

# Strontium Isotope study of the Peconic River Watershed Long Island, New York

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**Written in 1994**

Based on the MS Thesis by Geng Xin "Strontium Isotope Study of the Peconic River Watershed, Long Island, New York, Stony Brook University, 1993. Accessible in the Science and Engineering Library at Stony Brook University with call number x GB565.N72 P42 1993.

## **Abstract**

The Peconic River Watershed covers approximately 120 km<sup>2</sup> of pine barrens in eastern Long Island. This area is lightly populated and has a relatively simple groundwater system in that the only input of water is from precipitation and the dominant output of water is stream runoff with minor subsurface flow discharge to the sea. Forty-one samples of precipitation, throughfall, plants, soil, soil water, surface water and ground water collected during the calendar year 1991 were analyzed for strontium concentration and isotope composition. Our results suggest that soil weathering probably makes only a small contribution to the total Sr input. Dry precipitation accounts for approximately 90% of the total Sr input to the system with wet precipitation supplying the other 10. Biomass and adsorbed Sr on the surface of soil particles at shallow depth are the two major reservoirs of Sr and hold more than 90% of the Sr in the system. The estimated residence time for Sr within this system is approximately 50 years.

## **Introduction**

Several attempts have been made to distinguish the sources of the inputs of Sr in natural water systems (*e.g.*, Wickman et al., 1987 and Aberg et al., 1987) and to quantify the input and distribution of Sr within an ecosystem by using Sr isotopic composition as a tracer (Aberg et al., 1989; Graustein, 1989 and Gosz et al., 1989). In a pristine ecosystem such as the Peconic River Watershed, the major strontium inputs are from atmospheric deposition and weathering processes. The only source of water is precipitation. The major outputs of water and Sr are stream discharge and subsurface flow. However, the atmospheric and soil weathering contributions to the system are difficult to quantify because of inherent heterogeneities. This study uses Sr isotope compositions and concentrations to evaluate the annual strontium input from soil weathering and wet and dry precipitation by use of mass balance with isotopic composition control on the components as well as water balance in the Peconic River watershed, a relatively pristine area of Long Island with a relatively simple hydrology.

## **The Peconic River Watershed**

The Peconic River Watershed (Fig. 1) is located in central Suffolk County, Long Island, approximately 100 kilometers east of New York City. The Watershed is bounded on the north and south by the local ground water divides and on the east and west by the drainage area of the Peconic River. It occupies a densely wooded area of approximately 120 square kilometers. The Peconic River originates near the western boundary of the Brookhaven National Laboratory. It flows eastward some 20 kilometers where it discharges into Flanders Bay. It provides the only surface stream runoff in this watershed. Figure 2 shows hydrological boundaries, detailed geographic features, water table contours and surface water sample locations in the study area.

The ecosystem is defined by the drainage area of the Peconic River and its tributaries. Its surface boundaries are depicted in Figure 2. The northern and part of southern boundaries are confined by the two major ground water divides which traverse the area from west to east. In general, surface and near surface ground water from the area between the two branches of divides moves eastward to the Peconic River, flows and discharges into Flanders Bay. Both divides are not stationary but move north or south as the water table configuration changes. These changes occur seasonally and also during periods of recharge or drought. The configuration of the upstream boundary at the west side of the Peconic River Watershed is unknown, however, and is undoubtedly more complicated or variable than the nearly straight line indicated in Figure 1. The same applies to the downstream boundary, which is defined by two separate straight lines drawn perpendicular from the point of the Riverhead Gauge to the equipotential lines near the north and south divides. Based on this configuration, the surface area of the Peconic River Watershed is approximately 120 km<sup>2</sup> with a variability of 20 km<sup>2</sup> which corresponds to the fluctuation of the water table divides during winter and summer. The system is arbitrarily defined extending vertically to a depth of 5m

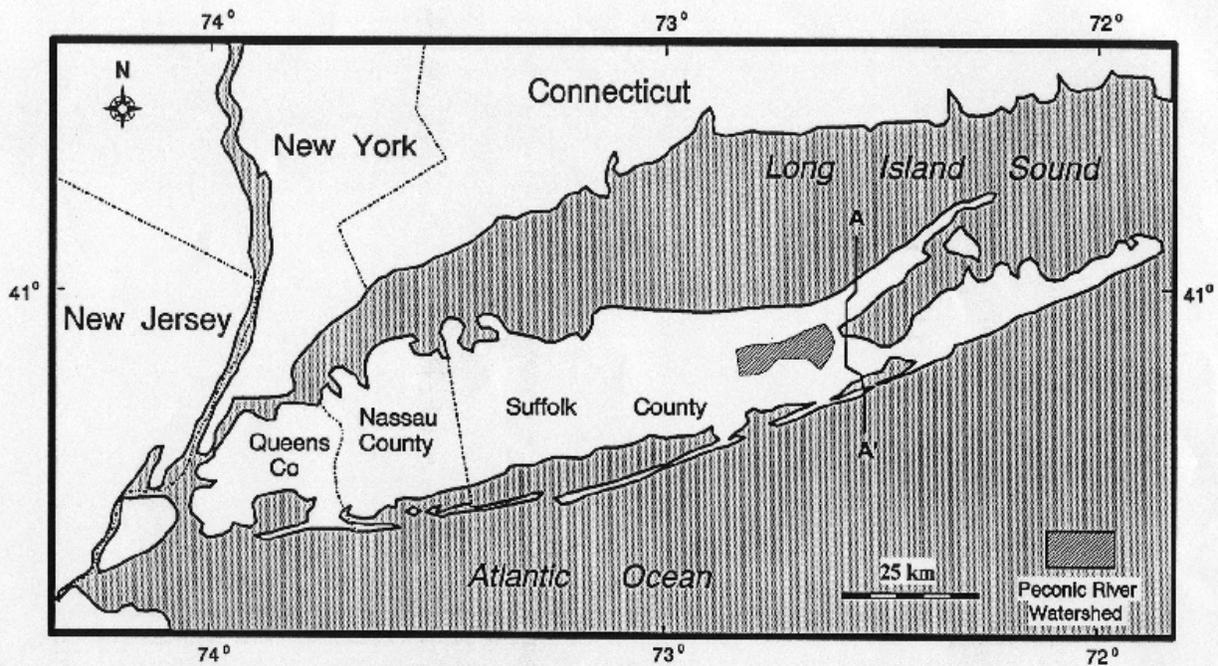


Figure 1 Map of Long Island and location of Peconic watershed.

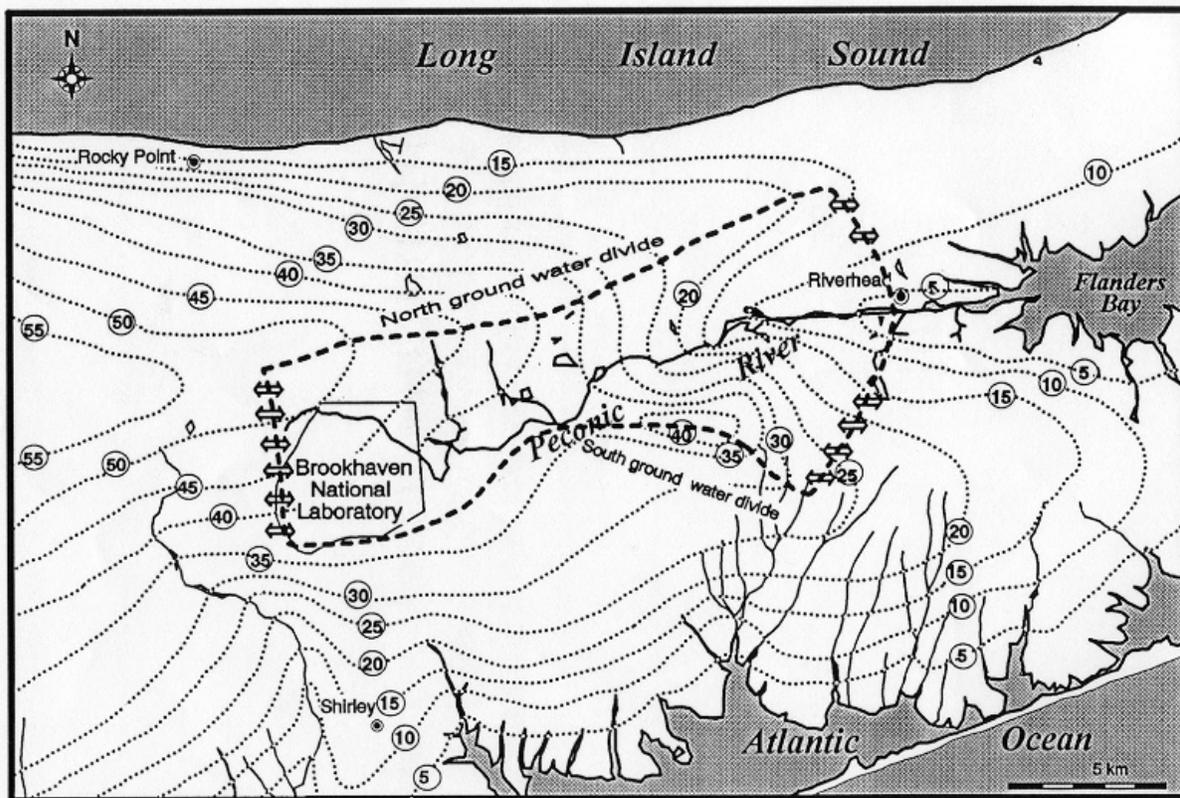


Figure 2. Map of the Peconic River Watershed

below the ground surface, since most Sr is held in the surface or near surface area by vegetation and organic soil

and most of glacial deposits are only slightly altered below this depth.

### Geology and Hydrology

The Peconic River Watershed is underlain by unconsolidated Cretaceous and Pleistocene siliciclastic sediments that rest unconformably upon the pre-Cretaceous crystalline basement complex consisting of essentially impermeable bedrock. The general geologic relationships are indicated diagrammatically in the cross-section A-A' in Figure 3. The formations strike northeast and dip to the southeast (Smolensky et al., 1989 and deLaguna, 1986). Most of glacial deposits are composed of stratified and highly permeable beds of sand and gravel of Wisconsin age (Sirkin, 1986).

The principle ground water reservoirs in the Peconic River Watershed are the upper glacial and the Magothy aquifer (Heath et al., 1966). The upper glacial aquifer is the major source of public water in this area (Krulik, 1986). The only source of water to the Long Island ground water system is recharge from precipitation. The average annual precipitation in this area during 1943-82 was 117.7 cm (Krulik, 1986). Approximately half of the precipitation returns to the atmosphere by evapotranspiration during years with close to the average annual rainfall (Fetter, 1976 and Bart and others, 1976).

Except for an average overland runoff of less than 5% the rest of the precipitation infiltrates through the surficial deposits to the water table and becomes shallow ground water (Fetter, 1976). Most of the shallow ground water moves laterally through the glacial deposits either northward or southward from the north and south ground water divides (Figure 2) and discharges into the Peconic River and to the Flanders Bay, Long Island Sound and the Atlantic Ocean. About 95% of the total stream flow under natural conditions is derived from local shallow ground water seepage (Pluhowski et al., 1964). Although the volume of the flow of the stream is relatively small, its combined base flow represents a significant amount of the total freshwater outflow from the watershed's hydrologic system (Prince et al., 1989). In 1991 for example, the Peconic River discharged 80% of the total water discharged. Study show 90% of the total recharge infiltrated into the ground ultimately discharges from the shallow ground water flow through the upper glacial deposits into sea (Heath et al., 1966).

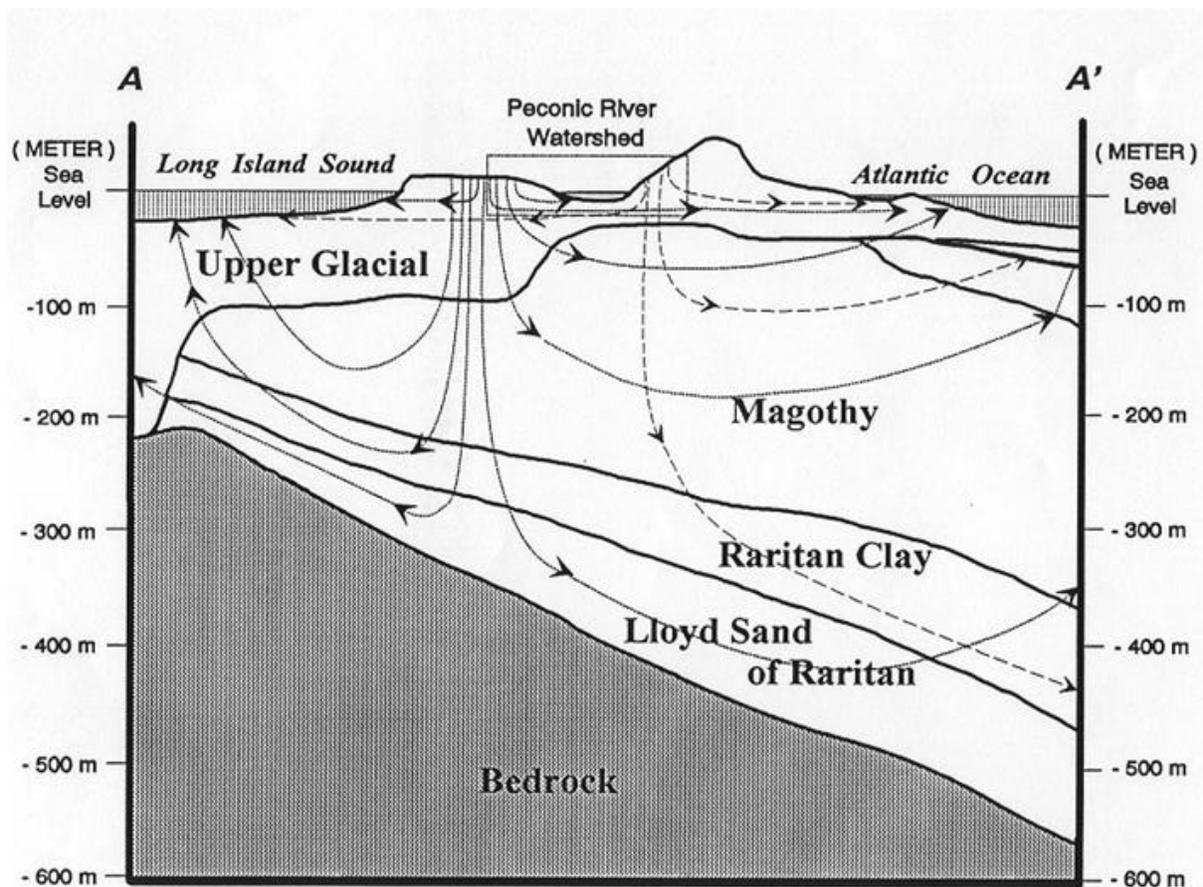


Figure 3. Schematic groundwater flow lines from the Peconic River Watershed. From cross section A-A' in Figure 1 Vertical exaggeration about 25 times.

## Climate, Vegetation and Soil

The climate in Long Island is relatively humid. The temperature extremes are modified by the Atlantic Ocean and to a lesser extent by Long Island Sound (Isbister, 1966). The area is relatively undisturbed and is covered by dense vegetation. The native trees around Fox Pond are pitch pine and white oak. Undergrowth is mainly high bush blueberries, huckleberry and shad bush (U.S. Dept. Agric., 1975).

The soils of the Peconic River Watershed are generally deep, excessively drained, coarse-textured, quartzose glacial sands with a high permeability and low natural fertility. The soils along the Peconic River and nearby ponds, which extend eastward from its headwaters at the west boundary of the Brookhaven National Laboratory to its mouth at Riverhead, are characterized by nearly level to gently medium textured and moderately coarse textured with moderate to high moisture capacities. The soils near Fox Pond, where many samples were collected, consist of deep, nearly level, somewhat poorly drained coarse-textured soils. Locally, some soil may be organic rich and contain black sand and peat beds (U.S. Dept. Agric., 1975). The compositions of soil from both A1 and B1 horizons were studied for mineral composition using electron microscopy. Both samples contain abundant angular quartz with minor angular feldspar and clay.

## Analytical Procedure

Sampling started in Aug. 1991 and ended in July 1992. Forty-one samples were collected representing wet precipitation, throughfall, soil water, ground water, surface water, soil, vegetation and vegetation litter. The Sr concentration and isotope composition analyses are shown in **Table 1**. Strontium was separated from each sample by cation exchange chromatography and was measured for concentration and isotope composition. All the strontium chemical analyses were conducted in the Isotope Geology Laboratory at the Department of Earth and Space, S.U. N.Y. at Stony Brook. The total strontium concentration of each sample was determined by isotope dilution using a calibrated spike enriched in  $^{84}\text{Sr}$ . Measurements were made on NBS design 6" radius, a thermal ionization mass spectrometer. Reproducibility of all isotope dilution measurements was generally better than  $\pm 1\%$ .

Measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were made on unspiked samples on the Finnigan MAT 262 mass spectrometer. All measured values of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio were corrected for isotope fractionation to a standard value of 0.1194 for the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio. Eleven replicate analyses, as well as seventeen runs on the strontium standard, suggest that the uncertainty of any one analysis was approximately  $\pm 0.00002$  at two standard deviations. The total chemical and loading blank for Sr was 50 pg. Samples for isotope composition analysis consisted of at least 50 ng of Sr. Thus, the blank was less than 0.1% of the sample.

The amount of sample used for each of IC and ID analysis was depended on the Sr concentration of each sample. Five milliliters of precipitation and one milliliter of other waters were used for each of isotope dilution analyses. One to 200 ml of water were used for isotope composition analyses depending on the Sr concentration in the sample.

## Results

Sr inputs from the atmosphere come from wet precipitation, aerosols or dust. Previous studies show that aerosols and dust are relatively enriched in Sr. Their concentrations can be up to 198 ppm (Gosz et al., 1989) and their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vary in the range of 0.7081 (Hurst et al, 1981) to 0.7471 (Biscaye et al., 1974). However, only the soluble portion of Sr in aerosols and dust will affect the Sr concentration and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in wet precipitation. Each storm will have different kinds and amounts of aerosols and dust with separate Sr characteristics dependent on its path. Different wind directions during precipitation also add complexity to the diverse origins of aerosols and dust. Thus, the Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for individual precipitation events are expected to be variable.

### Precipitation

Nine samples of wet precipitation were collected over the interval Feb. 1992 through July 1992. Five of them were collected at Fox Pond in the Peconic River Watershed, and four were collected at the main campus of the S.U.N.Y at Stony Brook which is approximately 20 miles west of Fox Pond. One sample of throughfall was collected at Fox Pond approximately one week after a 15 mm rain. The Sr in the rain water collected in this study represents dominantly the Sr in wet precipitation. This is because the sampling device was placed outside immediately before or during the storm and emptied immediately after. Thus, there was a minimum of inputs from dry aerosols and dust deposited prior to or after the storm. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of rain samples range from 0.7091 to 0.7099, close to the sea water value of 0.7092. This may indicate that most wet precipitation derives its Sr from the ocean. The Sr concentrations in the rain water samples are low, about 1 ppb or less. The one snow sample has a Sr concentration of 3.55 ppb and the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7089. This ratio is lower than that of seawater and suggests that it may contain a significant amount of aerosol and dust originated from materials which have low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. This snow storm traveled from the Southern Plains to Long Island (New York Times 3/22/92). There is no clear trend among Sr concentrations,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the corresponding storm path for the samples collected during this time period.

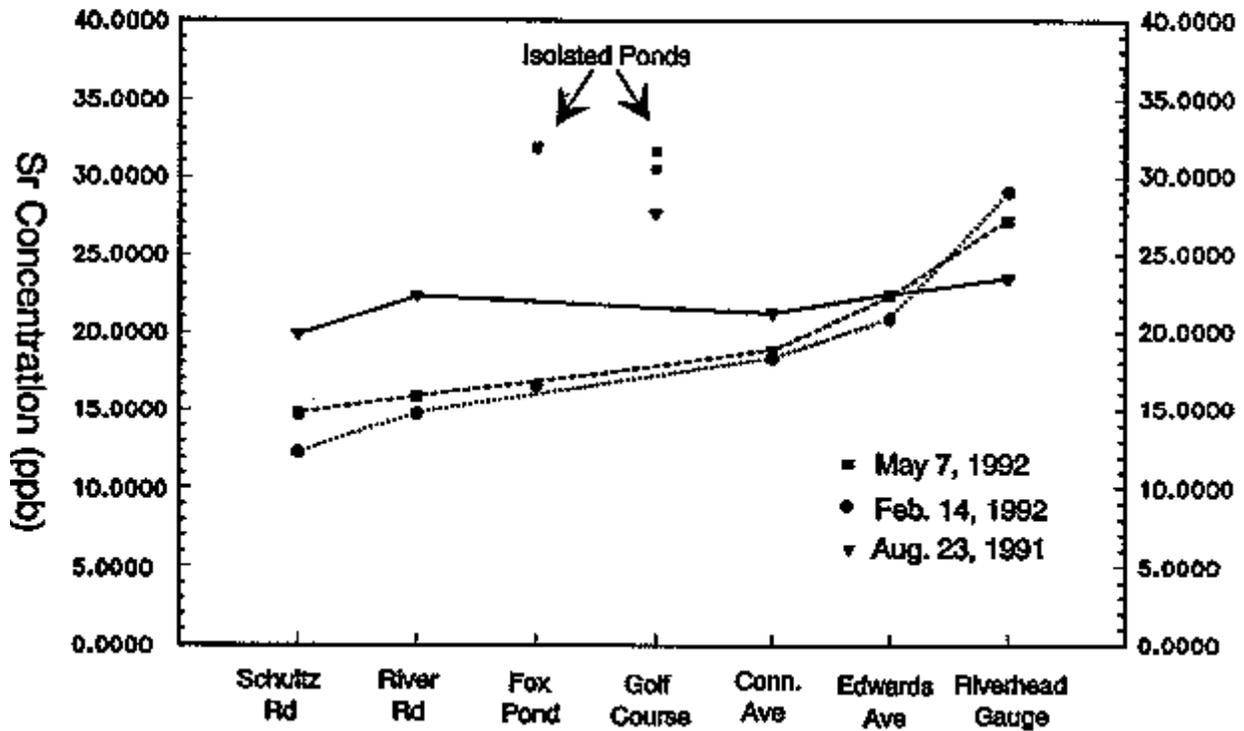
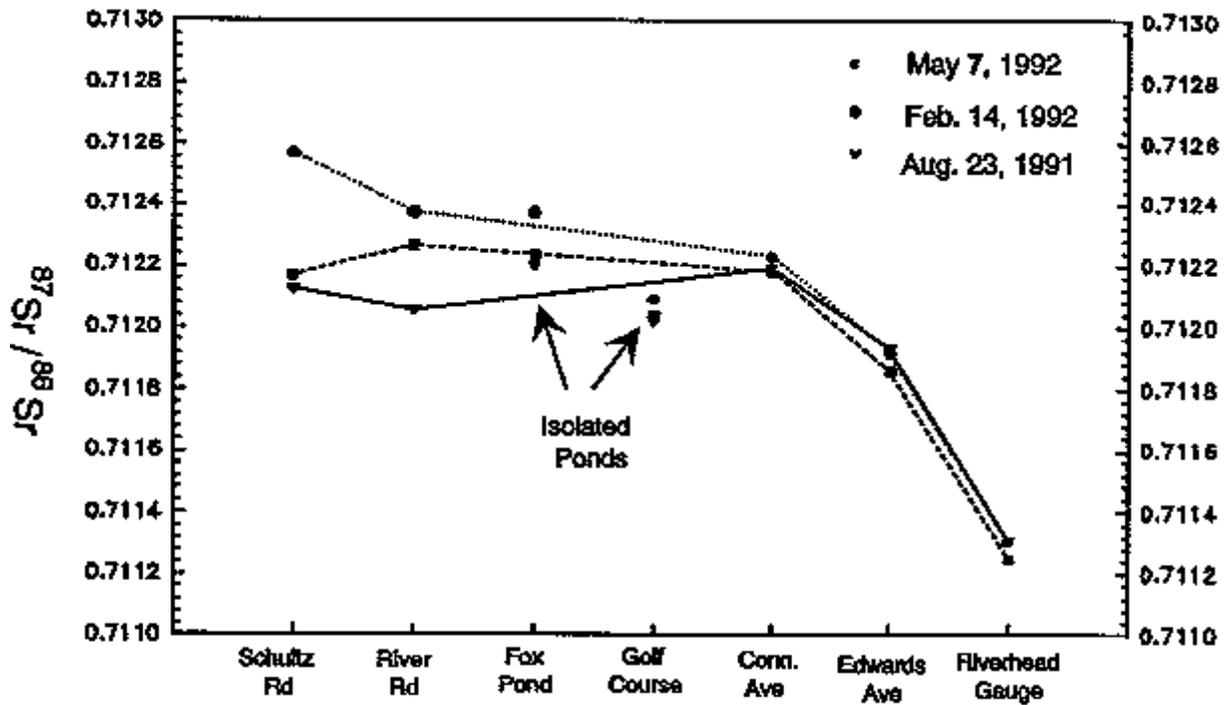


Figure 4  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and strontium concentrations for different sites from west (Schultz Rd.) to east (Riverhead Gauge) along the Peconic River at different times.

The Sr concentration in the throughfall sample was approximately 15 times higher than that in the rain-water collected at same time nearby. The addition of Sr from aerosols, dust and the vegetation was obviously the cause of this increase in its concentration. The throughfall also has a much higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio than that of rain-water. Since the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of average wet precipitation is 0.7093 and that of the vegetation is 0.7118, in order to bring the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio up to 0.7127, Sr with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios higher than 0.7127 must have been added to the throughfall from dry precipitation. Thus, it is reasonable to assume that the average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the dry precipitation between this and last storm was equal to or greater than 0.7127. Graustein and others (1983) show that the Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of throughfall typically exhibit large spatial and time variability. Up to 34% of the Sr in throughfall can be derived from botanically cycled Sr (Graustein 1989).

### **Vegetation and Litter**

Two vegetation samples were collected at Fox Pond. One was a dead branch of a live pine tree, and the other was litter collected at adjacent to this pine which consisted of pine needles, foliage, twig and bark. Vegetation and litter samples had Sr contents of 12.5 and 13.5 ppm respectively. Whether Sr is physiologically essential to the vegetation growth is not clear. However, the Sr in the vegetation is concentrated approximately 2 to 1000 times higher than the Sr in its surrounding lithosphere, hydrosphere and atmosphere (Trudinger et al. 1979). Vegetation plays a significant role in determining the chemical budget of the environment and is a large reservoir of Sr in an ecosystem.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of vegetation is generally homogeneous (Gosz et al., 1989). Different vegetation may have distinct Sr sources and the uptake of Sr from roots represents a mixture of Sr originating from atmospheric inputs and soil weathering products. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the pine tree and litter samples in this area were 0.7118 and 0.7124, between the ratio for average precipitation, 0.7093, and that of acid washed soil, 0.7244. The relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the vegetation reflects a relatively large contribution of atmospheric Sr. Perhaps the slightly higher Sr isotope ratio for the litter is a result of relatively insoluble aerosols and dust that accumulated on the ground.

### **Soil**

Two soil samples were collected at depths of 10 cm and 50 cm below the ground surface at Fox Pond where two lysimeters were buried. The 10 cm sample was organic rich consisting of sand with a dark black coating, clay and vegetation. The 50 cm sample was organic poor consisting of sand with a yellow-brown coating and clay. Analyses of both the acid wash and acid washed soil were performed for each sample. Acid wash analysis was to determine the amount and characteristics of the strontium adsorbed on the coating of soil particles. Acid washed soil was analyzed to determine the potential strontium within soil particles which may be released by chemical weathering.

The acid wash for soil at 10 cm below the surface had a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7125 and a Sr abundance of 676 ppb. The concentration is measured relative to the total weight of soil washed, not the concentration of the dissolved coating. The acid wash for soil at 50 cm had a similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, but a much lower Sr abundance 52.6 ppb.

The acid washed soil is clean, nearly white, quartz sand with minor feldspar and clay. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the acid washed soil, show the highest values, 0.7230 and 0.7258, in this study. This ratio is close to the average continental source of 0.719 (Faure, 1972). The acid washed soil has relatively low Sr concentrations of 7.3 and 5.1 ppm consistent with their quartz rich character. While the isotope composition of the washed soil could provide the higher ratio end member for the Sr in the system, the amount of Sr in the minerals available for leaching into the groundwater are limited because this Sr is in resistant minerals and not easily released.

### **Soil water and ground water**

Four soil water samples were collected using two self-made gravity lysimeters at Fox Pond. The lysimeters were installed approximately two weeks before the sampling and were placed one meter apart at depths of 10 cm and 50 cm below the surface. The groundwater table was at 80 cm. Prior to the rain the lysimeters were vacated to ensure that the water was collected only from this rain event. The soil water samples were collected approximately 24 hours after a heavy rain on two different dates and represent the change after the precipitation went through the soil. Two shallow ground water samples were collected also at Fox Pond at a depth of 150 cm below the ground surface through a previous installed PVC pipe. The PVC pipe was installed approximately two meters away from the locations of the lysimeters.

The four soil water samples in the vadoze zone have Sr concentration of 25 to 34 ppb and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7100 to 0.7113 which are slightly higher than the values for rain water of 0.7089 to 0.7099. The top soil O-horizon contains large proportions of dead vegetation and organic rich weathering products as well as aerosols and dust. As soon as wet precipitation reaches the ground, water drains through soils and the soluble Sr from its sur-

rounding sources is dissolved in the soil water. The groundwater at 1.5 m has a much lower Sr concentration of 4.5ppb and a higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, about 0.7132. These values are much different from the soil water. It is not clear whether the recent disturbance of the soil associated with the emplacement of the lysimeters may have contributed to the differences in Sr composition and concentration.

### **Surface water**

Twenty-one surface water samples were collected at seven sites along the Peconic River and adjacent ponds on three different dates. The seven sites include two upstream river sites at Schultz Rd and River Rd, three down stream river sites at Conn. Ave, Edwards Ave and the Riverhead Gauge and two pond sites at Fox Pond and the golf course.

Figure 4 shows the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr concentrations of the surface water at different seasons versus the sampling sites. Sr concentrations systematically increased from 13 ppb to 27 ppb and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios decreased from 0.7124 to 0.7112 as the stream water flowed from the west (Schultz Rd) to the east (Riverhead Gauge) during the period of sampling. For each of the sites, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were fairly constant during the sampling period at the three down stream sites, but varied at the two upstream sites. The relatively constant  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios over the time of sampling at the down stream sites suggest a rather well mixed ground water body or a large reservoir under these sites. Whereas the variations at the upstream sites suggest a smaller reservoir which might more easily be affected by local anthropogenic contaminants or by the different amounts of sea spray transported to these sites via the atmosphere

Figure 4 shows that Sr contents are the lowest during winter and the highest during summer at all sites except at the Riverhead Gauge. The increase in Sr concentrations during the summer is probably a result of increased evaporation. At the Riverhead Gauge, the Sr concentrations was found to be highest during winter and lowest during summer. The absolute Sr concentration at this site was also the highest compared with other sites during each sampling time. This suggest that Sr from local sources may have played an important role in controlling Sr concentration behavior at the Riverhead site.

Figure 4 shows that average Sr concentrations were systematically increased from 13 ppb to 27 ppb and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were decreased from 0.7124 to 0.7112 as the water flowed from the west (Schultz Rd) to the east (Riverhead Gauge) during the period of sampling. This variation could be contributed by two possible causes - sea water intrusion and local contamination. Edwards Ave and the Riverhead Gauge are very close to the sea water. Because of their locations, these sites could be more easily contaminated by salt water than the other sites. Even a small portion of sea water intrusion might result in a significant increasing of Sr concentrations and the decreasing of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios because Sr concentration in sea water (8 ppm) is relatively high and it has a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7092 (Faure, 1986). A small dam down stream of the Riverhead Gauge prevents the sea water intrusion from surface. Sea water might be brought up and added to the fresh water aquifer of the Peconic River Watershed through the percolation of deep ground water under artesian conditions. Since sea spray has the same Sr characteristic as the sea water, sea spray transported to these sites via the atmosphere might result in the same effect. The other possible cause for these Sr variations may be local contamination. For example, lime used as fertilizer needed to grow grass on Long Island has Sr isotope ratios similar to seawater.

Approximately 95% of the surface water in this area is thought to be derived from local shallow ground water seepage (Pluhowski et al., 1964). The similarity of the Sr isotope composition of ground water to that of stream water is consistent with ground water being the major source for Sr in the stream water. The increased extents of evaporation during the summer probably increased the Sr concentrations of the stream water as it flowed eastward. The addition of Sr to the stream from other sources, such as overland flow, dry aerosols and dusts and local contamination resulted in further alteration of the Sr ratios in the surface water.

### **Strontium Budget**

The strontium cycling in a terrestrial ecosystem participates in various biological and geological cycles of the earth through a system of inputs and outputs. The strontium inputs to an ecosystem may be derived from the lithosphere, atmosphere or biosphere. Inputs from the lithosphere include the strontium added by chemical weathering of soil minerals. Atmospheric inputs include the Sr in wet precipitation, aerosols and dust. Biologic inputs are material which originates elsewhere and is transported to the system, for instance fertilizers added by man. Strontium may leave an ecosystem as dissolved or particulate matter in stream water runoff, subsurface discharge, inorganic and organic bed load moving along stream bottoms (Strahler, 1963), wind transport, or human and animal activity. When the losses of strontium associated with dust or windblown materials and bed load are negligible, Sr losses from an ecosystem are limited to surface stream runoff, subsurface discharge and biologic output. Besides the Sr discharged from system via surface runoff and subsurface flow, part of the Sr is held by vegetation, soil water, ground water or adsorbed on the soil surface.

The strontium budget can be simplified if there is little human activity such as in the Peconic River Watershed. In which case, the biological input would probably be negligible or equal the biological output. The strontium budget for such a steady state ecosystem may be expressed as

$$\text{Strontium Inputs} = \text{Strontium Outputs} \quad 1)$$

$$\text{Geological Input} + \text{Atmospheric Input} = \text{Surface Stream Runoff} + \text{Subsurface Discharge} \quad 2)$$

The strontium cycle of an ecosystem is strongly related to the hydrologic cycle since the water moving into and out of an ecosystem carries significant amounts of strontium. The biological uptake and release of strontium are also closely related to water availability. Similarly, the nature and weathering rate of soil is also influenced by the hydrologic pattern because water is essential to the chemical weathering process. Thus the understanding of the water budget is important to the strontium cycle and budget study in the system. Any unbalanced water budget under a steady state condition might indicate over or underestimation of any water inputs or outputs to and from the ecosystem or water loss through other channels.

The ground water system in the Peconic River Watershed is under a steady state condition since the ground water is neither depleted nor accumulated during a long period of time resulting in the relative stability of the local water table. The only recharge to the aquifer is from the infiltration of precipitation through the surficial deposits to the water table. The water outputs occur as (1) evapotranspiration; (2) Peconic River stream runoff; and (3) subsurface discharge to the surrounding salt water bodies. The water budget can be expressed as:

$$\text{Water Inputs} = \text{Water Outputs} \quad 3)$$

$$\text{Precipitation} = \text{Evapotranspiration} + \text{Surface Stream Runoff} + \text{Subsurface Discharge} \quad 4)$$

$$140 \times 10^6 = 70 \times 10^6 + 55 \times 10^6 + 15 \times 10^6 \quad 5)$$

The annual precipitation measured at Brookhaven National in 1991 was 114.63 cm. This amounts to  $140 \times 10^6$  tons based on the annual precipitation and the drainage area of the Peconic River watershed. This input could vary by up to  $20 \times 10^6$  tons due to the seasonal fluctuations of the drainage area. Evapotranspiration was approximately  $70 \times 10^6$  tons, i.e., half of the annual recharge (Fetter, 1976; Bart and others, 1976). The Peconic River is the only stream which discharges water from this system. The annual output is given by the discharge measured at the Riverhead gauge by which has averaged approximately  $55 \times 10^6$  tons per year in recent years. The subsurface discharge is based on the water not accounted for in evapotranspiration and stream discharge. The annual subsurface discharge is thus  $15 \times 10^6$  tons or approximately 20% of total discharge. The uncertainty in subsurface discharges is approximately  $10 \times 10^6$  tons.

The Sr mass balance equations for both Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  under a steady state condition, i.e., when inputs equal outputs, are:

$$\text{Sr}_{\text{DPre}} + \text{Sr}_{\text{WPre}} + \text{Sr}_{\text{SW}} = \text{Sr}_{\text{SSR}} + \text{Sr}_{\text{SD}} \quad 6)$$

$$\begin{aligned} \text{Sr}_{\text{DPre}} \times (^{87}\text{Sr}/^{86}\text{Sr})_{\text{DPre}} + \text{Sr}_{\text{WPre}} \times (^{87}\text{Sr}/^{86}\text{Sr})_{\text{WPre}} + \text{Sr}_{\text{SW}} \times (^{87}\text{Sr}/^{86}\text{Sr})_{\text{SW}} \\ = \text{Sr}_{\text{SSR}} \times (^{87}\text{Sr}/^{86}\text{Sr})_{\text{SSR}} + \text{Sr}_{\text{SD}} \times (^{87}\text{Sr}/^{86}\text{Sr})_{\text{SD}} \end{aligned} \quad 7)$$

Equation 6 is a Sr mass balance equation and equation 7 is mass balance equation for Sr isotopic composition of  $^{87}\text{Sr}/^{86}\text{Sr}$  (Banner and Hanson, 1990). The symbols Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  stand for the annual weight of Sr input or output and ratios for dry precipitation (DPre), wet precipitation (WPre), soil weathering (SW), surface stream runoff (SSR) and subsurface discharge (SD). The unknown Sr input, output or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the system can be evaluated using the available Sr data of other input, output and mixing components.

**Dry precipitation:** The annual Sr input and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of dry precipitation is unknown. The Sr flux and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the dry precipitation is estimated to be 13 kg/(km<sup>2</sup> year) and 0.7127 based on the Sr concentrations and ratios of the throughfall and the wet precipitation.

**Wet precipitation:** The average Sr concentration in rain and snow is approximately 1 ppb and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is approximately 0.7094. The annual Sr input from wet precipitation is calculated to be  $140 \pm 20$  kg based on the estimated studying area of  $120 \pm 20$  km<sup>2</sup>.

**Surface stream runoff:** On the basis of the average Sr concentration of 26.4 ppb and annual discharge rate of  $55 \pm 5 \times 10^6$  tons in 1991 at the Riverhead Gauge, the annual Sr output from surface stream runoff is calculated to be  $1400 \pm 100$  kg with an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7113.

**Subsurface discharge:** The Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of subsurface discharge were assumed to be that of analyzed ground water, i.e., 4.6 ppb and 0.7132. Based on estimated subsurface discharge of  $15 \times 10^6$  tons in 1991, the strontium output from the subsurface discharge is calculated to be approximately  $70 \pm 50$  kg.

**Soil weathering:** The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the soil weathering input is assumed to be similar to the ratio of acid washed soil, i.e., 0.7244.

By substituting all the known values into the equations 6 and 7 and assuming  $\text{Sr}_{\text{sw}}$  is small, the average annual Sr input, its  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and variations due to seasonal change will be:

$$\text{Sr}_{\text{DPre}} + \text{Sr}_{\text{sw}} = 1330 + 130 \text{ kg}$$

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{DPre}} = 0.7116 \pm 0.0001$$

This result shows that the Sr input from the combination of the dry precipitation and the soil weathering accounts for approximately 90 % of total Sr input of 1,500 kg to the system in 1991. Although the exact amount of Sr input from the local soil weathering is not known, it is expected to be small compared with that from the dry precipitation input. The input from wet precipitation of 140 kg accounts for another 10% of total Sr input to this area. The Sr annual outputs are dominated by stream runoff and only a small percentage of outputs are contributed from subsurface discharge.

**Strontium within reservoirs**

The largest reservoirs of mobile Sr within the ecosystem are vegetation and labile Sr. Labile Sr is that Sr adsorbed on the surfaces of soil particles, which can be easily exchanged in the soil and ground water. The amount

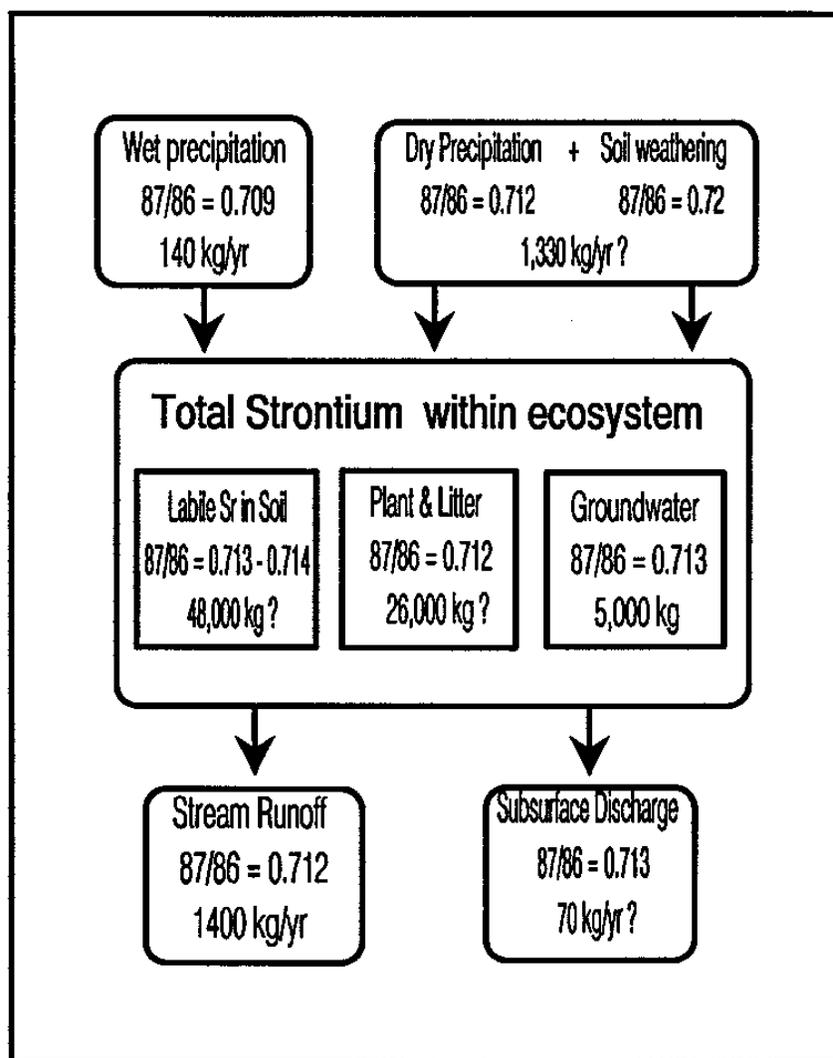


Fig. 5. The strontium budget in the Peconic River Watershed in 1991.

of Sr held by each of carriers within the system can be calculated based on its Sr concentration.

**Strontium in biomass:** The standing crop of dry matter in the plant community in this area, excluding humus, is approximately 10.1 kg/m<sup>2</sup> (Woodwell, 1968). For a Sr concentration of approximately 12 ppm with a consideration of geographic distribution as well as average biomass density, the Sr in biomass is 26,000 ± 4000 kg.

**The labile Sr adsorbed on soil:** Assuming appropriate average labile Sr concentrations and soil density of soils at different depths in this area, the total Sr contained within the labile soil between the ground surface and a depth of 5m is estimated to be 48,000 ± 8,000 kg.

**Sr contained within ground water:** In the Peconic River watershed the average depth to the Raritan Clay, which is relatively impermeable, is about 200 meters (Fig. 2). If the Sr concentration is 5 ppb and assuming a porosity of 50%, the total Sr held by the ground water is approximately 60,000 kg. We do not have good control of the hydrology in the area, but we would estimate that the ground water that contributes to Peconic River and also dominates the subsurface discharge probably is not deeper than about 5 meters below the ground water table. This seems reasonable since the maximum height of the water table in the area is about 15 meters. If we define the active part of the ecosystem to include only the groundwater within 5 meters of the groundwater table, the Sr held in the active part of the groundwater system is 1,500 kg. If the groundwater had the same concentration as river water (about 20 ppb) or if the groundwater that is active were two or three times as deep there would still be less than 20,000 kg. of Sr in the active groundwater system. Which is less Sr than that in the biomass or that adsorbed on the soil.

This study suggests that the vegetation and labile soil account for more than 95 % of the mobile Sr in the system. The total amount of mobile Sr is 83,000 ± 10,000 kg. Given annual Sr input or output in the system of approximately 1,500 kg, the residence time for the Sr is 50 years. The results of strontium budget study, including annual Sr input, output and within mixing components, are graphically present in Figure 5.

### Discussion

Because of the limited Sr data and the spatial and time variations, it is impossible at this stage to depict a thorough history for each component within the ecosystem without further comprehensive sampling. Several aspects should be studied further. The study of the dry precipitation is of importance because it is the major Sr input to the system and its variation can significantly change the Sr budget and the Sr characteristics in the mixing components and Sr outputs from the system. The distribution of throughfall in the ecosystem is also important since it reflects the amounts of Sr input directly to the system and is the key component in determining the Sr budget in the system. Examination of their spatial and time variation can further constrain the reliability of the Sr input from the dry precipitation. A more thorough examination of Sr in vegetation, adsorbed on soil surfaces, and in soil water for a longer period of time and more extensive sampling could provide a better understanding of the history of these components.

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**Table 1. Analytical Results****Stream and ground water samples**

SAMPLE	DATE	DEPTH (m)	LOCATION	SR CONC. (ppb)	<sup>87</sup> SR/ <sup>86</sup> SR	2SDM*
PEC68	8/23/91	SURFACE	SCHULTZ RD	19.87	0.712126	0.000008
PEC69	8/23/91	SURFACE	RIVER RD	22.25	0.712043	0.000009
PEC70	8/23/91	SURFACE	FOX POND	31.35	0.712199	0.000009
PEC71	8/23/91	SURFACE	GOLF COURSE	27.42	0.712023	0.000008
PEC72	8/23/91	SURFACE	CONN. AVE	21.18	0.712193	0.000009
PEC73	8/23/91	SURFACE	EDWARDS AVE	22.45	0.711936	0.000009
PEC74	8/23/91	SURFACE	RIVERHEAD GAUGE	23.44	0.711313	0.000008
PEC104	2/14/92	SURFACE	SCHULTZ RD	12.33	0.712566	0.000008
PEC105	2/14/92	SURFACE	RIVER RD	14.74	0.712374	0.000009
PEC106	2/14/92	SURFACE	FOX POND	16.13	0.712375	0.000009
PEC107	2/14/92	SURFACE	GOLF COURSE	30.55	0.712090	0.000009
PEC108	2/14/92	SURFACE	CONN. AVE	18.31	0.712230	0.000008
PEC109	2/14/92	SURFACE	EDWARDS AVE	20.81	0.711920	0.000008
PEC110	2/14/92	SURFACE	RIVERHEAD GAUGE	29.00	0.711306	0.000007
PEC119	5/07/92	SURFACE	SCHULTZ RD	14.77	0.712150	0.000007
PEC120	5/07/92	SURFACE	RIVER RD	15.88	0.712265	0.000008
PEC121	5/07/92	SURFACE	FOX POND	31.88	0.711229	0.000007
PEC122	5/07/92	SURFACE	GOLF COURSE	31.60	0.712040	0.000007
PEC123	5/07/92	SURFACE	CONN. AVE	18.83	0.712181	0.000010
PEC124	5/07/92	SURFACE	EDWARDS AVE	22.27	0.711860	0.000009
PEC125	5/07/92	SURFACE	RIVERHEAD GAUGE	26.83	0.711251	0.000009
GW-1	5/31/92	1.5	FOX POND	4.50	0.713161	0.000010
GW-2	6/07/92	1.5	FOX POND	4.69	0.713295	0.000008

**Wet precipitation and throughfall samples**

SAMPLE	DATE (1992)	LOCATION	PRECI. (inch)	AMT. (mm)	SR CONC. (ppb)	<sup>87</sup> SR/ <sup>86</sup> SR	2SDM*
Rain	2/24 - 2/26	Stony Brook	0.59	15	0.445		
Rain	3/10 - 3/11	Stony Brook	0.80	20	0.586		
Rain	3/19	Stony Brook	0.67	16	0.88		
Snow	3/22 - 3/23	Stony Brook	0.45	11	3.55	0.708858	0.000010
Rain	5/30 - 6/01	Fox Pond	1.90	47	0.289	0.709488	0.000012
Rain	6/05 - 6/06	Fox Pond	3.88	95	0.853	0.709084	0.000008
Rain	6/24	Fox Pond	0.65	17	1.29	0.709086	0.000010
Rain	7/14 - 7/16	Fox Pond	0.58	14	1.29	0.709939	0.000008
Rain	7/22 - 7/23	Fox Pond	0.48	12	0.494	0.709329	0.000011
Throughfall	7/22 - 7/23	Fox Pond	0.48	12	17.25	0.712693	0.000009

**Vegetation, soil and soil water samples**

SAMPLE	SAMPLE DESCRIPTION	DEPTH (CM)	LOCATION	STRONTIUM CONTENT	<sup>87</sup> SR/ <sup>86</sup> SR	2SDM*
Pine tree	Dead branch	surface	Fox Pond	12460 ppb	0.711811	0.000009
Vegetation lit- ter	pine needles, foliage, twig and bark	surface	Fox Pond	13455 ppb	0.712364	0.000008
S1-H	Soil digested with 2N HCL	10	Fox Pond	676 ug/kg	0.712528	0.000008
S2-H	Soil digested with 2N HCL	50	Fox Pond	52.6 ug/kg	0.714656	0.000011
S1-D	Soil digested with concentrate HF- HNO <sub>3</sub>	10	Fox Pond	7300ug/kg	0.722965	0.000007
S2-D	Soil digested with concentrate HF- HNO <sub>3</sub>	50	Fox Pond	5056ug/kg	0.725828	0.000008
sw1-1	Soil water	10	Fox Pond	33.7 ug/l	0.710027	0.000008
sw1-2	Soil water	50	Fox Pond	74.4 ug/l	0.710782	0.000009
sw2-1	Soil water	10	Fox Pond	24.5 ug/l	0.710243	0.000011
sw2-2	Soil water	50	Fox Pond	27.3 ug/l	0.711254	0.000012

a. Base from The New York Times Weather Report 1992

\* Two sigma standard deviation of mean in sixth decimal place