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EFFECTS OF BASIN SIZE ON LOW-FLOW STREAM CHEMISTRY AND SUBSURFACE CONTACT TIME IN THE NEVERSINK RIVER WATERSHED, NEW YORK

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ABSTRACT

The effects of basin size on low-flow stream chemistry and subsurface contact time were examined for a part of the Neversink River watershed in southern New York State. Acid neutralizing capacity (ANC), the sum of base cation concentrations (SBC), pH and concentrations of total aluminum (Al), dissolved organic carbon (DOC) and silicon (Si) were measured during low stream flow at the outlets of nested basins ranging in size from 0·2 to 166·3 km^2. ANC, SBC, pH, Al and DOC showed pronounced changes as basin size increased from 0·2 to 3 km^2, but relatively small variations were observed as basin size increased beyond 3 km^2. An index of subsurface contact time computed from basin topography and soil hydraulic conductivity also showed pronounced changes as basin size increased from 0·2 to 3 km^2 and smaller changes as basin size increased beyond 3 km^2. These results suggest that basin size affects low-flow stream chemistry because of the effects of basin size on subsurface contact time. © 1997 by John Wiley & Sons, Ltd.

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KEY WORDS subsurface contact time; stream chemistry; basin size

INTRODUCTION

Stream chemistry at a given location in a drainage basin during low-flow periods is determined by several factors. Among the most important factors are: (1) the chemistry of precipitation that falls on the basin draining to that location; (2) the biogeochemical processes that modify the chemistry of water as it drains along subsurface flow paths to the location of interest; and (3) subsurface contact time (i.e. the length of time it takes for water to drain along subsurface flow paths to the stream) (Johnson *et al.*, 1981; Wolock *et al.*, 1989). Subsurface contact time is important because geochemical processes, such as weathering, that modify the chemistry of water that moves along subsurface flow paths are kinetically dependent (Reuss and Johnson, 1986; Reuss and Walthall, 1989).

One factor that may reflect processes affecting stream chemistry at any location in a watershed is the size of the basin defined by that location. The effect of basin size on the spatial variability of stream flow response to precipitation has been a subject of debate (Beven *et al.*, 1988; Wood *et al.*, 1988, 1990; Garbrecht, 1991; Fan and Bras, 1995; Wolock, 1995). The concept of a ‘representative elementary area’ (REA) for stream flow response to precipitation was proposed by Wood *et al.* (1988, 1990). This concept suggests that the variability of stream flow response to precipitation between basins within a watershed is large when the basins are small; as basin size increases, the variability tends to decrease and then stabilize at more or less a constant level. Wood *et al.* (1988, 1990) refer to the basin size at which the stream flow response stabilizes as the REA. The size of the REA, in theory, is related to basin topography and soil characteristics (Wood *et al.*, 1988; Wolock, 1995).

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Only a few studies have addressed spatial patterns of stream chemistry within a basin (Merot and Bruneau, 1992). Previous studies have primarily examined the correlation between elevation and stream chemistry, between flow path length and stream chemistry, between stream order and stream chemistry and between soil catena and stream chemistry (Johnson *et al.*, 1981; Lawrence *et al.*, 1986, 1988; Lawrence and Driscoll, 1990). These studies, however, all focused on small watersheds, ranging in size from a few hectares to a few square kilometres.

The first objective of this study is to examine how low-flow stream chemistry varies with basin size across a wide range of basin sizes. Because low-flow stream chemistry is thought to be related to subsurface contact time, which in turn is determined by basin topography and soil hydraulic conductivity (Wolock *et al.*, 1989), the second objective is to examine the relationship of basin size to an index describing the subsurface contact time of water in the basin. This is done to see if similar patterns can be found for basin topography, soil hydraulic conductivity, subsurface contact time and stream chemistry with respect to basin size. These objectives are accomplished by analysing stream chemistry, topographic and soil hydraulic data for nested basins, ranging in size from 0·2 to 166 km^2, in the Neversink River watershed, New York.

STUDY AREA

The Neversink River watershed (Figure 1) in the Catskill Mountains of southern New York State was selected as the study area because stream flow and stream chemistry data have been made available through an intensive data collection programme conducted by the US Geological Survey (USGS) (Lawrence *et al.*, 1995a). The Neversink River watershed is an ideal site to examine the relationship between stream chemistry and subsurface contact time because the bedrock mineralogy of the watershed is mostly uniform (Murdoch, 1991).

The Neversink River watershed is drained by a clear, energetic mountain river, which is confined to a narrow valley with steep slopes. Underlying the watershed are flat-lying, Devonian age, sedimentary rocks overlain by glacial deposits and alluvium (Rich, 1934; Way, 1972). Bedrock underlying the watershed is about 60% sandstone and conglomerate and 40% shale and siltstone, which are dominated by slowly weathering silicate minerals. The bedrock of the watershed is overlain by till and coarse rocks derived from past glaciations.

Most of the soils are classified as inceptisols in the Arnot, Oquaga and Lackawanna series (Tornes, 1979; Seifried, 1989). Some spodosols occur beneath coniferous stands. The soils vary in thickness (about 0–1 m), and are excessively to moderately well drained, predominantly very steep and medium textured on the uplands. Some of the soils have a dense, cement-like fragipan beginning at a depth of 0·5–1 m below the land surface. The presence of a fragipan slows the infiltration of water into the soil profile and may result in perched groundwater during and after rainstorms. The soils tend to have a low base saturation, which reflects the base-poor local bedrock. The Neversink River basin receives high inputs of acidic deposition which are reflected in acidic stream water (Lawrence *et al.*, 1995a).

Vegetation is primarily northern hardwood forest, dominated by American beech, sugar maple and yellow birch. At elevations above 1000 m, balsam fir is the dominant tree species (*Kudish*, 1979). Stands of hemlock also occur in poorly drained soils and along stream channels.

The Neversink River watershed has a population of less than 1300 people with minimal development or agriculture. There has been only limited harvesting of forests over the past several decades (Lawrence *et al.*, 1995a).

EFFECTS OF BASIN SIZE ON STREAM CHEMISTRY

Stream flow was measured continuously at seven gauging stations (Figure 1). Because the stream flow hydrographs for all the gauges showed close temporal synchronism, the times when low stream flow occurred were determined by discharge values recorded at the Main Branch gauge (Figure 1). Low-flow periods were defined as times when stream flow at the Main Branch gauge was less than or equal to the 40th percentile value. Chemical data corresponding to the low-flow periods were obtained for stream sampling sites located

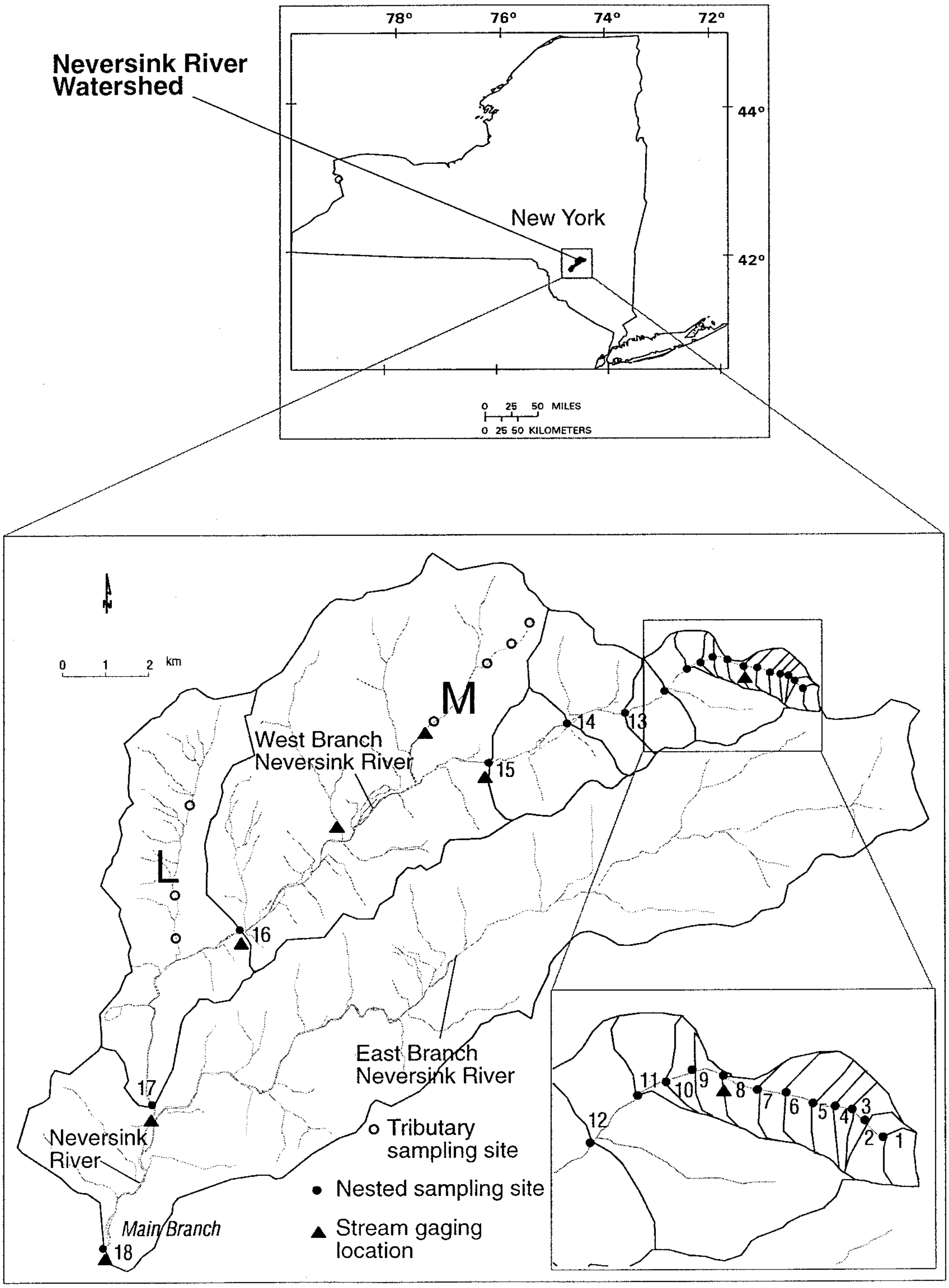


Figure 1. Location of the Neversink River watershed, 18 nested basins, sampling sites and stream gauging stations in the Neversink River watershed. The letters L and M show the location of lower and middle tributaries to the Neversink River where seven additional sites were sampled

Table I. Basin area and number of low-flow samples collected for 18 nested sampling sites in the Neversink River

Basin sampling site number	Basin area (km^2)	Number of samples
1	0·2	31
2	0·4	24
3	0·6	27
4	0·7	34
5	1·0	28
6	1·4	34
7	1·6	30
8	1·8	30
9	2·0	22
10	2·3	23
11	2·8	21
12	6·2	22
13	8·2	21
14	14·0	21
15	19·7	24
16	64·2	22
17	84·5	23
18	166·3	26

Table II. List of chemical constituents and their units of measurement

Chemical constituents	Definition and units
ANC	Acid neutralizing capacity, $\mu eq\ l^{-1}$
SBC	Sum of base cations (Ca^{2+}, Mg^{2+}, K^+), $\mu eq\ l^{-1}$
pH	Negative logarithm of H^+ activity
Al	Total aluminum, $\mu mol\ l^{-1}$
DOC	Dissolved organic carbon, $\mu mol\ C\ l^{-1}$
Si	Silicon (commonly in the form of H_4SiO_4), $\mu mol\ l^{-1}$

at the outlets of 18 nested sub-basins located along the West and Main Branches of the Neversink River (Figure 1). An additional seven sites in two tributaries (denoted M for middle and L for lower in Figure 1) of the West Branch were also sampled. The sites were chosen because multiple low-flow samples were available during the study period (October 1990–September 1993). Basin boundaries were generated automatically for the sites using the ARC/INFO geographical information system package (Environmental Systems Research Institute, Inc., Redlands, California). (The use of trade names is for identification purposes only and does not constitute endorsement by the USGS.) The size of the nested basins along the Neversink River ranged from 0·2 to 166·3 km^2 (Table I).

The stream chemistry data presented for the 18 nested sites in the Neversink River are the median (50th percentile), 25th, and 75th percentile concentrations for the low-flow samples. The samples were analysed for acid neutralizing capacity (ANC), the sum of base cation concentrations (SBC), pH and concentrations of total aluminum (Al), dissolved organic carbon (DOC), and silicon (Si) (Table II) at the USGS Albany District laboratory according to methods given in Lawrence *et al.* (1995b). Concentrations of sodium (Na^+) were not included when SBC was computed because of the potential confounding effects of road salt application near some stream reaches during the winter months. For the seven additional tributary sites, only mean ANC values are presented.

At some sampling sites, stream flow samples were collected biweekly for two years and monthly for the third year; other sites were sampled biweekly for the entire three-year period (Lawrence *et al.*, 1995a). The total number of low-flow samples included in the analysis ranged from 21 to 34 amongst the nested sampling sites in the Neversink River (Table I).

The low-flow stream chemistry concentrations varied as basin size increased from smaller to larger basins for the 18 nested sites in the Neversink River (Figure 2). The concentrations changed most rapidly when basin size was less than 3 km^2 and varied less for basin sizes greater than this threshold value. As basin size increased from 0·2 to 3 km^2, pronounced increases were observed in ANC, SBC and pH, whereas pronounced decreases were observed for Al and DOC concentrations. Si concentrations, in contrast, varied erratically as basin size increased from 0·2 to 3 km^2.

ANC, SBC and pH remained high for basin sizes greater than 3 km^2, with little variability up to 20 km^2 (Figure 2). Some variations of ANC, SBC and pH were observed when basin size increased further to 166 km^2, but the gradients of change in concentration were less. For basin sizes greater than 3 km^2, Al and DOC remained at low concentrations. A similar pattern was observed for total monomeric and organic monomeric aluminum (Fan, 1995). Si concentrations, in contrast, varied for basins larger than 3 km^2, but the gradient of change in concentration for basins larger than 3 km^2 was less than the gradient of change in concentration for basins smaller than 3 km^2.

The effects of basin size on low-flow concentrations of ANC, SBC, pH, Al and DOC were large compared with the temporal variability (as indicated by the range between the 25th and 75th percentile values) of these constituents at each sampling site (Figure 2). The effect of basin size on low-flow concentrations of Si, in contrast, was small relative to temporal variability at each sampling site. Temporal variability in Si concentrations was greater than the effect of basin size, even when the Si data were grouped by season (D. M. Wolock, unpublished data).

EFFECTS OF BASIN SIZE ON TOPOGRAPHY, SATURATED HYDRAULIC CONDUCTIVITY AND SUBSURFACE CONTACT TIME

Subsurface contact time reflects the length of time that water is in contact with soils and subsoils of a watershed before discharging into stream channels, and it is related to basin topographic and soil characteristics (Wolock *et al.*, 1989). Basin topography affects the distance that water has to travel to reach the stream channel and the rate at which water passes through the subsurface layer. Soil hydraulic conductivity also affects how rapidly water can drain through the system.

A subsurface contact time index, which is based on the conceptual framework of the watershed model TOPMODEL, was computed from readily available topographical and soil characteristics data (Wolock *et al.*, 1989); therefore, it is a direct representation of only those watershed characteristics on subsurface contact time.

The subsurface contact index for each basin was computed by dividing an estimate of the pore volume of the soil mantle by an index of the water flux through the soil. Beven (1986) has shown that an index of the subsurface flow rate for a basin can be expressed as $A_{\mathrm{tot}}K_{\mathrm{ave}}z_{\mathrm{ave}}\,\mathrm{e}^{-\lambda}$, where A_{tot} (m^2) is total basin area, K_{ave} (m d^{-1}) is the mean saturated hydraulic conductivity for the basin, z_{ave} (m) is the average soil thickness and λ is the mean of the topographic variable $\ln(a/\tan\beta)$ for the basin (a is the upslope area per unit contour length and $\tan\beta$ is the slope gradient). Because the soil mantle volume can be estimated as $A_{\mathrm{tot}}z_{\mathrm{ave}}n$ [n (fraction) is the mean soil porosity for the basin expressed as the ratio of pore volume to total soil volume], the subsurface contact time index [T_{c} (days)] can be derived as follows:

$$T_{\mathrm{c}} = \frac{\text{Volume}}{\text{Flux}} \tag{1}$$

$$T_{\mathrm{c}} = \frac{A_{\mathrm{tot}}z_{\mathrm{ave}}n}{A_{\mathrm{tot}}K_{\mathrm{ave}}z_{\mathrm{ave}}\,\mathrm{e}^{-\lambda}} \tag{2}$$

$$T_{\mathrm{c}} = \frac{n\,\mathrm{e}^{\lambda}}{K_{\mathrm{ave}}} \tag{3}$$

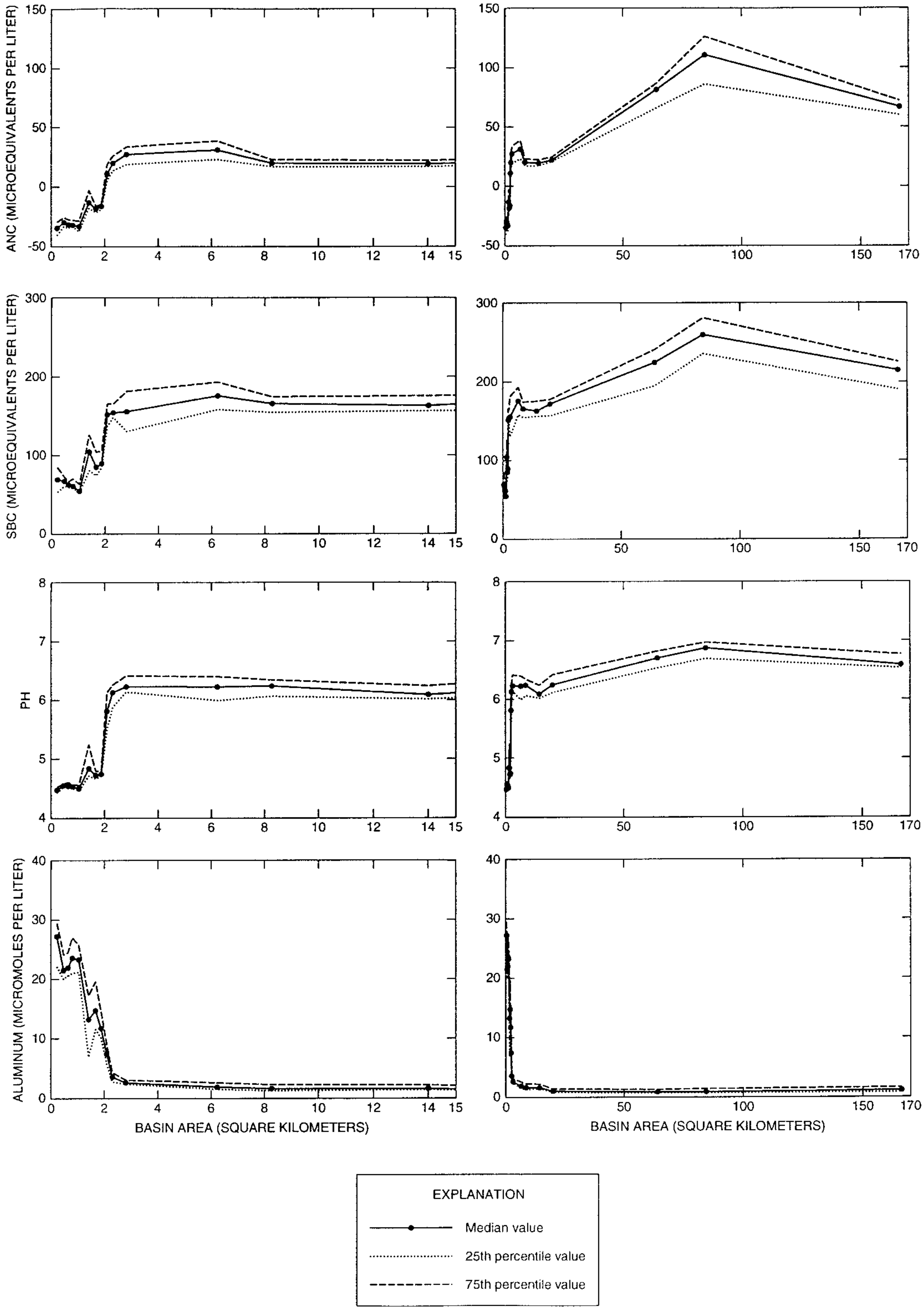


Figure 2. Caption on opposite page

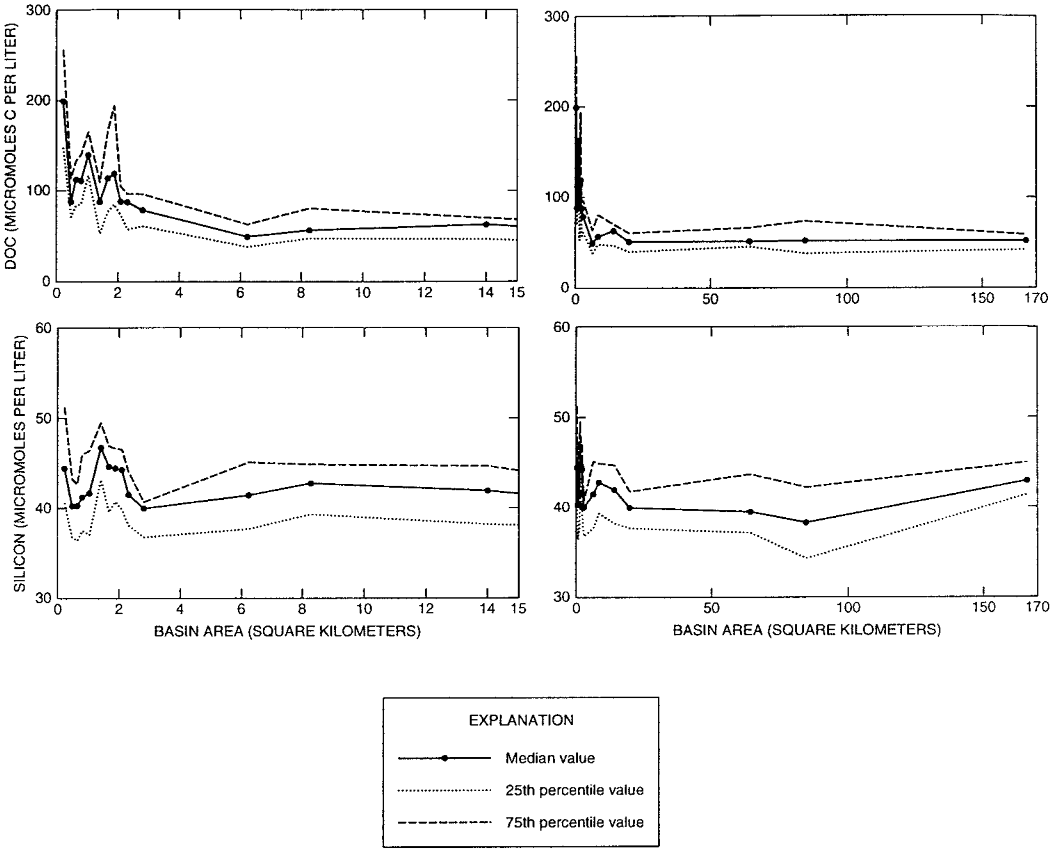


Figure 2. Relationships of median, 25th percentile, and 75th percentile low-flow stream chemistry concentrations with basin area for the 18 nested sites in the Neversink River. The graphs on the left show data for basins smaller than 15 km^2, and the graphs on the right show data for all basins

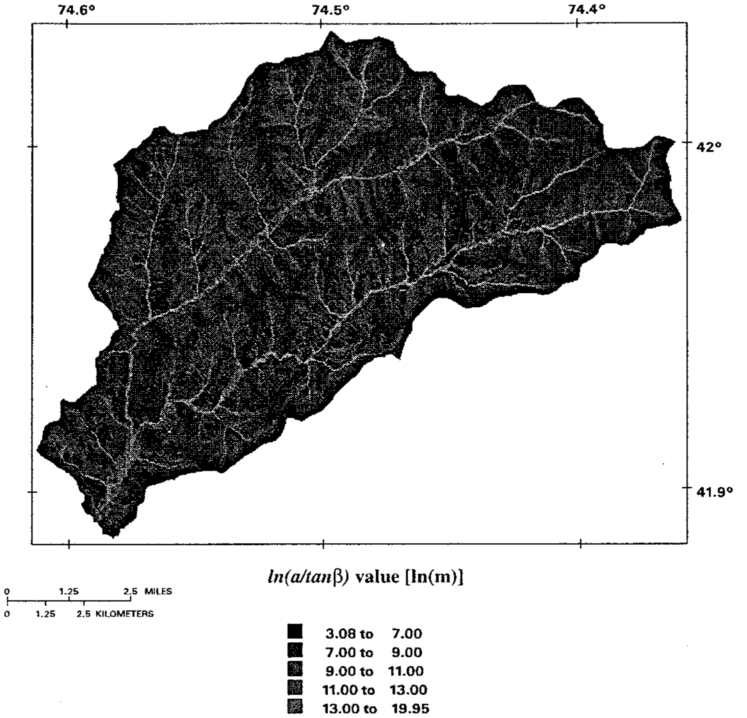
Equation (3) shows that the subsurface contact time index is related directly to the mean soil porosity and the mean of the $\ln(a/\tan\beta)$ distribution. The equation also shows that the subsurface contact time index is related inversely to the mean saturated hydraulic conductivity.

The topographic variable $\ln(a/\tan\beta)$ was computed using the GRID module of ARC/INFO from a digital elevation model (DEM), which is a gridded digital representation of the land surface topography. A multiple flow direction algorithm (Wolock and McCabe, 1995) was used to compute $\ln(a/\tan\beta)$ values at every point in a 30 m × 30 m resolution DEM for the study area. The spatial distribution of $\ln(a/\tan\beta)$ values for the Neversink River watershed above the Main Branch gauging station is shown in Figure 3.

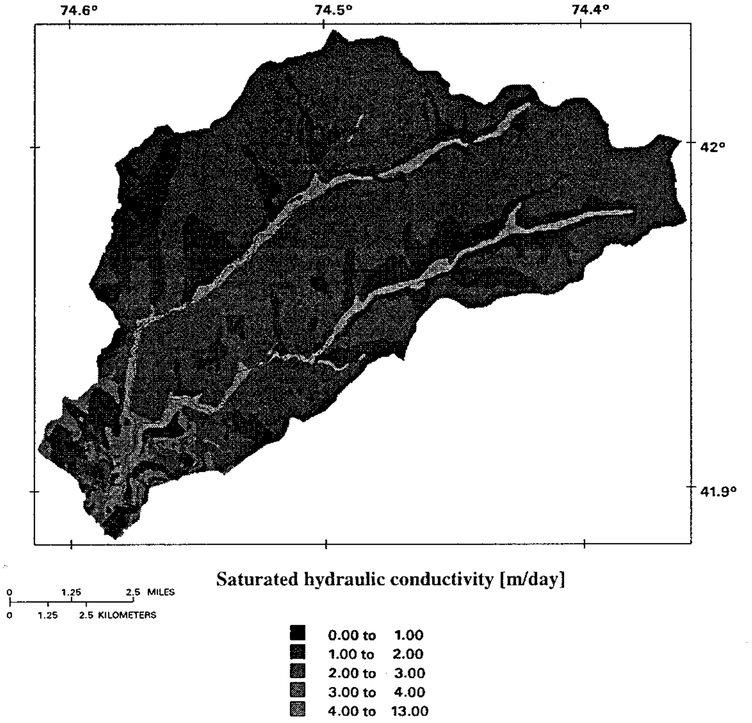
Soil hydraulic data (mean saturated hydraulic conductivity and porosity) were derived from digitized US Department of Agriculture Natural Resources Conservation Service (NRCS) soil survey maps (Tornes, 1979; Seifried, 1989). Figure 3 shows the spatial distribution of saturated hydraulic conductivity in the study area.

Mean values of $\ln(a/\tan\beta)$ and saturated hydraulic conductivity were computed for the basins defined by the stream sampling sites (see Figure 1) and used in Equation (3) to estimate subsurface contact time index values. Mean soil porosity was estimated from bulk density data assuming a particle density of 2·65 $\mathrm{g\ cm^{-3}}$. A single mean value (0·494) for soil porosity was used in Equation (3) for all the basins because bulk density values were not estimated everywhere in the two soil survey maps that cover the study area.

It is very unlikely that saturated hydraulic conductivity in the Neversink River watershed varies as smoothly over space as Figure 3 depicts. The smooth spatial pattern in the figure reflects the generalized



*ln(a/tan*β*)* **value [ln(m)]**



Saturated hydraulic conductivity [m/day]

Figure 3. Spatial distributions of $\ln(a/\tan\beta)$ and saturated hydraulic conductivity values for the Neversink River watershed (a is the upslope area per unit contour length and $\tan\beta$ is the slope gradient)

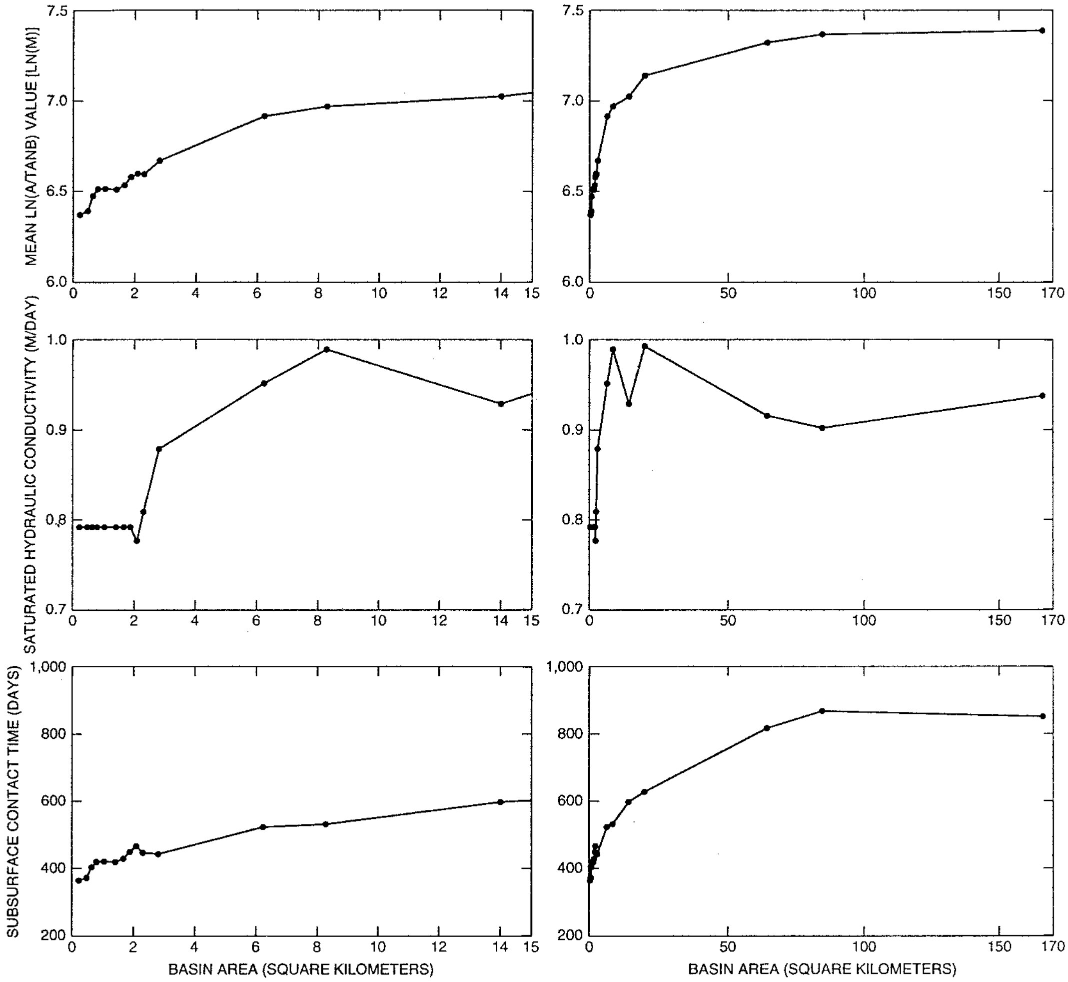


Figure 4. Relationship between mean ln(a/tan β) value, saturated hydraulic conductivity, subsurface contact time index, and basin area for the 18 nested sites in the Neversink River. The graphs on the left show data for basins smaller than 15 km^2, and the graphs on the right show data for all basins

nature of the NRCS soil survey maps. Soil characteristics such as the basin mean values for soil porosity and saturated hydraulic conductivity in Equation (3), however, are probably more affected by spatial aggregation than by the generalizations used to construct the soil survey map.

The mean ln(a/tan β) value ranged from 6·3, for the headwater basin, to 7·3, for the basin located furthest downstream in the Neversink River (Figure 4; see Figure 1 for basin locations). The lower mean values of ln(a/tan β) observed for the upstream basins occur for two reasons: (1) the hillslopes generally are steeper in the headwaters compared with the downstream tributaries, which results in higher values of tan β in the headwaters; and (2) the mean upslope area per unit contour length, a, is lower in the most upstream basins.

The gradient of increase in the mean ln(a/tanβ) value was greatest when basin size was less than 1 km^2 (Figure 4). A lower gradient of change in the mean ln(a/tan β) value occurred as basin size increased from 1 to 7 km^2, and an even smaller gradient of increase was observed as basin size increased from 7 to about 20 km^2. For basins greater than 20 km^2, the changes in the mean ln(a/tan β) values were very small. A similar pattern in mean ln(a/tan β) values was seen amongst sets of nested basins in the Sleepers River, Vermont watershed (Wolock, 1995).

Mean saturated hydraulic conductivity for the basins did not vary (0·79 m d^{-1}) when basin size was smaller than 2 km^2 (Figure 4). This constant value of mean saturated hydraulic conductivity for basins smaller than 2 km^2 is an artefact of the coarse resolution of the soil survey data; all basins smaller than 2 km^2 were contained entirely within a single soil mapping unit. Mean saturated hydraulic conductivity increased from 0·78 to almost 1·0 m d^{-1} when basin size increased from 2 to 10 km^2. When the basin size was greater than 10 km^2, mean saturated hydraulic conductivity varied between 0·9 and 1·0 m d^{-1}.

The subsurface contact time index [see equation (3)] increased from 295 to 803 days as basin size increased from 0·2 to 84 km^2 and then remained almost constant for larger basins (Figure 4). The gradient of change of the subsurface contact time index was greatest for the smallest basins. Increases in basin size from 2 to 10 km^2 were associated with increases in the mean $\ln(a/\tan\beta)$ values (λ) and increases in the mean saturated hydraulic conductivity (K_{ave}); the increases in these two variables had opposite effects on the subsurface contact time index because λ and K_{ave} are in the numerator and denominator of Equation (3), respectively.

Values computed for the subsurface contact time index are higher than preliminary on-site investigations using isotope analyses in the Neversink River watershed suggest, especially for the smaller upstream basins with steep slopes (D. A. Burns, USGS, written communication). The higher values of the subsurface contact time index compared with on-site estimates can be explained by the lack of consideration of macropore flow in the index. In the Neversink River watershed, the soil, subsoil and fractured bedrock provide numerous conduits for rapid subsurface transmission of water. Although the index is likely to overestimate the actual subsurface contact time in this watershed, this measure nevertheless provides an easily computed index that can be used to compare different basins in the watershed.

RELATION BETWEEN STREAM CHEMISTRY AND SUBSURFACE CONTACT TIME

Low-flow values of ANC, SBC and pH increased with increasing subsurface contact time, whereas Al and DOC low-flow concentrations decreased with increasing contact time; Si, in contrast, was unrelated to subsurface contact time (Figure 5 shows data for the 18 nested sites in the Neversink River).

The strength of a monotonic (constantly increasing or decreasing) relation between the stream chemistry constituents and the subsurface contact time index was measured by the Spearman rank correlation coefficient. The rank correlation coefficient was significant ($p = 0{\cdot}0001$) and positive for ANC, SBC and pH; the rank correlation coefficient was significant ($p = 0{\cdot}0001$) and negative for Al and DOC (Figure 5).

ANC, SBC, pH, Al and DOC showed pronounced changes as basin size increased from 0·2 to 3 km^2, but relatively small variations were observed as basin size increased beyond 3 km^2 (see Figure 2). This pattern can be attributed to subsurface contact time, which was estimated from basin topography and soil hydraulic characteristics. The greatest increases in the mean of the topographic variable, $\ln(a/\tan\beta)$ (see Figure 4), coincided with the greatest changes in low-flow stream chemistry. This suggests that topography, through its effect on subsurface contact time, is an important factor in determining the effects of basin size on low-flow stream chemistry. These results are consistent with the assertion made by Wood *et al.* (1988) that topography is an important watershed characteristic in determining the size of the 'representative elementary area' (REA). Although Wood *et al.* (1988) proposed the REA concept for stream flow response to precipitation, the results shown here suggest that the REA concept can be extended to stream chemistry.

The steep increase of ANC with basin size (see Figure 2), for basins smaller than 3 km^2, indicates that acid neutralization increases as basin size increases, possibly owing to greater opportunity for mineral weathering. At headwater locations, water passes quickly through subsurface layers; thus, there is a limited time for water to react with the silicate minerals of the basin. As basin size increases, acid neutralization also increases because the time that water is in contact with the subsurface layers may also increase. When basin size is greater than 3 km^2, the variations of most stream flow solutes with basin size become dampened; the results of this study suggest that this effect is related to the reduction of variations in subsurface contact time resulting from the reduction of variations in mean topographic and soil hydraulic characteristics.

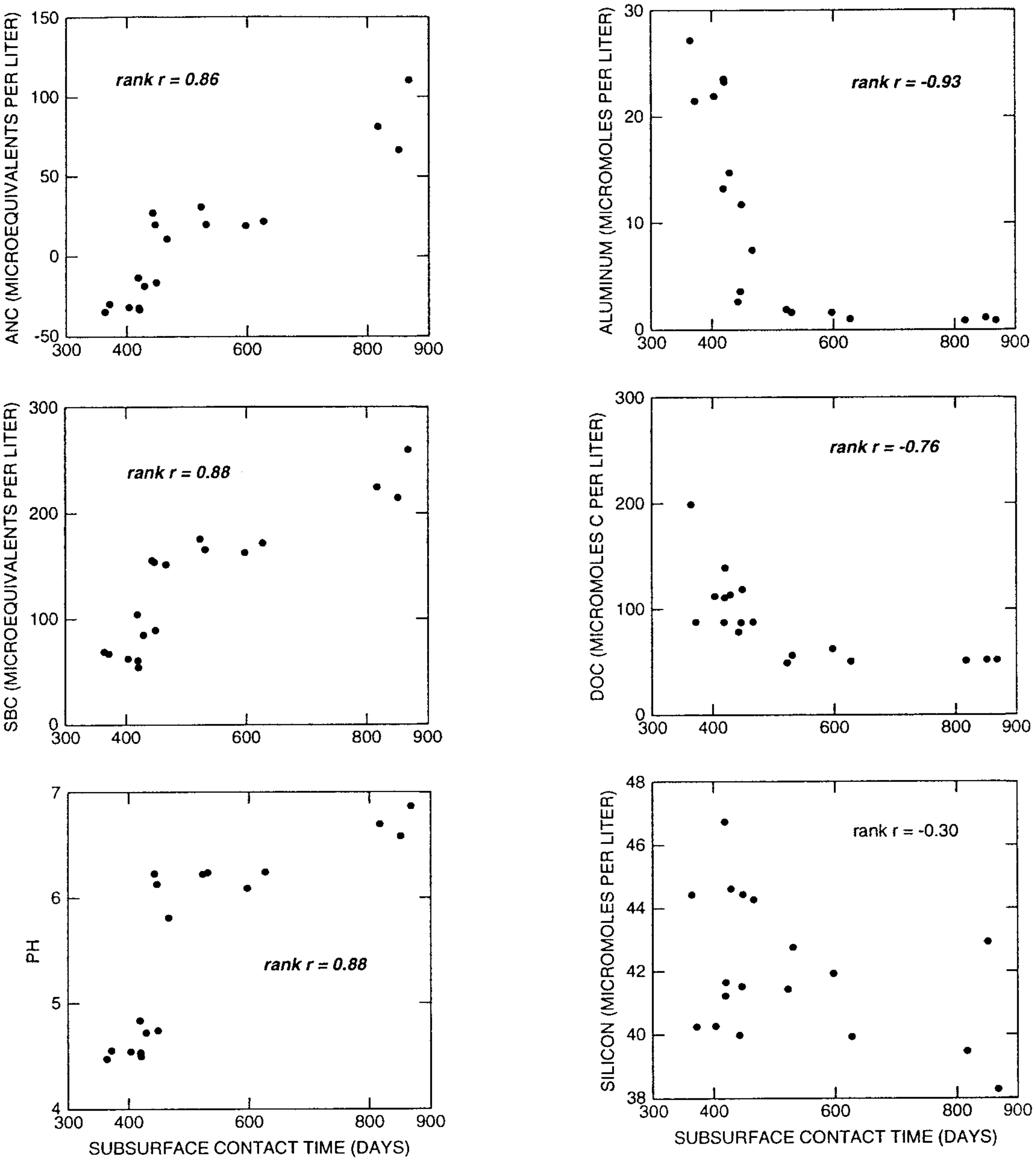


Figure 5. Relationship between median low-flow stream chemistry concentrations and subsurface contact time index values for the 18 nested sites in the Neversink River. The strength of a monotonic relation between the variables is measured by the Spearman rank correlation coefficient (rank *r*). Statistically significant ($p = 0{\cdot}0001$) values of rank *r* are shown in bold italics

The relationship between subsurface contact time and ANC was also evident for basins along tributaries in the middle and lower parts of the Neversink River watershed (Figure 6; see Figure 1 for the location of the tributaries). ANC increased with basin size among the sites in both the middle and lower tributaries (Figure 6a), and the changes in ANC were associated with increases in subsurface contact time (Figure 6b). These data also suggest that the differences in ANC between the middle and lower tributary basins are related to the differences in subsurface contact time.

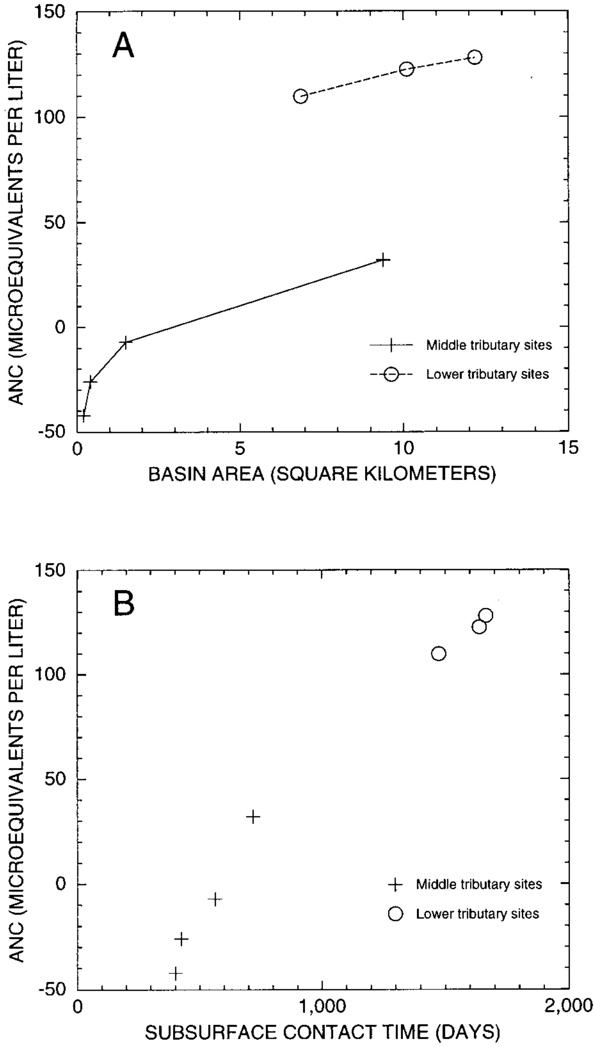


Figure 6. Relationship between mean low-flow acid neutralizing capacity (ANC) and (A) basin area and (B) subsurface contact time for seven sites in the lower and middle tributaries of the Neversink River. See Figure 1 for the location of the tributary sites

The increase of SBC with basin size (see Figure 2) for basins smaller than 3 km^2 is caused by weathering and neutralization processes. Once basin size is greater than 3 km^2, SBC concentrations do not vary substantially with further increases in basin size. The addition of stream flow from small tributary basins still alters the concentration of SBC, but for basins larger than 3 km^2, the effect of additional tributary inputs to stream flow on main stream concentrations is small. Variation in concentrations of SBC in stream water may reflect either the effect of varying contact times or spatial variations in bedrock, or soil geochemical characteristics. With our data it is impossible to rule out the effects of spatial variations in surficial mineralogy and soils, but the bedrock mineralogy of the watershed is considered uniform (Murdoch, 1991), and the data are consistent with the subsurface contact time explanation. If variations in mineralogy or soils were significant, it is unlikely that they would produce the systematic patterns that were observed throughout the basin. The effects of surficial mineralogy and soil geochemical variations may be limited to smaller geographical scales within the watershed and, if so, their potential importance would decrease with increases in basin size.

As with ANC and SBC, the rapid increase in pH with basin size for basins smaller than 3 km^2 suggests kinetically limited neutralization processes. In upland forested watersheds in the north-eastern US, stream flow pH tends to be lowest in the uppermost reaches and steadily increases in the downstream direction (Johnson *et al.*, 1981; Lawrence *et al.*, 1986; Driscoll *et al.*, 1988). Consistent increases in stream flow pH with decreasing elevation have been attributed to elevational gradients in soil water residence time in other watersheds where spatial variability of mineral weathering rates are considered to be minor (Johnson *et al.*, 1981). Al concentrations in stream water are controlled by pH and therefore decrease as pH and basin size increase.

The decrease in DOC concentrations with basin size can also be explained by increases in subsurface contact time. Longer subsurface contact times provide more opportunity for decomposition and oxidation of organic carbon, which leads to lower DOC concentrations. The relation between DOC concentrations and subsurface contact times may also reflect longer (in distance) flow paths, which would increase the amount of physical contact between subsurface water and mineral surfaces. This process would enhance adsorption of organic carbon and decrease DOC concentrations. Soils tend to be shallowest in headwater basins, often with little or no mineral soil. In this situation, there is minimal opportunity for carbon adsorption to mineral surfaces. Thus, variability in DOC concentrations between the basins may be caused by differences in soil depth rather than in subsurface contact time, but the effect is linked to subsurface flow path length, and, therefore, is not independent of subsurface contact time.

The lack of correlation between Si concentrations and the subsurface contact time index is inconsistent with geochemical control of Si solubility. It would be expected that longer subsurface contact time would be related to higher concentrations of weathering-derived Si. One possible explanation for this finding is that shallow soil near the land surface may contribute a substantial amount of Si to the stream. Build-up of soluble Si in the organic surface horizon (the primary rooting zone) from biocycling may provide a larger labile pool of Si than that achieved by weathering deeper in the subsurface. Biocycling of Si released by weathering has been shown to be an important control of Si concentrations in hardwood forested watersheds (Bartoli, 1983). The biocycling process and the prevalence of shallow organic soils in the headwaters may override the effect of subsurface contact time with respect to Si.

Most of the patterns of the stream chemistry variations at a basin size smaller than the 3 km^2 threshold size are related to acid neutralization. Once subsurface contact time is sufficient to achieve equilibrium with the solid phase, however, further increases in contact time would not be expected to increase concentrations of weathering products. Our results suggest that during low flow conditions the neutralization and weathering reactions are largely completed in the first-order drainage basin (about 2 km^2), which is consistent with the interpretation of Johnson *et al.* (1981) that in the Hubbard Brook Experimental Forest most of these reactions are accomplished within first- and second-order drainage basins.

CONCLUSIONS AND IMPLICATIONS

The results of this study showed that ANC, SBC, pH, Al and DOC show consistent patterns in response to varying basin size for a set of 18 nested basins in the Neversink River watershed. There seems to be a threshold basin size of 3 km^2 for concentrations of these stream chemistry constituents above which concentrations stabilize at relatively invariant values. For sampling sites in the Neversink River with basin areas larger than this threshold, most low-flow stream chemistry concentrations can be roughly estimated by the concentrations at a single sampling site.

Since this study only looked at one set of basins, the conclusions may not be directly applicable to other watersheds. For example, Merot and Bruneau (1992) found a critical basin size of about 1 km^2 for chloride and nitrate in a small watershed. The spatial pattern of stream chemistry constituents in areas not affected by acidic deposition may also differ from that in the Neversink River watershed. In addition, a different critical basin size may exist for a watershed during high-flow conditions.

Past concern about the effects of atmospheric deposition has resulted in the development of a number of process-based models that predict the effects of various deposition scenarios on water quality

(Christophersen and Wright, 1981; Cosby *et al.*, 1985; Gherini *et al.*, 1985). The structure of these models, typically, is derived from mechanisms that operate at the plot scale. Extrapolation to the small watershed scale is done by lumping or statistical averaging. This approach is dependent on the assumption that spatial variation can be described stochastically. However, our study in the Neversink River watershed suggests that spatial variations of low-flow stream chemistry are systematically related to subsurface contact time and basin size. These findings imply that to extend small watershed geochemistry models to larger watersheds, inclusion of the effects of scale on spatial patterns of basin characteristics would prove useful.

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