salinities and the variability in the DSi flux due to salinity is minimal. In the transition zone, however, salinity varies considerably and so does the DSi flux. The DSi flux appears to reach a maximum in late summer, when salinities in the transition zone are highest.

Macrofaunal irrigation is significant in the transition zone of the Potomac and generally peaks during late spring and early summer and decreases to a minimum during late fall. An example of macrofaunal irrigation (Callender and Hammond, 1982) is a polychaete worm ventilating its burrow with water currents, produced by ciliary action or muscular movements of its body. Callender and Hammond (1982), Lyons and others (1982), and Calvert (1983) have shown that macrofaunal irrigation can substantially enhance the diffusive flux.

Schink and others (1975) have shown that the flux of particulate biogenous silica into the sediments is one of the most important factors controlling the DSi flux out of the sediments. Rippey (1983) has shown that the DSi flux depends on the time since the last major deposition of biogenous particulate silica. Yamada and D’Elia (1984) similarly determined that the flux of DSi was directly proportional to the amount of biogenic silica applied to the sediment. This process appears to take place routinely in the transition zone. Figure 21, presented earlier, shows longitudinal plots of diatom cell counts that indicate a loss of cells in the transition zone. Estimated sinking rates for an “average” diatom in the Potomac range from 0.4 m/d (meter per day) to greater than 1.0 m/d. In view of the shallow depths and the long residence times in the transition zone, these sinking rates suggest that the diatom frustules generally would remain
in the transition zone and settle to the bottom. As an example of the effect of this die off, the decrease in diatoms from July 27 to August 17, 1981, as shown in figure 21, would result in approximately 10 to 20 mg/m²/d (milligrams per square meter per day) of biogenic silica being added to the sediment if all the diatom frustules settled to the bottom. For the Potomac, these factors have their greatest combined effect in the transition zone during late summer and early fall.

Resuspension

In addition to the benthic flux of DSi from the sediments, there is another process, of particular importance in the transition zone, that contributes DSi to the water column. This process is the resuspension of a thin layer of surface sediment during summer flood tides. Figure 24 shows turbidity concentrations, and figure 25 shows suspended-sediment concentrations, at three depths for a station in the middle of the transition zone during a complete tidal cycle. The large increase in both turbidity and suspended-sediment concentrations during

![Graph showing longitudinal distributions of total diatom cell counts for three months, 1981 water year.]

![Graph showing chlorophyll a concentrations at Piney Point, Md., 1980 and 1981 water years.]

\[1800 \text{ mg/m}^2/\text{d}\]

\[10,000 \text{ mg/m}^2/\text{d}\]

\[20,000 \text{ mg/m}^2/\text{d}\]

DISTANCE, IN KILOMETERS FROM CHESAPEAKE BAY

MONTH AND DAY OF WATER YEAR

**Figure 21.** Longitudinal distributions of total diatom cell counts for three months, 1981 water year.

**Figure 22.** Chlorophyll a concentrations at Piney Point, Md., 1980 and 1981 water years.
flood tide indicates that resuspension occurs. Figure 26 shows vertical DSi concentration profiles for both ebb and flood tides. During ebb tide, with no resuspension, the near-bottom DSi concentration was 0.4 mg/L higher than the surface concentration. During flood tide, with resuspension, there was an increase of 1.0 mg/L in the near-bottom DSi concentration, indicating that resuspension contributes additional DSi to the water column. The data in these three figures suggest that the bottom sediment has a thin layer of low shear strength that is easily disturbed. Postma (1980) calls this layer “fluid mud,” describes it as typically occurring in the turbidity maximum zone of estuaries, and says it is composed of sediments of very uniform size. Sediments and diatom frustules in this layer are continually agitated, tumbled, and reworked. Fournier (1960) and Siever (1962) have shown that tumbling quartz and amorphous silica increase the ambient DSi concentrations. This sediment layer seems to be susceptible to resuspension by water velocities greater than 35 cm/s. Similar results were reported by Vanderborgh and others (1977) for sediments along the Belgian North Sea coast and by Schubel (1968) for sediments in Chesapeake Bay. Resuspension was consistently observed in the transition zone from 1979 to 1982 and can be expected to recur owing to the strength of the upriver near-bottom flow of dense seawater each summer.
Table 7. Average in situ and diffusive dissolved-silica fluxes for the tidal river, transition, and estuarine zones
[In millimoles per meter squared per day]

<table>
<thead>
<tr>
<th>Hydrodynamic zone</th>
<th>Dissolved silica flux</th>
<th>Ratio of in situ to diffusive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In situ</td>
<td>Diffusive</td>
</tr>
<tr>
<td>Tidal river</td>
<td>7.9 ± 1.5</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>Transition</td>
<td>12.2 ± 2.5</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>Estuarine</td>
<td>5.9 ± 0.9</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 24. Turbidity at three depths and near-bottom water velocity for a complete tidal cycle at Stuart Wharf, Va., August 26, 1982.

Figure 25. Suspended-sediment concentrations at three depths and near-bottom water velocity for a complete tidal cycle at Stuart Wharf, Va., August 26, 1982.
Table 8. Annual benthic loads of dissolved silica to the overlying water column, 1979–81 water years

<table>
<thead>
<tr>
<th></th>
<th>1979 water year</th>
<th>1980 water year</th>
<th>1981 water year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tidal Transition</td>
<td>Estuarine zone</td>
<td>Tidal Transition</td>
</tr>
<tr>
<td>Diffusive flux</td>
<td>2,200</td>
<td>2,300</td>
<td>24,000</td>
</tr>
<tr>
<td>loads</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In situ flux</td>
<td>5,900</td>
<td>14,000</td>
<td>87,000</td>
</tr>
<tr>
<td>loads</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ground-Water Discharge

Three stratigraphic units that have potential for increasing DSi concentrations in the water column intersect the tidal Potomac River and Estuary. These units are described in Table 9. The outcrop areas of these units in the southern Maryland area are shown in figure 27.

The Paleocene Aquia Formation and the Eocene Nanjemoy Formation have high (20 to 50 percent) glauconite content (Chapelle and Drummond, 1983). Water in equilibrium with glauconite has a DSi concentration of approximately 15 mg/L. The Miocene Calvert Formation is very diatomaceous, and water in equilibrium with it should have a DSi concentration of approximately 120 mg/L. These formations are probably covered with muds (Callender and Hammond, 1982) in the river channel itself; however, they are available for dissolution along the shore and by the tributaries. Tributary runoff into the Potomac would be expected to have higher DSi concentrations and contribute sediment from these formations. Table 10 shows a comparison of DSi values for two tributaries and the main stem Potomac River. The drainage basins for these tributaries are primarily in the Calvert and Nanjemoy Formations. The DSi concentrations in May for the two tributaries are 2.6 and 2.0 mg/L greater than the DSi concentration in the river. The August concentrations for the two tributaries show a 5.2 and 3.6 mg/L increase over the concentration in the river. These higher concentrations compared with the May concentrations are probably due to ground-water discharge and the dissolution of the siliceous materials as water seeps through these formations.

The effect of ground-water discharge into the tidal Potomac River and Estuary is greatest in the transition zone. Chapelle and Drummond (1983) give representative DSi concentrations of 49 mg/L for the Piney Point-Nanjemoy aquifer and 12 mg/L for the Aquia aquifer. Ground-water-quality data from Woll (1978) for wells bordering the Potomac in the transition zone show a range in DSi concentrations from 11 to 62 mg/L. The high DSi concentrations in the Piney Point-Nanjemoy aquifer are attributed to vertical leakage of water through the Calvert Formation, which is highly diatomaceous. There are no data available to quantify the amount of ground water discharged into the transition zone, but the effect probably would be greatest during periods of lowest freshwater inflow at Chain Bridge.

Estuarine Mixing

An estuary is the area where a river meets the sea. This meeting results in the mixing of two water bodies of very different compositions: river water high in particulate matter and seawater high in cations and anions. The possible reactions between the dissolved species in seawater and the particulate matter in river water has been widely studied, particularly in relation to the effect on the surface.) Chapelle and Drummond (1983) give representative DSi concentrations of 49 mg/L for the Piney Point-Nanjemoy aquifer and 12 mg/L for the Aquia aquifer. Ground-water-quality data from Woll (1978) for wells bordering the Potomac in the transition zone show a range in DSi concentrations from 11 to 62 mg/L. The high DSi concentrations in the Piney Point-Nanjemoy aquifer are attributed to vertical leakage of water through the Calvert Formation, which is highly diatomaceous. There are no data available to quantify the amount of ground water discharged into the transition zone, but the effect probably would be greatest during periods of lowest freshwater inflow at Chain Bridge.

![Figure 26. Vertical dissolved-silica profiles for an ebb and flood tide at Stuart Wharf, Va., August 26, 1982.](image-url)
<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Stratigraphic unit</th>
<th>Thickness (meters)</th>
<th>Dominant lithologic character</th>
<th>Water-bearing properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td>Holocene</td>
<td>Lowland and upland deposits</td>
<td>0-58</td>
<td>Sand, gravel, and silt; tan to rusty orange; predominantly quartz.</td>
<td>Yields small to moderate amounts of water to wells. Utilized primarily as a water source for shallow, domestic, and farm wells. The upper recharging water-table aquifer to the Aquia and Piney Point-Nanjemoy aquifers in southern Maryland.</td>
</tr>
<tr>
<td>Tertiary (?)</td>
<td>Pleistocene (?)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tertiary</td>
<td>Miocene</td>
<td>St. Marys Formation</td>
<td>0-24</td>
<td>Clay, sandy, silty; greenish-blue to gray; fossiliferous.</td>
<td>Functions as a confining bed.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Choptank Formation</td>
<td>0-18</td>
<td>Clay, silty; olive-green to gray; fossiliferous.</td>
<td>Functions as a confining bed.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calvert Formation</td>
<td>0-55</td>
<td>Clay, silty; olive-green to gray; fossiliferous; lower member is diatomaceous and contains phosphatic pebbles.</td>
<td>Functions as a confining bed.</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Eocene</td>
<td>Piney Point Formation</td>
<td>0-24</td>
<td>Sand, grayish-green to grayish-white; medium- to coarse-grained; quartz is most common mineral; glauconitic; calcite-cemented shell beds common.</td>
<td>Important source of water in southern Calvert and St. Marys Counties. Hydraulically connected to the upper sandy portion of the Nanjemoy Formation.</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Eocene</td>
<td>Nanjemoy Formation</td>
<td>0-76</td>
<td>Sand, silt, clay; brackish-green to gray; quartz most common mineral; glauconitic (30 to 50 percent); the upper portion of formation is predominantly sand; the lower part is predominantly silt and clay.</td>
<td>The upper sandy portion is an important source of water in Calvert and St. Marys Counties and is hydraulically connected to the overlying Piney Point Formation. The lower portion of the formation functions as a confining bed.</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Paleocene</td>
<td>Marlboro Clay Formation</td>
<td>0-11</td>
<td>Clay, pinkish-red to silvery-gray; very plastic; thin lenses of pale gray silt.</td>
<td>Functions as a confining bed.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aquia Formation</td>
<td>0-70</td>
<td>Sand, greenish-black; quartz most common mineral; glauconitic (20 to 40 percent); lenses of silty-clay and shell beds common; calcite concentration common.</td>
<td>A primary source of water in southern Anne Arundel County and in St. Marys and Calvert Counties. An important source of water in southern Charles and Prince George Counties.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brightseat Formation</td>
<td>0-12</td>
<td>Silt, clayey; gray to dark gray; micaceous.</td>
<td>Functions as a confining bed.</td>
</tr>
</tbody>
</table>

Concentration of DSI. However, there has been little consensus as to the fate of DSI during this mixing process. A summary of the major researchers and their conclusions is presented in table 11.

To examine whether or not such reactions take place, DSI samples were collected through the whole range of salinity in the estuary and the resultant DSI concentrations were plotted against salinity (fig. 28). The data indicate (1) conservative mixing and simple dilution of DSI if the points fall along a straight line, (2) removal of DSI if the line through the points appears concave, and (3) addition of DSI if the line through the points appears convex. This type of graphical analysis assumes that steady-state conditions in discharge and concentration...
Figure 27. Approximate locations of outcrop areas for the Aquia, Nanjemoy, and Calvert Formations.
prevail at both end members of the study site long enough to bring the estuary into equilibrium with each end member. This is seldom the case in the Potomac and other estuaries. Therefore, during this type of sampling, the proximity of the river and sea end members to steady-state conditions must carefully be observed and the DSi-salinity plots interpreted accordingly. Figure 29 presents a series of DSi-salinity plots for the 1980 and 1981 water years plus two additional plots from the data of Smith and Herndon (1979, 1980c) for the 1977 and 1978 water years. The plots are arranged in chronological order according to month of year. More than 1 yr is shown for most of the months. Inspection of figure 28 shows that virtually all of the DSi-salinity plots are nonconservative. Most of the variability can be explained by fluctuating discharge. There is, however, a consistent trend in the plots. This trend is the development of a source of DSi beginning in June, reaching its maximum in August and September, and continuing on into November. It is important to remember that this source is present in the transition zone. Several possible contributors to this source have already been mentioned: benthic flux, resuspension of a thin layer of surface sediment, water-column dissolution of diatom frustules, dissolution of siliceous materials contained in the stratigraphic units that crop out in the transition zone, and the discharge of ground water with a high DSi concentration. Figure 30 shows three consecutive monthly plots of DSi as a function of longitudinal distance. The plots show the development of the DSi source in the transition zone in a different perspective than the DSi-salinity plots in figure 29. Figure 30 shows a consistent DSi concentration at Chain Bridge, a decrease in concentration in the tidal river, and an increase in concentration in the transition zone. Mass-balance calculations in table 12 confirm the above observations. This increase in DSi concentration has been observed for other subestuaries of Chesapeake Bay (Anderson, 1982; D'Elia and others, 1983) but is absent from the literature reporting studies of other estuarine systems (table 11). This increase in DSi appears to be caused by the following process. In early summer, phytoplankton in the tidal river and the upper

reach of the transition zone begin taking up DSi. The phytoplankton die off in the middle reach of the transition zone, probably because of increased salinity and turbidity. Subsequently, in the lower reach of the transition zone, they release DSi through (1) water-column dissolution, (2) near-bottom dissolution enhanced by resuspension, and (3) incorporation in the bottom sediments for later release through benthic flux. Table 13 indicates that the mass of DSi released from the sediment in the transition zone is similar to the mass of DSi trapped in the tidal river zone by phytoplankton. It appears that the biogenic silica from the tidal river zone "feeds" the benthic flux of DSi in the transition zone. However, because there are no data available on biogenic silica concentrations, dissolution rates, or uptake rates, the exact processes acting cannot be determined. The data in figure 29 represent four very hydrologically different water years, yet this process is one that routinely recurs each year in the transition zone of the Potomac.

| Table 10. Dissolved-silica concentrations for the Potomac River and two tributaries, 1978 |

<table>
<thead>
<tr>
<th>Tributary</th>
<th>Date</th>
<th>Dissolved-silica concentration in tributary</th>
<th>Dissolved-silica concentration in Potomac River</th>
<th>Difference between dissolved-silica concentration in the tributary and in the Potomac River</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potomac Creek</td>
<td>23 August 1978</td>
<td>5.9</td>
<td>0.7</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>2 May 1978</td>
<td>6.6</td>
<td>4.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Port Tobacco</td>
<td>23 August 1978</td>
<td>6.6</td>
<td>3.0</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>2 May 1978</td>
<td>6.1</td>
<td>4.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 28. Three responses of dissolved silica during estuarine mixing.
Table 11. Summary of previous work on behavior of dissolved silica during estuarine mixing

[Modified from Boyle and others (1974) and DeMaster (1981). USA, United States of America; UK, United Kingdom]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Estuary</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maeda (1952, 1953)</td>
<td>Various: Japan</td>
<td>Conservative</td>
</tr>
<tr>
<td>Bien and others (1958)</td>
<td>Mississippi, USA</td>
<td>100 percent removal by inorganic processes</td>
</tr>
<tr>
<td>Stefasson and Richards (1963)</td>
<td>Columbia, USA</td>
<td>Conservative in winter and little biological removal in summer</td>
</tr>
<tr>
<td>Fa-Si and others (1964)</td>
<td>Jiu-long, China</td>
<td>20 to 30 percent removal</td>
</tr>
<tr>
<td>Kobayashi (1967)</td>
<td>Kiso and Nagara, Japan</td>
<td>Conservative</td>
</tr>
<tr>
<td>Banoub and Burton (1968)</td>
<td>Southampton, UK</td>
<td>Conservative</td>
</tr>
<tr>
<td>Burton (1970)</td>
<td>Vellar, India</td>
<td>Mixing of two freshwater components of differing composition with seawater</td>
</tr>
<tr>
<td>Burton and others (1970)</td>
<td>Southampton, UK</td>
<td>Conservative</td>
</tr>
<tr>
<td>Hosokawa and others (1970)</td>
<td>Chikugogawa, Japan</td>
<td>20 to 30 percent removal</td>
</tr>
<tr>
<td>Liss and Spencer (1970)</td>
<td>Conway, UK</td>
<td>10 to 20 percent inorganic removal</td>
</tr>
<tr>
<td>Park and others (1970)</td>
<td>Columbia, USA</td>
<td>Conservative in winter and little biological removal in summer</td>
</tr>
<tr>
<td>Wollast and DeBroeue (1971)</td>
<td>Scheldt, Netherlands</td>
<td>Removal by diatoms</td>
</tr>
<tr>
<td>Stephens and Oppenheimer (1972)</td>
<td>St. Marks, USA</td>
<td>20 to 30 percent removal</td>
</tr>
<tr>
<td>Dengler (1973)</td>
<td>Various: New England</td>
<td>Conservative</td>
</tr>
<tr>
<td>Fanning and Pilson (1973)</td>
<td>Orinoco, Venezuela</td>
<td>Ambiguous due to lack of freshwater end-member value</td>
</tr>
<tr>
<td></td>
<td>Savannah, USA</td>
<td>Conservative</td>
</tr>
<tr>
<td></td>
<td>Mississippi, USA</td>
<td>Approximately 7 percent removal; mechanism unresolved</td>
</tr>
<tr>
<td>Liss and Pointon (1973)</td>
<td>Alde, UK</td>
<td>20 to 30 percent removal by unspecified mechanism</td>
</tr>
<tr>
<td>Boyle and others (1974)</td>
<td>Merrimack, USA</td>
<td>Conservative</td>
</tr>
<tr>
<td>Milliman and Boyle (1975)</td>
<td>Amazon, Brazil</td>
<td>25 percent removal</td>
</tr>
</tbody>
</table>
Dissolved-Silica Budget

Results from an unsteady-state nutrient-transport box model are presented in table 14. The table does not show the actual loads of DSi, which were presented by Bennett (1983), but rather the percentage of the incoming load to a hydrodynamic zone that was transported or delivered to the next lower zone. The table also shows the percentage of DSi lost in a zone—that is, the percentage of the incoming DSi load that was not transported to the next zone in the form of DSi. Because of the lack of biogenic and mineral silica data, the amount of the silica that was transported to the next zone in either of these two other forms cannot be determined. However, it has already been shown that the loss of DSi is associated with phytoplankton uptake and that the loss is probably due to its conversion to the biogenic form.

For the 1979–81 water years, the tidal river and estuarine zones served as net traps for DSi. The losses of 25 percent in the tidal river zone and 8 percent in the estuarine zone can be attributed to phytoplankton uptake. The transition zone served as neither a net source of nor a net sink for DSi for the 3 yr of the study period. This is due to a lack of phytoplankton uptake in this zone and the large dissolution input of benthic and water-column particulate silica. On the whole, 71 percent of the DSi load entering at Chain Bridge was transported into Chesapeake Bay. This is not to say that the DSi that entered at Chain Bridge is the same DSi that was exported to Chesapeake Bay. The DSi most likely goes through several cycles of conversion to biogenic silica and dissolution back to DSi before it leaves the system. D'Elia and others (1983) suggest that for Chesapeake Bay an atom of silica from fluvial sources would pass through the production-sinkage-dissolution-efflux cycle at least five to eight times between entering and leaving the system.

Loads of DSi for various sources and sinks are presented in table 15. Of the sources listed, riverine input at Chain Bridge and benthic inputs dominate. Seasonally, the riverine input is most important during the wetter winter and spring months. The benthic input is most important in the summer, when water temperatures and salinities increase to cause the rate of efflux to increase.
The influence of sewage-treatment-plant effluent is essentially confined to the tidal river.

The lack of biogenic silica data indicates the need for further study of biogenic silica production and dissolution rates and concentrations. Understanding the processes that control the behavior of DSI can aid in the study of other, more complicated nutrients.

SUMMARY AND CONCLUSIONS

The following is a summary of the analysis of data relating to dissolved silica collected during the 1979-81 study period:

1. The major riverine source of DSI is the Potomac River at Chain Bridge: 77,000 Mg of DSI passed Chain Bridge during the 1979 water year, 85,000 Mg during the 1980 water year, and 26,000 Mg during the 1981 water year.

2. The discharge-weighted mean DSI concentration for the 1979-81 water years at Chain Bridge was 5.6 mg/L. The DSI concentration is positively correlated with discharge at Chain Bridge. Variations in monthly mean discharge explain half of the variation in the monthly mean DSI concentration. Other important factors affecting DSI concentration at...
Chain Bridge are phytoplankton, dilution during extreme flood events, and the hysteretic response of DSI to changes in river discharge.

3. Sewage-treatment-plant effluent in the Washington, D.C., metropolitan area contributes substantial amounts of DSI to the tidal river. On the average, the effluent concentration is 4.1 mg/L higher than that at Chain Bridge. Sewage-treatment plants supply 7 percent of the combined Chain Bridge-sewage treatment plant input for the study period.

4. Effluent from the Blue Plains Sewage-Treatment Plant has a strong influence on the DSI concentration at Alexandria, Va. Seventy-eight percent of the variation in the DSI concentration at Alexandria can be explained by adding the Blue Plains DSI load to the Chain Bridge DSI load.

5. The longitudinal DSI distribution is conservative when discharges at Chain Bridge are high. During summer, when discharges are typically low, other processes, such as phytoplankton uptake and benthic inputs, dominate and the DSI distribution becomes nonlinear.

6. The range of DSI concentrations observed during the 3-yr study period was 0.0 to 9.5 mg/L. Concentrations in the estuarine zone are generally the lowest because of dilution by Chesapeake Bay.

Figure 30. Longitudinal distributions of dissolved silica for July, August, and September 1980.
Table 12. Mass-balance calculations of dissolved silica, 1980 water year
[Loads of dissolved silica in megagrams]

<table>
<thead>
<tr>
<th>Month</th>
<th>Incoming load at Chain Bridge</th>
<th>Dissolved silica loss in tidal river zone</th>
<th>Dissolved silica gain in transition zone</th>
<th>Benthic dissolved silica input to water column based on in situ flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>2,700</td>
<td>-1,100</td>
<td>1,300</td>
<td>1,500</td>
</tr>
<tr>
<td>July</td>
<td>2,300</td>
<td>-2,100</td>
<td>1,300</td>
<td>1,700</td>
</tr>
<tr>
<td>August</td>
<td>2,400</td>
<td>-2,300</td>
<td>1,800</td>
<td>1,700</td>
</tr>
<tr>
<td>September</td>
<td>1,300</td>
<td>-1,400</td>
<td>3,300</td>
<td>1,600</td>
</tr>
<tr>
<td>October</td>
<td>800</td>
<td>-800</td>
<td>420</td>
<td>1,300</td>
</tr>
<tr>
<td>November</td>
<td>1,200</td>
<td>-670</td>
<td>1,500</td>
<td>930</td>
</tr>
<tr>
<td>Total</td>
<td>11,000</td>
<td>-8,300</td>
<td>9,600</td>
<td>8,700</td>
</tr>
</tbody>
</table>

7. The tidal river zone is consistently a sink for DSi because of the uptake of DSi by phytoplankton. The greatest loss of DSi in the tidal river zone occurs during summer, when conditions become optimal for phytoplankton growth. Concentrations often approach 0 mg/L during summer, when phytoplankton biomass reaches a maximum.

8. The transition zone can be characterized by its lack of phytoplankton biomass and DSi loss. During summer, transition zone DSi concentrations consistently increase because of increased benthic inputs of DSi and water-column dissolution. Benthic processes, such as resuspension, benthic efflux, and groundwater discharge, exert their strongest influence during summer.

9. The benthic processes appear to be fed by the transport of phytoplankton from the tidal river zone to the transition zone, where they typically die because of increased salinity, turbidity, and mean cross-sectional water depth.

10. During the 3-yr study period, the estuarine zone lost approximately 9 percent of all DSi transported into the zone. The prominent factors affecting DSi concentrations in this zone are phytoplankton and advective exchange with Chesapeake Bay. Chesapeake Bay water typically has lower DSi concentrations than Potomac River water, and the advective exchange between the two results in dilution of the Potomac water.

11. DSi concentrations in the pore water of Potomac River sediments is essentially always higher than the concentration in the overlying water column, resulting in a constant flux of DSi to the water column.

12. The primary factors that appear to affect the rate of DSi flux are macrofaunal irrigation, salinity, temperature, and rate of input of biogenic silica.

13. The annual DSi load based on benthic flux calculations is estimated to be 67,000 Mg. This annual...
**Table 14.** Results from transport box model for 1979-81 water years showing percentage of load delivered to next zone and percentage of load trapped in zone

[A negative value indicates a source of DSi in that zone]

<table>
<thead>
<tr>
<th>Zone</th>
<th>1979 water year</th>
<th>1980 water year</th>
<th>1981 water year</th>
<th>Combined 1979-81 water years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage</td>
<td>Percentage</td>
<td>Percentage</td>
<td>Percentage</td>
</tr>
<tr>
<td></td>
<td>delivered to</td>
<td>trapped in zone</td>
<td>delivered to</td>
<td>trapped in zone</td>
</tr>
<tr>
<td></td>
<td>next zone</td>
<td></td>
<td>next zone</td>
<td></td>
</tr>
<tr>
<td>Tidal river zone</td>
<td>75</td>
<td>25</td>
<td>81</td>
<td>58</td>
</tr>
<tr>
<td>Transition zone</td>
<td>89</td>
<td>11</td>
<td>104</td>
<td>-4</td>
</tr>
<tr>
<td>Estuarine zone</td>
<td>133</td>
<td>-33</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>Total percent</td>
<td>94</td>
<td>6</td>
<td>63</td>
<td>37</td>
</tr>
</tbody>
</table>

**Table 15.** Dissolved-silica budget for the tidal Potomac River and Estuary, 1979-81 water years

[Mass in megagrams of SiO₂]

<table>
<thead>
<tr>
<th>Source</th>
<th>1979</th>
<th>1980</th>
<th>1981</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riverine supply at Chain Bridge</td>
<td>77,100</td>
<td>85,100</td>
<td>26,300</td>
<td>Blanchard and Hahl (1985)</td>
</tr>
<tr>
<td>Sewage-treatment-plant effluent</td>
<td>5,500</td>
<td>7,000</td>
<td>4,200</td>
<td></td>
</tr>
<tr>
<td>Nonpoint sources</td>
<td>34,400</td>
<td>25,100</td>
<td>9,000</td>
<td>Hickman (1984)²</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>86</td>
<td>86</td>
<td>86</td>
<td>Hickman (1984)</td>
</tr>
<tr>
<td>Benthic input</td>
<td>67,800</td>
<td>67,700</td>
<td>66,700</td>
<td></td>
</tr>
<tr>
<td>Ground water</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Water-column dissolution of biogenic silica</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

**Sink**

<table>
<thead>
<tr>
<th></th>
<th>1979</th>
<th>1980</th>
<th>1981</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion to biogenic silica</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Net loss to Chesapeake Bay</td>
<td>124,000</td>
<td>81,000</td>
<td>12,500</td>
<td>Bennett (1983)³</td>
</tr>
</tbody>
</table>

¹Sewage-treatment-plant loading based on Blue Plains Sewage-Treatment-Plant loads presented in table 1 plus an additional 25 percent of the Blue Plains load to account for the other sewage-treatment plants along the Potomac.

²Nonpoint-source loadings are tributary inputs to the main stem of the Potomac.

³Benthic loading is estimated from the average of the loadings calculated from diffusive and in situ flux measurements presented in table 8.

⁴Estimated from the results of an unsteady-state nutrient-transport model.
benthic load is based on the average of the diffusive and in situ fluxes.

14. Resuspension has repeatedly been observed in the transition zone. Resuspension acts on the surface layer of bottom sediment by tumbling and reworking the sediment, thereby increasing benthic input of DSI to the overlying water column.

15. Ground-water discharge into the tidal Potomac River and Estuary has its greatest potential for effect in the transition zone. DSI concentrations in ground water from aquifers that discharge into the transition zone range from 12 to 49 mg/L. The rate of discharge, however, has not been determined.

16. Considerable attention has been given to the fate of DSI during the mixing of fresh river water and seawater. The majority of the work to date has shown that conservative behavior is one response and the loss of DSI because of phytoplankton uptake or biological removal is another response. The Potomac River is somewhat unique in that DSI mass increases have been shown to occur during summer in the mixing zone. This is attributed to benthic processes and possibly to water-column dissolution of biogenic silica. The biogenic silica is transported from the tidal river to the transition zone as diatom frustules, which act to feed the benthic and water-column processes that convert the biogenic silica to a dissolved form.

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the Aquia aquifer, Maryland: Groundwater, v. 21, no. 3, p.
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APPENDIX: LONGITUDINAL DISSOLVED-SILICA AND SALINITY PROFILES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Date</th>
<th>Page</th>
</tr>
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<tr>
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<td>H42</td>
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<td>October 7, 1979</td>
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<tr>
<td>A3</td>
<td>January 17, 1980</td>
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</table>
Figure A1. Longitudinal dissolved-silica and salinity profiles, August 2, 1979.

Figure A2. Longitudinal dissolved-silica and salinity profiles, October 7, 1979.

Figure A3. Longitudinal dissolved-silica and salinity profiles, January 17, 1980.

Figure A4. Longitudinal dissolved-silica and salinity profiles, February 18, 1980.

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Figure A5. Longitudinal dissolved-silica and salinity profiles, March 19, 1980.

Figure A6. Longitudinal dissolved-silica and salinity profiles, May 20, 1980.

Figure A7. Longitudinal dissolved-silica and salinity profiles, June 18, 1980.

Figure A8. Longitudinal dissolved-silica and salinity profiles, July 23, 1980.
Figure A9. Longitudinal dissolved-silica and salinity profiles, August 19, 1980.

Figure A10. Longitudinal dissolved-silica and salinity profiles, September 18, 1980.

Figure A11. Longitudinal dissolved-silica and salinity profiles, October 22, 1980.

Figure A12. Longitudinal dissolved-silica and salinity profiles, November 18, 1980.
Figure A13. Longitudinal dissolved-silica and salinity profiles, December 16, 1980.

Figure A14. Longitudinal dissolved-silica and salinity profiles, February 5, 1981.

Figure A15. Longitudinal dissolved-silica and salinity profiles, March 4, 1981.

Figure A16. Longitudinal dissolved-silica and salinity profiles, April 16, 1981.
Figure A17. Longitudinal dissolved-silica and salinity profiles, May 20, 1981.

Figure A18. Longitudinal dissolved-silica and salinity profiles, July 1, 1981.

Figure A19. Longitudinal dissolved-silica and salinity profiles, July 28, 1981.

Figure A20. Longitudinal dissolved-silica and salinity profiles, August 19, 1981.
Figure A21. Longitudinal dissolved-silica and salinity profiles, September 22, 1981.
METRIC CONVERSION FACTORS

For use of readers who prefer to use metric (SI) units, conversion factors for terms used in this report are listed below:

<table>
<thead>
<tr>
<th>Multiply</th>
<th>By</th>
<th>To obtain</th>
</tr>
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<tbody>
<tr>
<td>Length</td>
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</tr>
<tr>
<td>inch (in)</td>
<td>25.4</td>
<td>millimeter (mm)</td>
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<tr>
<td>foot (ft)</td>
<td>0.3048</td>
<td>meter (m)</td>
</tr>
<tr>
<td>mile (mi)</td>
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<td>kilometer (km)</td>
</tr>
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<td>acre</td>
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<td>square inch (in²)</td>
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<td>square centimeter (cm²)</td>
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<td>Volume</td>
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<td>gallon (gal)</td>
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<td>cubic meter (m³)</td>
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<tr>
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<td>cubic meter (m³)</td>
</tr>
<tr>
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<td>cubic meter (m³)</td>
</tr>
<tr>
<td>Flow</td>
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<tr>
<td>foot per second (ft/s)</td>
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<td>meter per second (m/s)</td>
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<tr>
<td>foot per day (ft/d)</td>
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<td>meter per day (m/d)</td>
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<tr>
<td>cubic foot per second (ft³/s)</td>
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<td>cubic meter per second (m³/s)</td>
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<td>cubic meter per day (m³/d)</td>
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<td>cubic meters per second (m³/s)</td>
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<td>gram (g)</td>
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<td>ton, short</td>
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<td>megagram (Mg)</td>
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<tr>
<td>Temperature</td>
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<tr>
<td>degree Fahrenheit (°F)</td>
<td>°C = 5/9(°F-32)</td>
<td>degree Celsius (°C)</td>
</tr>
</tbody>
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Preliminary Determination of Epicenters (issued monthly).

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