

ABSTRACT

Title of Dissertation: **IMPACT OF ISOTOPIC HETEROGENEITY IN
SHALLOW SYSTEMS ON MODELING OF
STORMFLOW GENERATION**

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A major uncertainty in hydrologic and geochemical modeling of stormflow generation in watersheds has been quantification of the contributions of water and solutes from different sources and hydrologic pathways to streamwater. Isotopic techniques have recently gained widespread acceptance as useful tools in the investigation of sources of stream flow, but considerable debate still surrounds the question of whether the spatial and temporal variations in the isotopic and chemical compositions of water components are negligible.

At Panola Mountain, Georgia, a 2-year study of temporal and spatial variability in rain and throughfall has determined that average throughfall is enriched by 0.5‰ in $\delta^{18}\text{O}$ and 3.0‰ in δD relative to rain; site-specific differences in canopy cause up to 1.2‰ variation in $\delta^{18}\text{O}$ among collectors for the same storm; and throughfall ^{18}O enrichment takes place throughout the storm, not just at the beginning. Evaporative losses are greater and throughfall is generally slightly enriched in ^{18}O in conifer forests relative to

deciduous forests. However, throughfall shows little evidence of evaporative fractionation; instead, the high deuterium-excess values suggest considerable exchange with re-evaporated waters.

A 490-m² artificial catchment in China was used to investigate the effects of temporal variations in rain composition, and temporal and spatial variations in dominant water flowpath, on the development of isotopic and chemical heterogeneity in soil waters and groundwater. In response to changes in storm intensity, variability in the amounts of water transported via piston versus macropore flow caused a 4‰ range in $\delta^{18}\text{O}$ of groundwaters. Selective storage of early rain in shallow soils makes characterization of the isotopic composition of infiltrating rain water problematic.

Seasonal and hydrologic differences in the sources of alkalinity were investigated at four watersheds at Catoctin Mountain, Maryland, by analyzing the dissolved inorganic carbon in streamwater for $\delta^{13}\text{C}$. Because of short residence times, the isotopic signatures of the two primary carbon sources, calcite and soil-derived carbonic acid, do not appear to be appreciably overprinted by exchange reactions, biological recycling, or degassing; hence, $\delta^{13}\text{C}$ seems to be a useful semi-conservative tracer of water flowpaths and carbon sources.

ON MODELING OF STORMFLOW GENERATION

by

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Preface

Some of the data reported in this thesis have appeared in previously published works. In 1986, a year after I had initiated the study described in Chapter 3 and knew that it was going to "work", a student of mine at George Washington University analyzed a small subset of the available samples for her master's degree thesis (Mills, 1988). Short summaries of some of the data in Chapter 2 (Kendall and Gu, 1992) and Chapter 3 (Kendall et al., 1992c) have appeared in symposium proceedings. In each of these collaborative papers, I was responsible for the design of the study, the analysis of results, and the writing of the papers. I am grateful for the assistance and comments which my co-authors provided, but the originality of the material presented in those short articles and in this thesis is consistent with the requirements for doctoral research.

"The tragedy of science
is the heartless murder of beautiful theories
by ugly facts."

Gregory Benford

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The fieldwork for Chapter 1 was supported by the Acid Rain Program of the U.S. Geological Survey; USGS personnel stationed in Atlanta GA collected most of the samples discussed in this chapter. Others were collected by Rosanna Cappellato and analyzed for water chemistry as part of her dissertation at Emory University (Cappellato, 1991). I wish to thank Jake Peters and Rick Hooper (USGS, GA) for their assistance in designing this study and for maintaining the massive Panola database; Ed Drake (USGS) for rebottling splits of water samples for me; and Rosanna Cappellato for helping with the statistical analysis of the throughfall data.

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IMPACT OF ISOTOPIC HETEROGENEITY IN SHALLOW SYSTEMS ON MODELING OF STORMFLOW GENERATION

INTRODUCTION

The last few decades have seen increased interest in the topic of streamflow generation, primarily due to concern about anthropogenic acid deposition. Sensitive, low-alkalinity surface waters throughout North America and Europe have already been acidified, and many streams not currently acidic may suffer acid episodes during large rainstorms or spring snowmelt (Wigington, 1989), causing serious damage to local ecosystems. New awareness of the potential danger to water supplies posed by the use of fertilizers, pesticides, and other potentially toxic materials deposited at or near the earth's surface has also focused attention on rainfall-runoff processes. Determination of the amount of water potentially leaching the soil zone during storm events is an important step towards understanding the fate and transport of these pollutants in shallow unsaturated and saturated systems.

Prior to the last few decades, studies of the sources of streamflow during storm runoff were concerned only with the physics of the processes involved. Horton (1945) developed the concept that streamflow is generated by overland flow of the portion of rainfall which falls at intensities exceeding

the infiltration capacity of the soil. Hewlett (1961) showed that the water draining from the soil contributed to baseflow. Betson (1964) suggested that only certain parts of drainage basins -- where the infiltration capacity is frequently exceeded by rainfall -- contributed runoff during most storms (the partial-area contribution concept). Hewlett and Hibbert (1967) proposed that during storms, ephemeral streams expanded upstream by collecting overland flow and shallow subsurface runoff along their channels (the variable source area concept), emphasizing the role of soil water and groundwater in streamflow generation. In contrast, Dunne and Black (1970) determined that stormflow is dominated by overland flow on areas where the water table had risen to the surface, and introduced the term "saturated overland flow" to distinguish this flow from that of Horton, which occurs on unsaturated soil. In general, the Hortonian model is now considered to be inappropriate for humid temperate areas. Although there has been considerable debate on the role of soil water and groundwater in stormflow generation, on the whole, these physically-based models came to the conclusion, reasonable to any layman, that new rainwater was the dominant source of streamwater during most storms.

The relative contributions of rain and groundwater to streamwater can also be estimated by monitoring selected chemical species in streamwater during storm events; such determinations are called chemical hydrograph separations. The basic premise is that since rain is usually more chemically dilute than the groundwater that feeds streams during baseflow conditions, the dilution of the streams during storms should be a function of the relative amounts of rain and groundwater in the streamwater. In contrast to the many early physically-based models, most chemical hydrograph separation

studies to date have found less-than-expected dilutions in stream water and therefore have concluded that groundwater was the dominant source of runoff (Pinder and Jones, 1969; Neal et al., 1988; Wels et al., 1991). Kennedy and Malcolm (1977) and Pilgrim et al. (1979) have suggested that the smaller-than-expected dilutions may be a result of underestimation of the concentration of solutes in pre-event water, and that subsurface flow can rapidly acquire a load of solutes from brief contact with the soil. Hence, it is better to regard chemical tracers as indicators of water flowpaths, and only indirectly as indicators of water sources (Kennedy et al., 1986; Wels et al., 1991).

Because of the questions about non-conservative behavior by chemical tracers, the use of naturally-occurring isotopes and chemical solutes to track the movement of water has gained widespread acceptance in recent years. The basic principle behind isotope hydrograph separations is that if the isotopic compositions of the sources of water contributing to streamflow during storm events are known and are different, then the relative amounts of each source can be determined. In most low-temperature environments, deuterium (D) and oxygen-18 (^{18}O) in water behave conservatively in the sense that any reactions with matrix material will have a negligible effect on the D and ^{18}O content of water. As parts of the water molecule, these isotopes are ideal hydrologic tracers of water sources. In contrast, solutes are only carried by the water and can be gained or lost by passage through the matrix materials along different flowpaths. Natural variations in the isotopic compositions of precipitation, surface waters, and groundwaters enable storm water runoff to be separated into pre-event water(s) (old

water(s) that existed in the watershed prior to the storm) and event water (new rain water).

The conclusion generally drawn from isotope hydrograph studies is that pre-storm groundwater is by far the dominant source of runoff in humid, temperate environments (Sklash et al., 1976; Pearce et al., 1986; Bishop, 1991). This is opposite to what was previously concluded from physically-based studies and is in general agreement with chemical hydrograph studies; however, the contributions of groundwater to stream water estimated using both isotopic and chemical tracers for the same storm may vary in magnitude (Hooper and Shoemaker, 1986; Obradovic and Sklash, 1986; Sklash et al., 1986).

In its earliest and traditional applications (Fritz et al., 1976; Sklash and Farvolden, 1979, 1982), the use of isotope techniques to runoff studies required several assumptions:

1. Groundwater and baseflow can be characterized by a single constant isotopic composition.
2. Rain or snowmelt can be characterized by a single isotopic composition, or the variations are documented.
3. The isotopic composition of rain water is significantly different from that of groundwater/baseflow.
4. Contributions from soil water are negligible, or the isotopic composition is identical to that of groundwater.
5. Contributions from surface-water bodies (such as ponds) are negligible.

If these assumptions are assumed to be valid, then one can write two mass balance equations for the composition of stormflow at any time, one for water flux and one for isotope flux:

$$Q_s = Q_r + Q_g$$

$$Q_s \delta_s = Q_r \delta_r + Q_g \delta_g$$

where Q is streamflow in terms of discharge; δ (Delta) is the D or ^{18}O content, in permil (‰) or parts per thousand, defined as $\delta = [(R_x/R_s) - 1]/1000$, where R_x is the ratio of D/H or $^{18}\text{O}/^{16}\text{O}$ of the sample and R_s is the comparable ratio for the standard VSMOW (Vienna Standard Mean Oceanic Water; Hut, 1987); and the subscripts s, r, and g represent the stream, rain, and groundwater, respectively. These equations can then be solved for the amounts of stream water contributed by rain and groundwater (ie., new versus old water).

The utility of these equations for any particular storm event is a function mainly of the magnitude of $(\delta_g - \delta_r)$ relative to the analytical error of the isotopic measurements, and the extent to which the aforementioned assumptions are indeed valid (Pearce et al., 1986). Clearly the relative amounts of new versus old water are affected by many environmental parameters, including soil thickness, ratio of rainfall rate to infiltration rate, steepness of the watershed slopes, vegetation, antecedent moisture

conditions, lateral permeability of the soil, amount of macropores, and storage capacity of the catchment.

In the last decade, the validity of several of the simple assumptions for the use of the isotope hydrograph separation technique has been evaluated by a number of investigators, including Sklash and Farvolden (1979), Kennedy et al. (1986), McDonnell et al. (1991), Bishop (1991). First and foremost, rain is not constant in isotopic composition over storm events, as was assumed, and temporal variations in rain isotopic composition have been found to have an appreciable effect on hydrograph separations (McDonnell et al., 1990). In addition, several investigators have concluded that soil waters are not only an important component to storm runoff but often are isotopically or chemically distinct from groundwater (Kennedy et al., 1986; DeWalle et al., 1986; Hooper et al., 1990). A few recent studies have determined that shallow soil and groundwaters can be sufficiently heterogeneous in isotopic composition for hydrograph separations to be ill-advised (McDonnell et al., 1991; Ogunkoya and Jenkins, 1991). Although none of these re-evaluations of the assumptions behind use of the hydrograph separation method has caused any significant change in the basic conclusion of most isotope and chemical hydrograph studies to date--namely, that most stormflow in humid-temperate environments is old water (Bishop, 1991), there clearly is a need to address the potential impact of natural isotopic variability on the use of isotopes as tracers of water sources.

This thesis focuses on the question of how much spatial and temporal variability there is in the isotopic compositions of new and old water in small catchments, and how this variability impacts our ability to model how the catchments "work". The first two chapters focus on the main types of δD

and $\delta^{18}\text{O}$ variability in small catchments. The third chapter suggests a possible solution to the problems raised by the $\delta^{18}\text{O}$ and δD variability of subsurface waters -- an alternative, independent isotopic method for determining the relative amounts of water flowing along different subsurface flowpaths.

Chapter 1 investigates the possibility that the $\delta^{18}\text{O}$ and δD composition of rain may be significantly affected by interception with the tree canopy at a USGS research watershed at Panola Mountain, GA. Some 30 storms over a 2-year period were analyzed to assess intrastorm and spatial variability in rain and throughfall under deciduous and coniferous canopy. Currently, most isotope hydrology studies use the $\delta^{18}\text{O}$ and δD compositions of rain samples collected in open areas as indicators of the isotopic composition of recharge water entering the system. But much of the land surface is forested and if interception of rain with the tree canopy significantly affects the isotopic composition of the rain water, then we might be incorrectly estimating the composition of the actual recharge water. This might be important for paleoclimatic reconstructions, groundwater-recharge studies, and atmospheric water budget calculations--as well as for isotope hydrograph separation studies.

Chapter 2 investigates the development of isotopically heterogeneous subsurface waters in the Hydrohill catchment, a small (490 m²) artificial catchment in China designed for the investigation of storm runoff. Rain water showing a 4‰ intrastorm range in $\delta^{18}\text{O}$ from a 12-cm storm was monitored as it moved through the soil zone and was discharged from various soil horizons; flow through preferential flowpaths plus mixing with pre-storm water results in the development of persistent temporal and spatial

variability in the chemical and isotopic composition of pore waters. The Hydrohill catchment contains an impressive number of piezometer wells, neutron probe access holes, and lysimeters at several horizons allowing the independent determination of the amounts and compositions of surface and subsurface waters flowing along different pathways in the catchment, and the calculation of isotope mass balance budgets.

The extent of temporal and spatial isotopic variability in rain, throughfall, and shallow subsurface waters, as documented in the first two chapters, poses serious problems for the use of isotopes for quantitative determination of the relative amounts of stormflow contributed from different sources. In addition, chapter 2 examines the problems with attempts to determine sources and flowpaths of water using combinations of isotopic, chemical, and hydrologic data and models. At this point, it seems likely that it will be very difficult to adequately estimate the isotopic composition of soil water in many normal-sized catchments. Hence, if soil water is an important source for stormflow, our isotope hydrograph separations will necessarily be less accurate than hoped.

One solution to the problem that our current isotope tools seem inadequate for determining how catchments "work" is to try some new isotope tools. In a series of abstracts (Mills and Kendall, 1987; Kendall and Mills, 1989; Kendall, 1990; Bullen and Kendall, 1991; Kendall et al., 1992a; Kendall et al., 1992b) and a short symposium paper (Kendall et al., 1992c) I have suggested that carbon isotopes, possibly combined with strontium isotopes, appear to be useful for distinguishing between deep and shallow flowpaths, and combined with oxygen isotopes, for distinguishing between water sources. In particular, the stable carbon isotopic composition ($\delta^{13}\text{C}$) of

dissolved inorganic carbon in waters in the soil zone appears to be distinctively different from waters derived from deeper groundwater. If this holds true elsewhere, we might be able to use the carbon isotopic composition of streamwater as an indicator of the relative amounts of water from these two sources, providing a method that is independent of the oxygen and hydrogen isotopic compositions

However, before advocating the use of carbon isotopes as a way of improving the accuracy of isotope hydrograph separations and other models of stormflow generation, it is necessary to demonstrate that carbon does indeed behave semi-conservatively in small catchments. A tracer intermediate in conservativeness between chemical tracers and water isotopes, with some attributes of both, would be useful. Unlike oxygen and hydrogen isotopes, reactions of carbon-bearing species at low temperatures usually involve measurable changes in the isotopic compositions of both the reactant and product (ie., isotope fractionation). The focus of chapter 3 is the demonstration that $\delta^{13}\text{C}$ values of dissolved inorganic carbon are useful tracers of sources of stream alkalinity in small catchments. This paper necessarily precedes the planned papers actually using the combined isotope approach to determining hydrograph separations.

Chapter 1

TEMPORAL, SPATIAL, AND SPECIES-RELATED VARIATIONS IN THE $\delta^{18}\text{O}$ AND δD OF THROUGHFALL

INTRODUCTION

Most isotope hydrology studies use the δD and $\delta^{18}\text{O}$ of rain samples collected in open areas as the indicator of the isotopic composition of recharge water entering the system. But much of the world is forested and if interception of rain with the tree canopy significantly affects the isotopic composition of the rain water, then we might be incorrectly estimating the composition of the actual recharge water. This might be important for paleoclimatic reconstructions, groundwater-recharge studies, stormflow hydrograph separations, and atmospheric water budget calculations.

If the isotopic composition of throughfall is significantly different than rain, we should either be measuring the isotopic composition of throughfall instead of rain or we need to be able to correct the measured rain isotopic compositions for the effects of canopy interception. Obviously, accurate information about potential canopy effects is more critical in areas with dense tree cover than in bare arid zones. Post-infiltration processes in the subsurface such as evaporation or exchange with soil vapor may also alter the isotopic composition of percolating recharge, hence compounding the

problem of accurate determination of the composition of recharge waters (Gat and Tzur, 1967).

Isotopic variations in meteoric waters are generally explained by "isolated air mass" models based on Rayleigh condensation with immediate removal of precipitation (Dansgaard, 1964; Friedman et al., 1964) or with a part of the condensate being kept in the cloud during rain-out (Craig and Gordon, 1965; Gat and Dansgaard, 1972). On a global scale, the isotopic compositions of rain samples produced by rain-out fall along a line in δD - $\delta^{18}O$ space called the global meteoric water line (GMWL) (Craig, 1961a):

$$\delta D = 8 \delta^{18}O + 10 .$$

There is an excellent correlation of average volume-weighted δD and $\delta^{18}O$ values from different stations, with $r = 0.997$ (Gat and Gonfiantini, 1981). The isotopic compositions of mean monthly rain also plot within the same locus of points, with isotopically depleted rain in the winter and isotopically enriched rain in the summer. The seasonality in isotopic compositions at mid-latitude stations is a product of seasonal temperature changes at mid-latitudes which induce variations in the total amounts of water rained-out of the atmosphere as the air masses are transported towards the pole (Craig, 1961a).

Dansgaard (1964) has defined the deuterium excess parameter (d) as:

$$\delta D = 8 \delta^{18}O + d .$$

Air masses of different geographic origin have water vapors with different d-excess values (Hubner et al., 1978) and frontal and convective storms have different isotope enrichment patterns (Miyake et al., 1968). Processes affecting the d-excess value of rain in a partially closed system include ratio of precipitation to evapotranspiration, temperature of precipitation, degree of rain-out, humidity, amount and isotopic composition of evaporated water. Seasonality in d-excess values can be generated by two mechanisms: higher d-excess values in the vapor source of the rain (perhaps derived from evaporation under low-humidity conditions), and evaporation of falling raindrops under low-humidity conditions (Rozanski et al., 1982). The lower d-excess values seen in the summer have been explained by seasonal differences of water balance over the continent; in the summer, transpiration returns to the atmosphere substantial amounts of water isotopically enriched in the heavy species relative to air moisture derived from oceanic sources. This backwards flux of vapor reduces the effect of rain-out and the corresponding isotopic depletion of rain during the summer (Rozanski et al., 1982).

Although it has been realized for a long time that there are large variations in the isotopic composition of precipitation over short time scales (Dansgaard, 1953; Epstein, 1956), there have been surprisingly few studies of intrastorm variations. Bleeker et al. (1966) correlated intrastorm variations in isotopic composition with movements of warm and cold fronts into the area. Matsuo and Friedman (1967) also found that sequential samples of rain varied isotopically over short time intervals, especially at the

beginning of storms when rain intensity was low; during intense rain, isotopic compositions were more constant. In contrast, Pionke and DeWalle (1992) found that the $\delta^{18}\text{O}$ values changed most rapidly during high intensity storms. The first shower of a storm often was enriched in D and ^{18}O relative to later showers; this was attributed to progressive removal of enriched rain from the cloud combined with partial evaporation of raindrops in the undersaturated air (Ehhalt et al., 1963). Nativ and Mazor (1987) also found that the first part of a rain storm is often isotopically enriched and termed this the "front effect". Rains associated with the passage of a frontal system are often characterized by a V-shaped pattern (or W-shaped pattern for multiple fronts), with depleted rain values associated with peak rain intensity (Rindsberger et al., 1990). Falling rain droplets rapidly reach approximate isotopic equilibrium with the atmospheric vapor (Friedman et al., 1962; Stewart, 1975)). Studies of the changes in the isotopic composition of rain with elevation are common (Dansgaard, 1964; Smith et al., 1978) but little is known about small-scale ($< 1 \text{ km}^2$) spatial variations.

Studies of the isotopic variations in throughfall are even more rare. Gat and Tzur (1967) estimated that enrichments in ^{18}O of recharge waters due to evaporation of rain water on tree canopy probably do not exceed 0.5‰ , and predicted that such samples would plot along a slope of about 5 on $\delta\text{D}-\delta^{18}\text{O}$ plots. Pearce et al. (1986) reported an enrichment in ^{18}O of 0.11‰ of throughfall relative to rain for one storm. Saxena (1986) measured the amounts and $\delta^{18}\text{O}$ values of rain and throughfall during summer storms in a pine forest in Sweden and found that throughfall was generally enriched in ^{18}O by a few tenths of a permil relative to the original rain for

interception losses of about 40%; a few storms showed comparable isotopic depletions instead. He developed a model incorporating mixing of rain with a Rayleigh-fractionated evaporated component; using estimated humidity and temperature values, model simulations agreed well with observed fractionations. Gat (1988) also developed a theoretical model of isotope enrichment during canopy interception, based on the mixing of new rain with partially evaporated remnants of water on the leaves.

Several studies have attempted to use the isotopic compositions of water in the soil-plant-atmosphere system to estimate the contributions of evapotranspiration (ET) from various sources (Bariac et al., 1983; Walker and Brunel, 1990). Although transpiration does not cause any significant net isotopic fractionation and returns to the atmosphere water isotopically similar to the soil/groundwater utilized by the plants (Zimmermann et al., 1967), the isotopic compositions of different components of plants may be fractionated. The higher the transpiration rate, the greater the enrichment of leaf water relative to the water source and consequently the further the leaf waters are from equilibrium with atmospheric vapor (Walker et al., 1989). Other factors such as temperature, humidity, uptake patterns, and species differences have also been linked to enrichment (Leaney et al., 1985; Allison et al., 1985; Cooper and DeNiro, 1989). Evaporation, on the other hand, produces isotopically depleted vapor and isotopically enriched residual water via two consecutive isotopic enrichment steps: an equilibrium fractionation caused by the phase change and a kinetic fractionation during transport. Depending mainly on the humidity, kinetic fractionations result in slopes as low as 3 below the GMWL in δD - $\delta^{18}O$ space.

The purpose of the paper is to explore whether interception with the tree canopy significantly affects the isotopic composition of the recharge water, how the fractionation between rain and throughfall varies over the storm, how this fractionation depends on plant species and local environmental conditions, and how significant this fractionation is to studies of isotope hydrology.

For this study, two different kinds of samples were collected: incremental sequential samples during individual storms and total event samples. Both kinds of samples were collected in the open and under two kinds of canopy (deciduous and coniferous).

SITE DESCRIPTION

The Panola Mountain Research Watershed, a 41-ha catchment established by the USGS in 1984 within the Panola Mountain State Conservation Park (Panola), is located in the Piedmont province of Georgia (84°10'W, 33°38'N), about 25 km southeast of Atlanta in Rochdale County (Figure 1). The watershed is underlain primarily by the so-called "Panola Granite"; a prominent 3-ha granodiorite dome is exposed in the headwaters. Soils are classified as Entisols near the base of the dome and as highly weathered Ultisols on hillslopes and ridges (Hooper et al., 1990). The temperature averages 16.3°C, the mean annual precipitation is 112 cm, and winds come mainly from the northwest (Cappellato et al., 1992). The site is

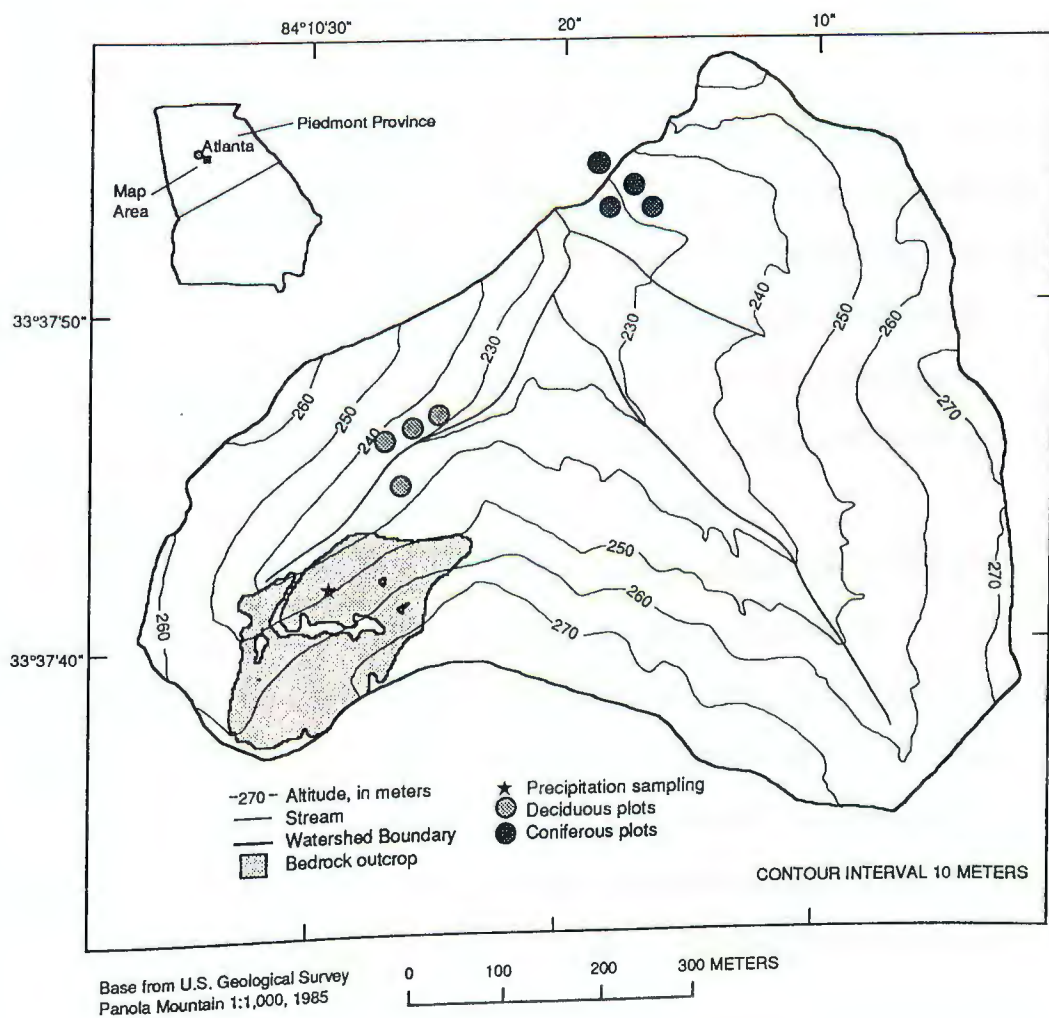


Figure 1. Index map showing the location of the Panola Mountain Research Watershed and the locations of plots and collectors within the watershed.

completely forested, except for the dome, and is characterized by 29% deciduous (oak, hickory, and tulip poplar), 22% loblolly pine, and 31% mixed coniferous/deciduous forests (Cappellato, 1991).

Four 0.04-ha plots each were selected in the deciduous and coniferous forests for the installation of throughfall, stemflow, and litterfall collectors (Figure 1). The throughfall and stemflow collectors were designed to collect bulk intercepted water for individual events. Each plot contained four throughfall collectors, for a total of 16 deciduous and 16 coniferous collectors. Open-air precipitation was collected for each event from a collector located about 40 m from the deciduous plots.

Sequential incremental rain, deciduous throughfall (site 610), and coniferous throughfall (site 110) samples were also collected using custom-made collectors located near the plots; the timing and amounts of throughfall were measured using adjacent tipping-bucket recorders. Rain amount was measured at five sites, and climatic parameters such as temperature, humidity, solar radiation, and wind speed were measured at several sites within the watershed; in addition, a WMO station is located 15 km west of the site.

METHODS

A storm "event" is operationally defined as the time during which rain fell and was collected. At Panola, the rain gages operated continuously and

whenever a rain storm dropped more than about 0.3 mm of rain, the water was removed the next weekday at the end of the shower.

Over a 2-year period October 1987 to November 1989, 29 storms were sampled for spatial and species-related variations in the chemistry of throughfall and stemflow by Cappellato (1991), and dozens of storms were sampled and analyzed for intrastorm variability in water chemistry. Samples were archived for most storms and a subset of 15 storms with incremental samples and 16 storms with spatially distributed samples were later selected and analyzed for δD and $\delta^{18}O$ for this paper; four of these storms had both incremental and spatial samples. Two-thirds of these selected storms were in the growing season (April to October) and one-third were in the dormant season (November to March). All storms had at least 0.4 cm of rain, up to a maximum of 8 cm. The dates used for the storms in this paper are the dates the rain storms started.

Precipitation quantity was determined by weighing the sample in the automatic wet/dry collector (Aerochem Metrics 301¹) for each event; these amounts were verified by comparison with the several tipping-bucket records. Solute fluxes were determined by adjusting the solute concentrations for the collector area.

The storm-event throughfall collectors each consisted of a 16.8-cm diameter screen-covered funnel that was connected to a 1-L collector bottle by 1-cm-diameter tubing looped to reduce evaporation. Stemflow was collected from polypropylene collars 20-cm wide wrapped around tree trunks at breast height. The collars were attached to 220-L carboys with 3-cm tubing. Twelve collectors were installed on the most important deciduous

species and four on loblolly pines. The isotopic composition of stemflow was analyzed for three storms.

All the spatial collectors were rinsed with distilled water immediately before each storm and air dried; the amount of water remaining in the collectors was negligible. All samples were retrieved from the collectors within about 12 hours after the storm ended (Cappellato, 1991). Within 24 hours after collection, all solutions were analyzed for pH and conductivity, and then refrigerated; splits for isotope analysis were usually archived a few days later. The isotope samples were completely full 16-ml glass bottles with tightly sealed polyseal caps; all bottles were waxed to prevent evaporation.

Three types of incremental sequential samples were collected: incremental rain, incremental coniferous throughfall, and incremental deciduous throughfall. The incremental samplers were identical and consisted of a 28.6-diameter funnel located within the wet-side of an Aerochem sampler which was attached to a set of 12 polyethylene bottles connected in series with 1-cm-diameter Tygon tubing. The first eight bottles collect the equivalent of 0.18 cm of rain each, followed by two bottles of 0.33 cm each, and then two bottles of 0.66 cm each. During a storm, each bottle fills in turn, overflows, and new water is routed to the next bottle. On the basis of several tests with chemically different waters, the amount of cross-contamination of the incremental samplers is less than 5% (N.E. Peters, personal communication, 1989). The incremental sample bottles were removed from the collector within 24 hours of the end of the storm, and capped; isotope samples were archived as above.

The incremental-sample collection system had several flaws. First and foremost, exact times for when each bottle was filled are not available because the tipping bucket recorders that recorded the time of each one-hundredth of an inch (0.0254 cm) of precipitation were adjacent to, but not connected to, the water collectors. Although spatial variability in throughfall intensity, and to a lesser extent, rain intensity, would cause the recorders to measure slightly different amounts of rain than was collected in the samplers, it had been expected that it would be very simple to use the tipping bucket records to assign times for the cumulative volumes of water collected in successive bottles in the sequential samplers. However, in-line losses with the sequential samplers and leaks in the hose connections caused considerable uncertainty in assigning times to when the bottles were filled. Times were assigned to the incremental samples by normalizing the cumulative volumes to the amount that was measured by the adjacent recorder and distributing the "losses" evenly among bottles; by this method, the losses are treated as though they were all in-line losses (due to water trapped in the tubes connecting the bottles). The samplers frequently failed to collect complete sets of samples for storms that dropped more than 2.5-4.0 cm of rain.

The samples were analyzed in the U.S. Geological Survey-Water Resources Division stable isotope laboratories in Reston, VA and Menlo Park, CA. Water was prepared for oxygen-isotope analysis by equilibration with carbon dioxide (Epstein and Mayeda, 1953). About 10% of the oxygen-isotope samples were prepared in duplicate, on different days. Most

waters were prepared for δD analysis by the zinc reduction technique (Kendall and Coplen, 1985); the rest were prepared by equilibration with hydrogen gas (Coplen et al., 1991). All δD samples were prepared and analyzed at least in duplicate, on different days. All gases were subsequently analyzed on double-collecting stable isotope mass spectrometers.

All the isotopic compositions are normalized to the VSMOW-SLAP scale and are expressed as δ values in units of permil (‰ or parts per thousand) relative to the standard VSMOW (Hut, 1987). Analytical precisions and long-term reproducibility (2σ) were 0.10‰ for $\delta^{18}O$ and 2.0‰ for δD . Isotopic enrichment factors (ϵ) are the differences in the isotopic compositions between two samples, eg. throughfall and rain. Details of the analysis procedures are included in Appendix 1. All the isotope data are tabulated in Appendix 2.

RESULTS

Two kinds of meteoric water were collected at Panola -- precipitation (P) in open areas and throughfall (T) under tree canopy. Both incremental (I) fractions of the storm and the total event (E) samples were collected for both rain and throughfall. Incremental throughfall (TI) was collected under both deciduous (dec) and coniferous (con) canopy; multiple samplers were located under the two canopy types to detect any spatial variations in throughfall during individual events. Accordingly, the different types of

water samples are abbreviated as PE (precipitation event), PI (incremental precipitation), TEcon (event throughfall under conifers), etc.

All precipitation events (PE) larger than about 2 mm from July 1986 to July 1989 were collected and analyzed for isotopic composition; the local meteoric water line (LMWL) derived from a linear regression of these data is $\delta D = 7.38\delta^{18}O + 9.48$ ($n=176$, $r^2=0.94$) (Table 1). This slope is slightly lower than the slope of 8 generally regarded as reflecting equilibrium condensation (Craig, 1961a). Based on the isotopic compositions of these 176 storms over three years (222.3 cm of rain), the volume-weighted average $\delta^{18}O$ and δD values of precipitation at Panola are -5.38‰ and -29.5‰ , respectively; the averages for the individual years were within $\pm 0.28\text{‰}$ of the $\delta^{18}O$ value and $\pm 4.2\text{‰}$ of the δD value of the 3-year average. Storm size significantly affects the equation of the LMWL (Table 2). Selection of different size fractions can shift the slope of the linear regression by about 0.5 and the y-intercept by about 7‰ . Despite this, there is very little correlation of storm size and $\delta^{18}O$ or δD , with r^2 values of 0.14 and 0.11 for $n = 176$, respectively.

Figure 2 shows the isotopic compositions of event and incremental samples of both rain and throughfall collected at Panola. A number of linear regressions can be derived from these data (Table 1). The equations for all these different types of meteoric water are almost identical but, in general, the throughfall data have slightly higher slopes and y-intercepts than the rain, and incremental samples have slightly higher slopes and intercepts than the event samples. The standard errors (S.E.) for the y-intercepts all overlap but a few of the equations have slopes that are statistically distinct.

Table 1. Linear Regressions of the δD and $\delta^{18}O$ Values of Rain and Throughfall at Panola Mountain, Georgia.

Precipitation type	Linear regression equation	r^2	n	1σ (y-int.)	1σ (slope)
storm-event rain (PE)	$\delta D = 7.38 \delta^{18}O + 9.48$	0.94	176	5.95	0.14
incremental rain (PI)	$\delta D = 8.09 \delta^{18}O + 14.43$	0.96	158	6.04	0.14
all rain samples (PE+PI)	$\delta D = 7.72 \delta^{18}O + 11.70$	0.95	334	6.16	0.10
storm-event coniferous throughfall (TEcon)	$\delta D = 7.63 \delta^{18}O + 12.34$	0.90	115	4.28	0.24
storm-event deciduous throughfall (TEdec)	$\delta D = 7.70 \delta^{18}O + 12.34$	0.92	119	3.84	0.21
all storm-event throughfall samples (TE)	$\delta D = 7.66 \delta^{18}O + 12.34$	0.91	234	4.05	0.16
incremental coniferous throughfall (TIcon)	$\delta D = 8.06 \delta^{18}O + 14.42$	0.97	108	5.45	0.15
incremental deciduous throughfall (TIdec)	$\delta D = 8.37 \delta^{18}O + 16.16$	0.96	103	5.63	0.17
all incremental throughfall samples (TI)	$\delta D = 8.20 \delta^{18}O + 15.21$	0.96	221	5.54	0.11
all throughfall samples (TE+TI)	$\delta D = 8.06 \delta^{18}O + 14.11$	0.95	445	4.86	0.08

Table 2. Effect of Storm Size on the Linear Regression Equations of the δD and $\delta^{18}O$ of Rain.

Storm size	Percent of total	Linear regression	r^2
All (n=176)	100	$\delta D = 7.38 \delta^{18}O + 9.48$	0.94
> 0.5 cm	93	$\delta D = 7.67 \delta^{18}O + 11.49$	0.95
≤ 0.5 cm	7	$\delta D = 7.18 \delta^{18}O + 8.25$	0.89
> 0.2 cm	98	$\delta D = 7.71 \delta^{18}O + 11.81$	0.95
≤ 0.2 cm	2	$\delta D = 6.77 \delta^{18}O + 4.96$	0.88

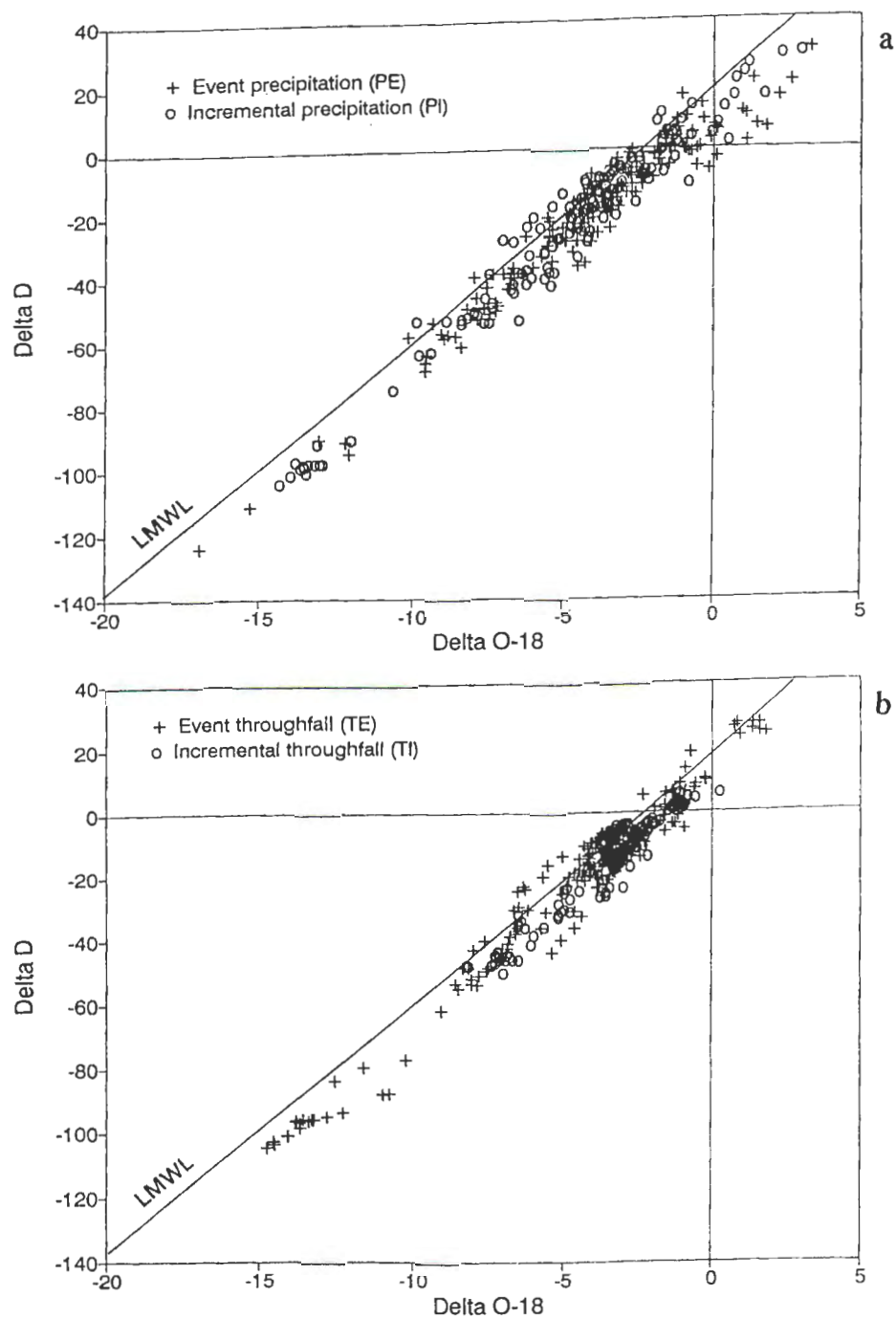


Figure 2. Isotopic compositions of event rain (PE) and incremental rain (PI) samples (a); spatial throughfall (TE) and incremental throughfall (TI) at Panola (b). The linear regression through the PE data, the Local Meteoric Water Line, is labeled LMWL. Analytical uncertainties (2σ) are smaller than the symbols.

A broad data envelope around the local meteoric water line is an indication that humidity conditions showed considerable variation and/or water sources were variable in a locality. Hence, to investigate processes responsible for fractionating throughfall relative to rain, it would probably be more useful to compare the rain and throughfall isotopic compositions from the same storms (Table 3).

Spatial variations in throughfall:

The spatial variations in throughfall amounts and chemistry were determined for the 16 deciduous (TEdec) and 16 coniferous (TEcon) storm-event collectors for 29 storms (Cappellato, 1991). However, only a subset of these were analyzed for $\delta^{18}\text{O}$ and δD : three conifer and three deciduous samples semi-randomly chosen for each of 16 storms. Later, complete suites of samples were analyzed for five of the storms which spanned the range of responses observed. Given the variability in isotopic composition and water amounts for the different collectors, it is possible that biases were created in the data by the sample selection. However, frequency diagrams of water amounts for the entire set and for the subset analyzed for isotopes showed that the subset reflected the distributions of water amounts in the entire set.

The water yields of the individual throughfall collectors were generally less than the yields from the open-air (bulk) rain collectors. For

Table 3. Volume-Weighted Isotopic Compositions and Average Interception Losses for Rain (PE) and Spatial Throughfall (TE).*

Date	PE (cm)	Interception loss (cm)		$\delta^{18}\text{O}$ (‰)			δD (‰)			n
		TEdec	TEcon	PE	TEdec	TEcon	PE	TEdec	TEcon	
10/26/87	1.12	14.6	10.8	-5.50	-4.96	-4.65	-27.0	-24.1	-25.8	5
01/01/88	1.64	4.8	11.1	-3.80	-3.18	-3.29	-11.5	-6.9	-5.7	32
07/21/88	0.39	54.5	38.7	-2.50	-2.75	-2.99	-6.5	-10.0	-12.7	6
07/22/88	1.54	21.8	14.9	-8.20	-8.20	-8.18	-49.5	-47.8	-47.6	6
08/30/88	2.23	12.4	7.8	-4.25	-4.00	-3.90	-18.5	-16.8	-17.0	6
10/31/88	1.20	10.4	17.4	-4.25	-3.63	-3.51	-12.5	-7.3	-7.3	6
11/16/88	0.50	22.8	33.5	-1.30	-1.17	-0.97	0.0	+2.2	+2.9	29
01/03/89	1.11	3.9	12.4	-2.50	-2.56	-2.19	-8.0	-7.0	-4.6	31
02/27/89	1.75	10.5	21.5	-7.35	-6.44	-6.47	-39.0	-35.1	-33.9	6
03/21/89	4.40	3.5	10.0	-5.75	-5.17	-5.00	-38.5	-30.4	-31.4	6
03/30/89	1.13	12.2	18.6	-3.45	-3.28	-3.09	-18.0	-15.7	-13.1	32
04/09/89	1.40	4.2	15.5	-3.90	-3.58	-3.55	-26.0	-25.0	-24.6	6
05/01/89	3.89	6.1	17.0	-7.65	-7.29	-7.15	-49.0	-45.4	-44.8	6
06/05/89	0.82	13.5	27.0	-2.95	-2.71	-2.73	-13.5	-11.4	-10.0	6
07/02/89	2.51	4.9	9.7	-3.65	-3.55	-3.58	-13.5	-13.4	-13.3	31
07/19/89	2.87	9.4	23.1	-3.20	-3.21	-3.08	-13.0	-12.7	-11.2	6

* Interception Loss = PE - (TE + SE)

the subset of collectors analyzed for isotopes, the average interception losses $((PE-TE)/PE*100)$ and 1σ standard deviations for the deciduous and coniferous collectors were $10.6\% \pm 9.9\%$ and $21.1\% \pm 7.4\%$, respectively. These values are similar to the average losses determined for the entire set of throughfall collectors for these same 16 storms, $14.2\% \pm 12.0$ and $20.3\% \pm 8.8$ (Cappellato, 1991).

These water losses are not true (total) interception losses because they do not take into consideration the amount of rain which is intercepted by the trees and runs down the trunks as stemflow. For the storms analyzed for isotopes, the average amounts of the total rain intercepted as stemflow are 1.1% and 2.0% for deciduous and coniferous trees, respectively. For specific storms, the average amount of stemflow (SE) collected under the two canopy types varied from 0.2 to 5.4% of the total rain, with little correlation with season. Therefore, the average interception losses caused by evaporation and canopy storage $((PE-TE-SE)/PE)$ for all the collectors for the 16 storms are 13.1 and 18.1% for deciduous and coniferous canopy, respectively.

The isotopic compositions of the throughfall event (TE) samples (Figures 3a-c) form "clumps" in δD - $\delta^{18}O$ space rather than trending parallel to the local meteoric water line because the range in isotopic compositions for different collectors for the same storm is relatively small. The average range in $\delta^{18}O$ for a set of collectors is 0.5‰ but for some storms was as high as 1.2‰ (Figure 4). Almost all the throughfall samples for each storm are enriched in ^{18}O and D relative to the corresponding PE samples. Some of the variability might be due to small amounts of water remaining on the

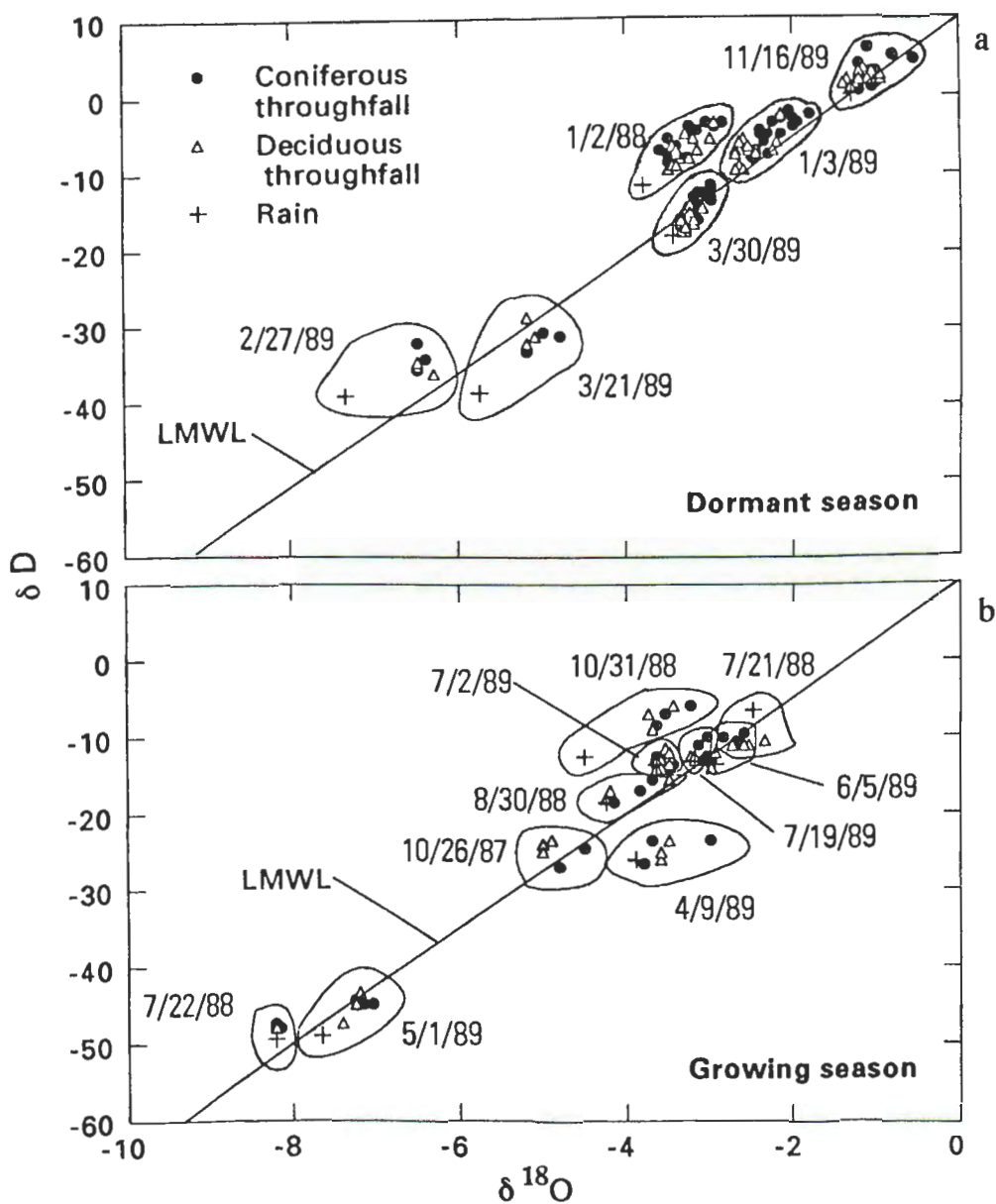


Figure 3. Isotopic compositions of spatial throughfall and corresponding event samples for the 16 storms: (a) Dormant season storms, November - March; (b) Growing season storms, April - October. Analytical uncertainties (2σ) are smaller than symbols.

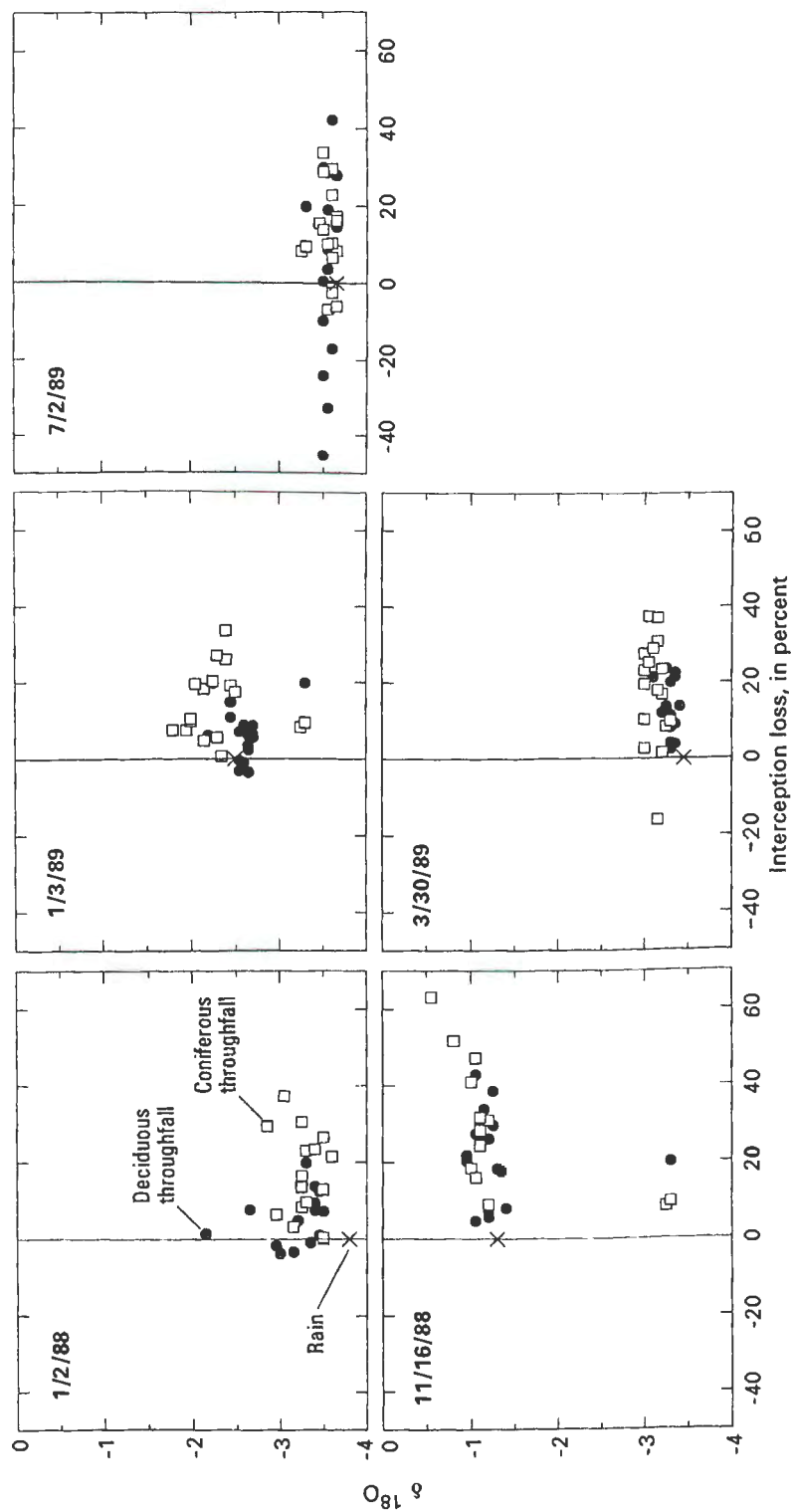


Figure 4. Comparison of $\delta^{18}\text{O}$ values of event rain and throughfall samples and interception losses for five storms. The 2σ analytical uncertainty is 0.1‰ .

canopy from previous storms. Two of the storms with the largest variability (8/30/88 and 4/9/89) occurred within 12 hours after a previous storm; the other storms show no correlation of variability and hours since the previous storm.

The volume-weighted $\delta^{18}\text{O}$ and δD values of TE samples (from the multiple collectors) for each of the 16 storms (Table 3) are enriched in ^{18}O and D relative to the rain samples for almost all storms (Figure 5); only throughfall for the 7/21/88 storm shows depletion in both isotopes relative to rain. Conifer throughfall is enriched relative to PE by $\delta^{18}\text{O} = +0.43\text{‰} \pm 0.59\text{‰}$ and $\delta\text{D} = +2.2\text{‰} \pm 2.4$ (n = 115). Deciduous throughfall is enriched relative to PE by $\delta^{18}\text{O} = +0.32\text{‰} \pm 0.61\text{‰}$ and $\delta\text{D} = +3.2\text{‰} \pm 2.8\text{‰}$ (n = 115). Hence, throughfall collected under conifers is enriched in ^{18}O by an average of $+0.11\text{‰}$ and enriched in D by an average of 1.0‰ relative to throughfall under deciduous trees. These average differences are well within the 2σ analytical error bars, but are nonetheless real; one-sided t tests indicate that the differences are significant at the 2.5% level for $\delta^{18}\text{O}$ and the 0.25% level for δD . The volume-weighted $\delta^{18}\text{O}$ values of coniferous throughfall are enriched in ^{18}O by an average of 0.2‰ relative to deciduous throughfall for about 55% of the storms, are identical ($\pm 0.05\text{‰}$) for 30%, and are depleted by an average of 0.2‰ for 15% of the storms.

There is no correlation between % water loss and the volume-weighted average throughfall enrichments for the entire set of samples for the 16 storms ($r^2 < 0.1$ for both isotopes and both canopy types). For the five storms where almost-complete sets of TE samples were analyzed, only one (11/16/88) showed a moderate positive correlation

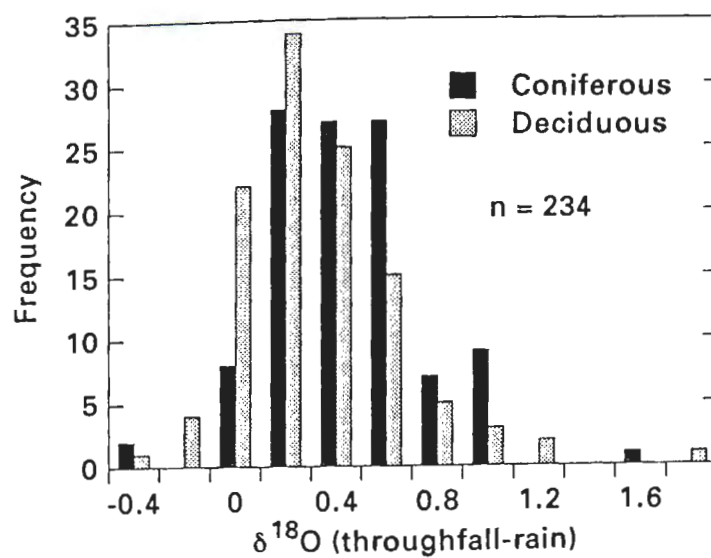


Figure 5. Histogram of the enrichments in ^{18}O of coniferous and deciduous throughfall collected for entire events, relative to rain collected for the same time periods. The 2σ error bars are 0.14‰ .

($r^2 = 0.3$) of % water loss and isotopic enrichment of samples (Figure 4b). The other four storms (Figure 4a,c,d,e), and the storms where only about six samples each were analyzed, showed correlations of less than $r^2=0.1$. In general, the coniferous collectors showed more isotopic enrichment and higher water losses than the deciduous collectors.

For the three storms where stemflow samples from the 12 collectors were analyzed for isotopic composition, all the SE samples were enriched in ^{18}O and D relative to the rain (Table 4), and showed more variability in composition than the corresponding TE samples. The 1/1/88 storm showed the most variation: more than 1‰ in $\delta^{18}\text{O}$ and 10‰ in δD , and a good positive correlation ($r^2 = 0.51$) of water amount and $\delta^{18}\text{O}$. In δD - $\delta^{18}\text{O}$ space, the three sets of stemflow samples plot along slopes of 10 ± 0.5 with y-intercepts of 20 ± 5 ‰; as a group, stemflow samples have a d-excess value of +16‰. The stemflow data plot above the lines formed by other rain and throughfall samples for the same storms.

Problems associated with incremental collectors:

The total amount of PI collected in the sequential collector should be only slightly less than the amount of PE (because of edge-effects with small funnels), and the amounts of TI should only be slightly smaller than the PI because of the additional losses resulting from evaporation and storage; the isotopic compositions of PE and volume-weighted PI should also be very similar. Because differences between PE and PI amounts and isotopic

Table 4. Isotopic Compositions of Rain (PE), Throughfall (TE), and Stemflow (SE) for Three Storms.

Date	$\delta^{18}\text{O}$ (‰)				δD (‰)			
	PE	TE	SE	1 σ (SE)	PE	TE	SE	1 σ (SE)
01/01/88	-3.80	-3.23	-2.80	0.31	-11.5	-6.4	-3.1	3.5
01/03/89	-2.50	-2.39	-2.41	0.13	-8.0	-6.0	-6.3	1.4
07/02/89	-3.65	-3.57	-3.51	0.06	-13.5	-13.2	-12.3	1.0

compositions should be solely a function of sampler problems, comparison of the PE and PI data should allow a realistic evaluation of the magnitude of any possible biases introduced by these two types of collections. Sample recovery problems with the incremental collectors could cause various biases in the amounts and isotopic compositions of waters, making determination of strictly canopy-effects of incrementally collected throughfall samples difficult.

There is an excellent correlation ($r^2 = 0.98$) between total PE and PI amounts for 50 storms 1987-89 (Figure 6a) selected by the following criteria: (1) both PE and PI were collected; (2) there were no known problems with the collectors; (3) it was clear that the PI and PE samples were collected for identical time intervals; and, (4) $PE > PI$. The average water loss associated with the incremental rain collector for these 50 storms is 19% ($\pm 10.7\%$) of the total PE. There is no correlation ($r^2 < 0.1$) between the size of the storm and the percent water loss.

The amounts of precipitation collected by the PI, Tldec, and TIcon samplers are plotted relative to the amount of PE on Figure 6a; the line derived from the correlation of PI and PE for the 50 storms is plotted here for comparison. Except for the 7/27/88 storm where the PI sampler failed, all the other PI amounts plot close to the line; hence, the PI sampler was behaving "normally" for all but one of the storms analyzed for isotopic composition.

The percent of the total rain (PE) collected by the incremental rain samplers for the 15 storms ranged from 70.9 to 99.3%, with an average of 83%. It is unclear how much of this difference was due to: (1) problems

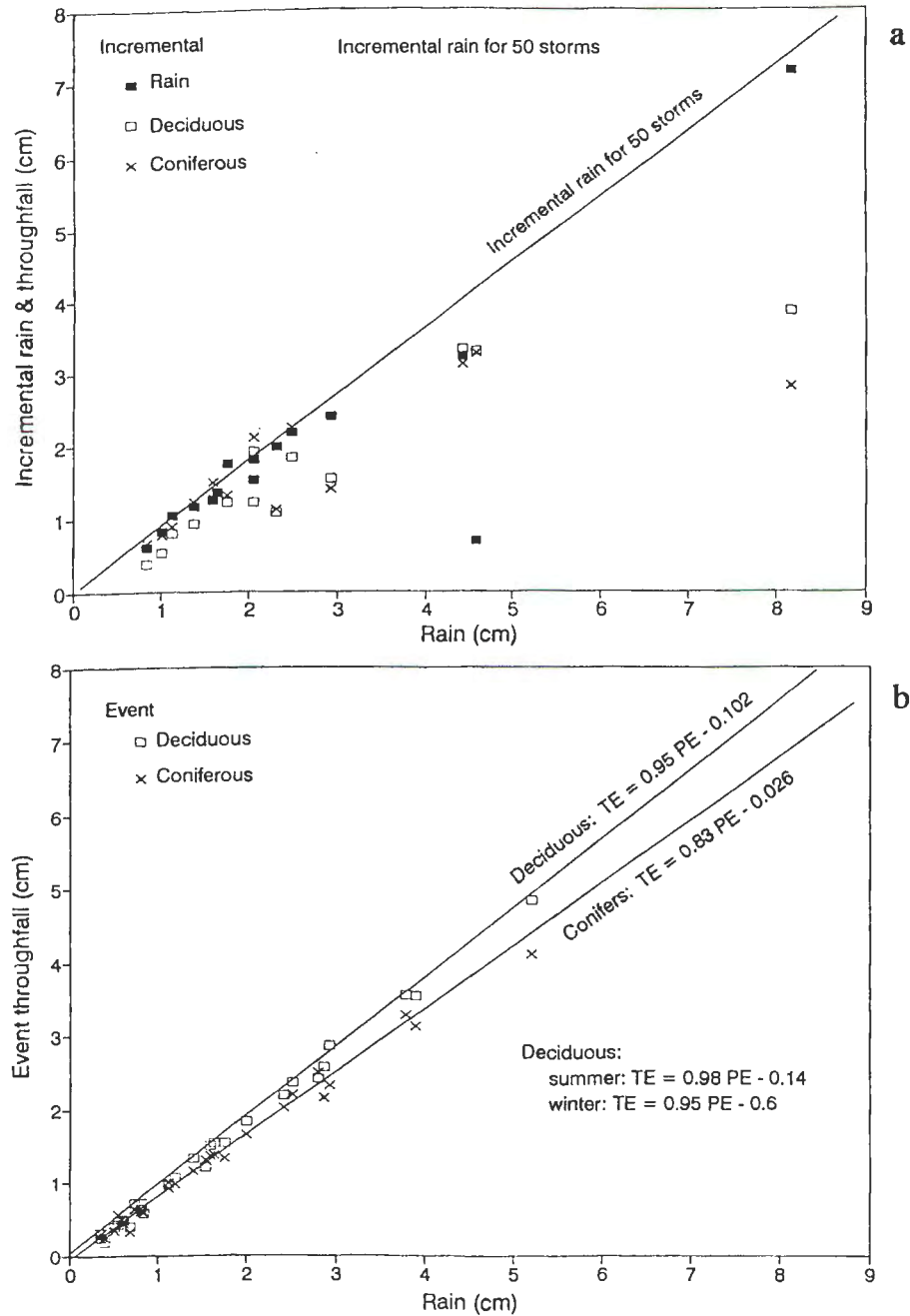


Figure 6. Comparison of amounts of water collected in throughfall samplers with amounts collected in rain samplers. (a) Volume-weighted averages of incremental rain (PI), incremental coniferous throughfall (TIcon), and incremental deciduous throughfall (TIdec); (b) Linear equations derived from volume-weighted throughfall event (TE) data. See text for more detailed explanations.

with collecting rain in a small funnel (i.e., wind effects, edge effects, etc.; Crockford and Johnson, 1983); (2) water remaining in the tubes connecting the bottles; and, (3) water leakage through the vent hoses on each bottle. Samples were collected and appropriately bottled within 24 hours after the end of the storm so evaporative losses were probably negligible.

The volume-weighted average $\delta^{18}\text{O}$ and δD values of incremental samples for the 15 storms are listed in Table 5. Problems with the collectors caused substantial losses for several storms, particularly for the 7/27/88 and 9/3/88 storms (Figure 3a). Unfortunately, the volume-weighted isotopic compositions of the PI samples are not identical with those of the corresponding PE samples (Table 5). For the 13 storms where the collectors behaved normally, the average volume-weighted $\delta^{18}\text{O}$ value for PI is 0.17‰ (± 0.37) heavier than for PE, with a range of +0.76 to -0.65‰ for specific storms; for a third of the storms, the PI $\delta^{18}\text{O}$ values are within ± 0.2 ‰ of the PE compositions. The average volume-weighted δD value for PI is +2.5‰ (± 2.9 ‰) with a range of +7.2 to -3.7‰. There is no correlation ($r^2 < 0.1$) between percent water loss and the shift in $\delta^{18}\text{O}$ or δD of the PI samples relative to the PE samples; hence, evaporation does not appear to be the main cause of the frequent enrichment of the PI samples relative to PE.

The PI data show that neither the amounts of water collected in the incremental samplers nor the volume-weighted isotopic compositions accurately represent the original rain. Because the incremental throughfall and rain collectors were identical and hence have the same kinds of potential biases, detailed comparisons of the TIcon or TIdc incremental data with either the PI or PE data are unwarranted. However, given that the average

Table 5. Isotopic Compositions for Total Rain (PE), Incremental Rain (PI), and Throughfall (TI).

Date	$\delta^{18}\text{O}$ (‰)				δD (‰)			
	PE	PI	TIdc	TIcon	PE	PI	TIdc	TIcon
1/01/88	-3.80	-3.90	-3.14	--	-11.5	-11.6	--	-5.0
1/03/88	-13.10	-13.30	-12.27	--	-90.0	-93.7	--	-84.4
5/10/88	-4.10	-3.74	-3.20	-3.13	-29.0	-25.4	-20.5	-19.8
5/15/88	-5.75	-5.99	-6.34	-6.67	-42.0	-37.4	-40.7	-38.4
6/02/88	+1.35	+1.64	+1.37	+1.22	+21.0	+25.8	+26.3	+25.1
6/09/88	-2.35	-1.90	-1.94	-2.10	-9.5	-4.2	-4.7	-3.2
6/19/88	-1.50	-1.33	-1.73	-1.35	+0.0	+1.8	+4.0	+2.3
7/27/88	-3.50	-3.68	-3.70	-3.55	-19.5	-17.9	-17.7	-17.9
9/03/88	-6.65	-6.37	-4.71	-4.73	-40.0	-38.3	--	--
9/04/88	-12.10	-12.75	-12.66	-13.26	-94.5	-90.9	-96.4	-94.4
9/16/88	-4.10	-3.92	-5.84	-6.03	-11.5	-11.6	-15.9	-15.6
10/01/88	-4.45	-4.18	-4.53	-4.76	-16.0	-15.8	-19.3	-19.6
1/03/89	-2.5	-2.44	-2.49	-2.34	-8.0	-5.1	-4.0	-6.1
2/28/89	-7.35	-6.74	-6.28	-6.70	-39.0	-31.8	-31.4	-27.6
3/30/89	-3.45	-3.47	-3.13	-2.91	-18.0	-15.7	-12.0	-14.0

storm showed a 3.5‰ (± 2 ‰) decrease in $\delta^{18}\text{O}$ over the event, the average total offset of +0.17‰ is relatively unimportant for evaluating intrastorm changes in composition. There is no correlation ($r^2 < .01$) between amount of intrastorm variability and the $\Delta\delta(\text{PE-PI})$ values. The seemingly erratic nature of the water losses prevents prediction of how any sampler will behave isotopically during a storm. However, error bars on the probable shift in $\delta^{18}\text{O}$ of any specific sequential sample can be estimated as follows:

If the water loss is indeed proportional to the volume collected (as Figure 6a implies), then the isotopic effect of a 20% loss in each bottle can be calculated. The $\delta^{18}\text{O}$ values of successive PI samples change gradually over time and, in general, decrease during the storm (Figure 7a-c).

Volume-weighted PI has a slight tendency to be heavier than PE and since evaporation is apparently not the cause, slightly more of the loss must occur in bottles collected at the end of the storm than at the beginning. The maximum intrastorm change in $\delta^{18}\text{O}$ observed during the storms studied is 7‰; the biggest shift in $\delta^{18}\text{O}$ between any two successive bottles is about 3‰. If I assume that the isotopic composition changed monotonically by 3‰ during the time a bottle is filling and that all the loss occurred either at the beginning or ending of the filling time, this loss would cause a shift in $\delta^{18}\text{O}$ of about 0.5‰ ($\pm 2\sigma = 0.1$ ‰) from the "true" composition of the incremental sample. The corresponding worst-case shift in δD is about 4.0‰ ($\pm 2\sigma = 2.0$ ‰). This worst-case scenario is probable because the overflow water between the filling of adjacent bottles has the highest likelihood of being lost either by venting through the air hoses or by in-line losses. For the more average $\delta^{18}\text{O}$ change of 4‰ over the storm, a 20%

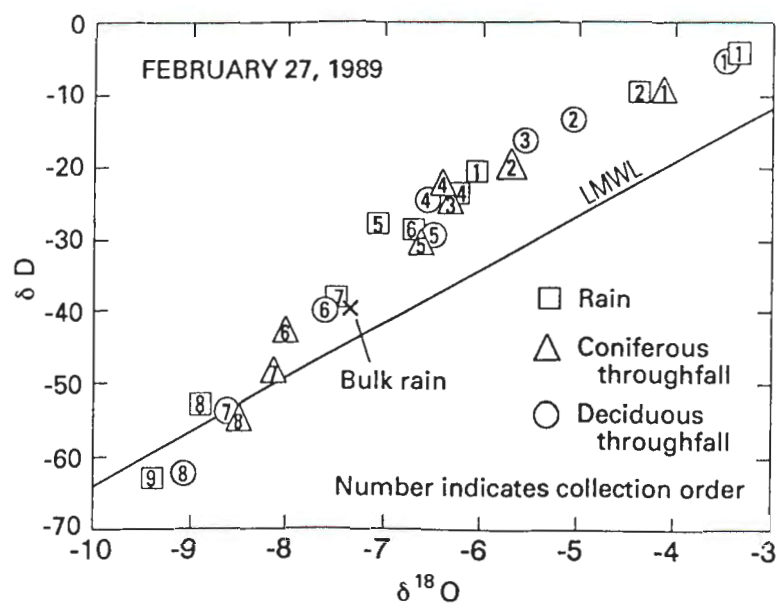


Figure 7. Intrastorm changes in δD and $\delta^{18}O$ for: rain (PI); deciduous throughfall (TDec), and coniferous throughfall (TIcon) for the 2/27/89 storm. Successive samples are labeled in numerical order. 2σ error bars may be as high as 0.6‰ for $\delta^{18}O$ and 6‰ for δD because of collector problems.

loss would cause a shift of about 0.1‰. Depending on whether the loss occurs at the start or end of the bottle filling, the shift in $\delta^{18}\text{O}$ would be positive or negative. Hence, the error bars on the $\delta^{18}\text{O}$ values of individual incremental samples due to leakage and in-line loss are probably less than 0.5‰; these same error bars also apply to the identical throughfall collectors.

The deciduous incremental collector has both larger water losses and greater enrichments in ^{18}O and D relative to the PE samples than observed for the coniferous incremental collector; in contrast, the TE samples generally show greater water losses and enrichments under conifers. The opposite finding with the two incremental samplers is probably an example of the type of site-specific effects seen in Figure 4; not all the conifer sites showed more water loss and greater enrichment than all the deciduous sites. However, greater water losses are generally correlated with greater enrichments. The coniferous TI collector was located under much sparser canopy than was typical for the spatial TE collectors. Comparison of Figure 6a with 4, which shows the relation between amounts of PE versus TE amount for the deciduous and coniferous collectors, suggests that the amount of variability seen for TI collectors in Figure 6a is not necessarily due to problems with the incremental samplers but, in part, represents natural site and storm-dependent variability.

For the storms analyzed for isotopic composition, the average water losses for the coniferous and deciduous TI collectors relative to PE are 27 and 35%, respectively, compared to the average loss of 17% for PI. Thus, assuming that the TI collectors suffered the same types of leakage and in-line

water losses as the identical PI collectors, the canopy interception losses for the deciduous and coniferous collectors are about 10 and 17%, respectively; these values are within the range of losses observed for the 32 TE collectors (Cappellato, 1991). The volume-weighted $\delta^{18}\text{O}$ values of TI for individual storms range from 2‰ enriched to 2‰ depleted in ^{18}O relative to the PE. This is considerably more variability than was seen in the $\Delta\delta(\text{PE-PI})$ values and much greater than the estimated error bars for leakages associated with incremental collectors; hence, this greater variability probably reflects interactions with the canopy, not just collector problems.

In summary, the unfortunate leakage of the incremental collectors limits the potential usefulness of the incremental data. Even though there is a 10-17% water loss associated with the TI samples that cannot be explained by collector problems and a general isotopic enrichment of volume-weighted TI relative to PE or volume-weighted PI, I cannot determine if the TI for storms is truly isotopically distinct from the PE or PI for the same storms because the $\Delta\delta$ values fall within the range of deviations caused by collector leakages. Given that the $\delta^{18}\text{O}$ of volume-weighted PI differs from PE for the same storm by an average of +0.17‰, comparisons of average $\delta^{18}\text{O}$ values of incremental samples is probably unwarranted. However, intrastorm patterns among the three incremental collectors are still interpretable because the $\delta^{18}\text{O}$ of individual samples are probably shifted by less than $\pm 0.5\text{‰}$. Hence, the best use of the TI and PI data is to investigate intrastorm processes where trends are more important than absolute isotopic compositions.

Intrastorm variations in rain and throughfall:

Figures 6a and 6b show the intrastorm changes in δD and $\delta^{18}O$ for the three incremental samplers during the 2/27/89 storm, a typical winter storm. Successive samples are labeled in numerical order. Plots for the other 14 storms are included in Appendix 3. During most storms, throughfall continued to drip from the trees for up to an hour after rain had ceased. The first incremental samples are commonly enriched relative to the rest of the storm, which could be a product of normal rain-out and/or evaporative enrichment of raindrops falling through an unsaturated airmass; this enrichment can then be compounded by throughfall interception on relatively warm, dry leaf surfaces. The $\delta^{18}O$ and δD values of the incremental samples generally decrease during the course of the storms. The TIcon samples are almost always enriched in ^{18}O relative to PI and TIdéc samples; this is especially true after slight decreases in rain intensity and at the ends of the storms when evaporation would reasonably have more of an effect on the composition of the water dripping through the canopy. The last TIcon is almost always considerably enriched relative to the last TIdéc sample.

Individual winter storms showed gradual monotonic 3 to 7‰ decreases in $\delta^{18}O$ over time. TI samples track the PI samples fairly well but are usually enriched relative to PI samples for the entire storm, especially at the end. The $\delta^{18}O$ composition for TIcon is consistently enriched relative to PI. The TIdéc, on the other hand, is usually very similar to PI, which is

reasonable because during the winter the leafless deciduous trees intercept very little rain. On δD - $\delta^{18}O$ plots, the isotopic compositions of successive samples do not plot along straight lines; instead, they form bow-shaped, concave-down curves. The TI samples form curves slightly more bow-shaped than the PI samples, mostly because the last TI sample is especially enriched in ^{18}O . The best examples of bow-shaped curves are the five winter storms, four of which have both TI and TE data (Table 6) that are in good agreement. A few of the summer storms also are vaguely bow-shaped in δD - $\delta^{18}O$ space (Appendix 3).

The worst-case 2σ error bars on incremental samples, caused by collector problems, is about 0.6‰ for $\delta^{18}O$ and 6.0‰ for δD ; because of high correlation coefficient between $\delta^{18}O$ and δD of waters ($r^2 = 0.95$ for all the rain data in this study), the error correlation is estimated to be about 0.9. When second-order polynomials equations are fitted to the incremental data with the above error bars (Appendix 4), the winter storm data still form concave-down bow-shaped curves that are similar in shape (equation) among sets of samples collected for the same storm. Except for the May storms, the rest of the summer storms are characterized by widely different equations among sets of samples for the same storms. Thus, despite problems with incremental collectors, the bow-shaped curves are "real" and appear to be characteristic of winter storms at Panola.

There are two types of storms during the growing season: convective storms that have very rapid decreases in $\delta^{18}O$ over short time intervals during periods of intense rain, and frontal storms where the longer periods of gentle rain are associated with considerable intrastorm isotopic variability. During

Table 6. Isotopic Compositions of Rain PE) and Throughfall
for Four Storms where both Incremental (TI) and Spatial (TE) Samples were Collected.*

Date	$\delta^{18}\text{O}$ (‰)				δD (‰)				Slope of line in $\delta\text{D}-\delta^{18}\text{O}$ space	
	PE	TE	TI	PE	TE	TI	TEdec	TEcon		
01/01/88	-3.80	-3.23	-3.14	-11.5	-6.4	-5.0	7.4	11.4		
01/03/89	-2.50	-2.39	-2.42	-8.0	-5.9	-5.0	--	11.0		
02/27/89	-7.35	-6.45	-6.49	-39.0	-34.6	-29.5	4.3	5.8		
03/30/89	-3.45	-3.19	-3.04	-18.0	-14.4	-13.9	13.5	13.6		

* Conifer and deciduous data averaged together.

intense rain, the rapid changes in the isotopic composition of PI are closely mimicked by the TI, both forming bow-shaped curves. For frontal storms, the TI tracks the PI only moderately well, showing the same types of oscillations as the PI but generally damped and not exactly in phase with the PI.

The equations of linear regressions derived for PI, TIdec and TIcon for the 15 storms are slightly different (Appendices 5 and 6), but no trends are apparent and the 95% confidence bands for the different equations for the same storm generally overlap. For storms where δD and $\delta^{18}O$ are highly correlated ($r^2 \geq 0.80$), the slopes of the linear regressions range from 3 to 11, with average slopes of 8 to 9. When "Yorkfit" linear regressions -- which weigh each point according to its x and y errors plus any x-y error-correlations -- are derived for the same data (Appendix 7), the equations are similar to ones derived using normal linear regressions, again with average slopes of 8 to 9. These equations are indistinguishable from those of PE and TE samples (Table 1) at the 95% confidence level. Because rain formed by equilibrium condensation generally plots along a slope of 8, the variability in slope indicates that there is more going on than just equilibrium condensation.

DISCUSSION

Although rain condensation is generally thought to take place in isotopic equilibrium with the atmospheric vapor (Dansgaard, 1964), as the

rain drops fall through a lower air mass with a different air temperature, humidity, and vapor isotopic composition, the drops are subject to both evaporation and isotopic exchange. Plotting rain data on δD - $\delta^{18}O$ plots often provides useful information about the evolutionary controls on the isotopic compositions of these waters. Evaporation, for example, usually causes the residual waters to plot along so-called evaporation lines of slopes less than 8; the resulting evaporated vapor typically has a higher d-excess value than the ambient atmosphere. Equilibrium evaporation at humidities close to 100% causes the residual waters to become progressively enriched along the MWL. Atmospheric vapor with a large component of evaporate is characterized by a higher d-excess than the original vapor, and precipitation from this mixed air mass or exchange of rain droplets with it will produce rain with a higher d-excess value. Hence, it is possible to use the d-excess value as a diagnostic tool for recognizing the addition of evaporated moisture into the local atmosphere (Gat and Matsui, 1991; Gat et al., 1993).

The same evaporation-exchange processes later affect the isotopic compositions of the intercepted rain water on the tree canopy, part of which drips down as throughfall or drips down the tree trunk as stemflow, and the rest evaporates back into the atmosphere. Hence, the isotopic composition of the throughfall which reaches the soil and eventually may result in storm runoff or recharge, may not be the same isotopic composition as the original rain. The magnitude and direction (i.e., enrichment or depletion in the heavy isotope) of the isotopic change of throughfall relative to rain is a function of evaporation rate, temperature, humidity, and the difference between the isotopic compositions of the rain and atmospheric vapor.

Intrastorm variability in rain and throughfall:

Similarity of PI and TI: The general similarity of the PI and TI equations (Appendices 5 and 7) and their curves in δD - $\delta^{18}O$ space (Figure 7) for sets of samples from the same storm is unexpected and not easy to explain. One conclusion to be drawn is that the throughfall samples show little evidence for any additional post-rainfall kinetic fractionation resulting from additional evaporation on the canopy surfaces. Not even the first samples of each storm, which are almost always enriched in ^{18}O and D relative to the remaining rainfall and often plot below the other storm samples in δD - $\delta^{18}O$ space (but not much below the LMWL), show any evidence for evaporative enrichment. The linear regression through the first samples of TI and PI ($n=39$) is $\delta D = 8.04\delta^{18}O + 12.22$ ($r^2 = 0.94$), similar to the equations for various linear regressions in Table 1. Thus, although there has been an average 10-17% loss of water for TI samples relative to PI samples, and a general isotopic enrichment of TI relative to PE, the TI samples do not generally plot along evaporation lines in δD - $\delta^{18}O$ space.

The PI and TI curves are most similar during convective storms, particularly in the winter. This makes sense because one would expect less opportunity for enrichment if the storm is intense and the canopy is sparse. The main differences between the winter PI and TI data are that the first TI samples are not as enriched, nor are the last TI samples as depleted, as the

rain. For the deciduous collectors for several of these storms, the amount of water lost to evaporation was small--less than or equal to the amount stored on the canopy (Table 7); hence, the early depletion of TI samples relative to PI samples could be explained by evaporation of part of the first bottle-volume of rain on dry leaves, and the latter enrichment could be caused by storage of the final rain water. However, for TI on the evaporative losses were 5-10 times greater than the amount of water stored.

During frontal storms in the growing season, the first PI samples occasionally fall very slightly below the LMWL. Otherwise, the oscillations seen in PI, both parallel to the LMWL and erratic movements away from the LMWL, are usually broadly mimicked by the TI. Because $\delta^{18}\text{O}$ values varied during these storms, selective storage of various waters could cause all sorts of variable isotopic patterns in the resulting throughfall. Despite large evaporative losses -- particularly by conifers -- relative to open rain samples, the TI samples are not always enriched relative to the PI samples.

Incremental vs spatial samples: There are systematic differences between incremental and event data. Inspection of Table 1 reveals that PI samples plot on a line in δD - $\delta^{18}\text{O}$ space with a higher slope and y-intercept than PE samples; although the 1σ standard error values for the y-intercepts overlap, the slopes of the PE and PI lines are indeed different at the 95% confidence level. The d-excess values for PE and PI are +11.95‰ and +13.97‰, respectively. The TI samples also plot along lines with higher slopes (at the 95% confidence level) and y-intercepts than the TE samples; the d-excess values are +13.50‰ for TE and +14.32‰ for TI. While the higher slopes

Table 7. Percentages of Event Rain (PE) Lost to Various Water Reservoirs.

Date	PE (cm)	Percent of PE lost to different reservoirs			Enrichment of TE relative to PE		Selective storage could cause most of the $\delta^{18}\text{O}$ enrichment
		Storage	Stemflow	Evaporation	$\delta^{18}\text{O}$ (‰)	δD	
Deciduous							
10/26/87	1.125	12.4	0.4	2.1	0.54	2.9	+
01/01/88	1.643	3.7	1.4	1.2	0.62	4.6	
07/21/88	0.399	35.1	0.0	19.3	-0.25	-3.5	+
07/22/88	1.549	9.0	0.3	12.8	0.00	1.7	+
08/30/88	2.794	5.0	1.0	7.4	0.25	1.7	+
10/31/88	1.203	5.0	0.7	5.3	0.62	5.2	
11/16/88	0.500	12.0	0.2	10.4	0.13	2.2	+
01/03/89	1.592	3.8	1.8	0.1	-0.06	1.0	
02/27/89	1.754	3.4	2.1	7.1	0.91	3.9	
03/21/89	3.785	1.6	2.5	1.9	1.58	8.1	
03/30/89	1.134	5.3	0.9	6.9	0.17	2.3	+
04/09/89	1.407	3.6	1.6	0.6	0.32	1.0	
05/01/89	3.892	3.6	3.0	2.5	0.36	3.6	
06/05/89	0.827	7.3	0.2	6.2	0.24	2.1	+
07/02/89	2.510	2.4	1.0	2.5	0.10	0.4	
07/19/89	2.871	4.9	0.6	4.7	-0.01	0.3	+
averages	1.053	2.5	1.4	10.3	0.197	0.9	

Date	PE (cm)	Percent of PE lost to different reservoirs			Enrichment of TE relative to PE		Selective storage could cause most of the $\delta^{18}\text{O}$ enrichment
		Storage	Stemflow	Evaporation	$\delta^{18}\text{O}$ (‰)	δD	
Conifers							
10/26/87	1.125	2.67	0.62	8.18	0.85	1.2	
01/01/88	1.643	1.83	5.36	9.31	0.51	5.8	
07/21/88	0.399	7.52	0.50	35.84	-0.49	-6.2	
07/22/88	1.549	1.94	0.90	12.91	0.02	1.9	+
08/30/88	2.794	1.07	2.58	6.69	0.35	1.5	
10/31/88	1.203	2.49	1.75	14.88	0.74	5.2	
11/16/88	0.500	6.00	0.40	27.20	0.33	2.9	
01/03/89	1.592	1.88	2.64	10.49	0.31	3.4	
02/27/89	1.754	1.71	2.28	19.84	0.88	5.1	
03/21/89	3.785	0.79	3.30	9.17	1.75	7.1	
03/30/89	1.134	2.65	0.88	15.96	0.36	4.9	
04/09/89	1.407	2.13	2.49	13.36	0.35	1.4	
05/01/89	3.892	0.77	2.80	16.24	0.50	4.2	
06/05/89	0.827	3.63	0.36	23.34	0.22	3.5	
07/02/89	2.510	1.20	2.75	8.45	0.07	0.2	+
07/19/89	2.871	1.04	1.50	22.19	0.12	1.8	
averages	1.812	2.457	1.944	15.878	0.429	2.7	

and intercepts of incremental samples could to some extent reflect data scatter, or some storm-specific or seasonal bias, most of the linear regression equations determined for PI and TI from individual storms (Appendix 5) also have slopes and intercepts higher than the LMWL defined by the PE and TE samples.

The observation that incremental samples fairly consistently plot along lines with slightly greater slopes and y-intercepts than event samples points to the existence of processes operating on different time scales that cause different fractionation effects. The effects of processes acting on meteoric waters during storms may be camouflaged in sets of event data by volume-weighting, larger-scale spatial variations, or seasonal effects. A possible explanation for different equations for incremental samples lies with the bow-shaped, concave-down nature of incrementally collected data in δD - $\delta^{18}O$ space. Each equation for incremental samples is defined by very few points, and the bow-shaped nature of the curves in δD - $\delta^{18}O$ space causes the slope to be strongly affected by the position of single points. Because the isotopic composition changes rapidly during the initial high-intensity portion of the storm, most of the data points lie on the lower end of the bow-shape, thus causing relatively high slopes to be calculated.

The early PI and TI samples lie near or above the LMWL, the last samples lie on or below the LMWL, and the intermediate samples always lie above the line. The close match of curves seen with the three incremental collectors argues that leakage problems have had minimal effect on the basic pattern of decreasing isotopic composition during the storm. It is curious that the first PI and TI samples fail to plot significantly below the LMWL;

because the ambient airmass was probably relatively unsaturated at the beginning of the storm, it might be expected that these samples would be substantially affected by evaporation of falling raindrops.

Exchange of falling rain with atmospheric vapor containing a large fraction of evaporated moisture could explain the higher d-excess values of rain during the middle of the storms. At the beginning and end of the storms, the evaporative enrichment, however minimal, appears to have a stronger effect than does exchange. Perhaps the slight evaporative signature at the beginning and end is a result of "edge effects" between moving air masses. In any case, the wide range of slopes in δD - $\delta^{18}O$ observed for PI and TI samples indicates that there has been significant amounts of exchange between the falling raindrops and local air masses of variable isotopic composition and humidity; in general, the slopes with values significantly different from 8 demonstrate that equilibrium condensation effects have been overprinted by isotopic exchange.

An alternate explanation for the bow-shaped curve of successive samples of rain is that it is an inherent product of the condensation process. The global meteoric water line is a remarkably straight line for what is generally assumed to be a continuous fractionation process. Gat (1980) noted an explanation for the straightness of the GMWL and its slope of 8 in δD - $\delta^{18}O$ space proposed by Harmon Craig: that the GMWL represents a mixing line between marine moisture and drier air from the top of large cloud systems that is very depleted in both isotopes.

Causes of enrichment in throughfall samples:

The degree of isotopic enrichment ϵ in throughfall samples does not seem to be controlled by any single environmental factor. There is a slight correlation of ϵ and season (Figure 8). For both the spatial and temporal storms, the amount of enrichment is slightly greater in the winter than in the summer. There is little correlation ($r^2 < 0.2$) between the $\delta^{18}\text{O}$ of PE, which has a seasonal change in composition, and ϵ . There is little correlation between ϵ and the storm size ($r^2 < 0.2$ for both isotopes).

It is surprising that: (1) there isn't a greater correlation of ϵ and season, and (2) that throughfall samples are not more enriched relative to rain in the summer than in the winter rather than the reverse. It had been expected that enrichments would show a definite seasonal cycle, with greater enrichments in the summer for deciduous trees because of their greater leaf surface area, and lesser enrichments or maybe no enrichments for deciduous trees in the winter when the trees are bare. An explanation for the first oddity is that the enrichment process seems to be affected by a number of factors besides canopy density and that 16 storms may be too small a number for the effects of these factors to be accurately distinguished. The inverse seasonal relation suggests that evaporative enrichment is not well correlated with canopy surface area.

It has been suggested that if the leaf surfaces were still wet with the water from an earlier shower, the first throughfall samples of the new storm could contain small amounts of highly evaporated water (Gat and Tzur,

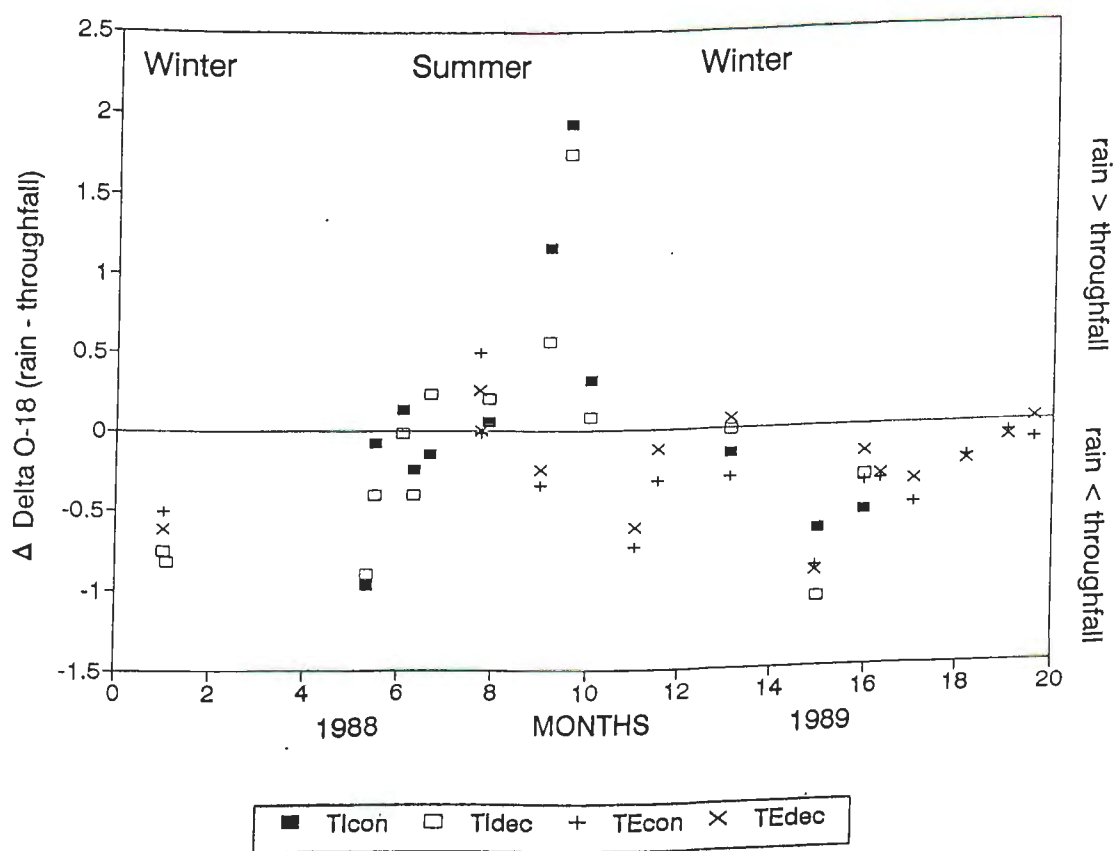


Figure 8. Seasonal changes in the $\delta^{18}\text{O}$ differences between rain (PE) and throughfall, both for event (TE) and incremental samples (TI); $\Delta = (\text{PE} - \text{TE})$ or $\Delta = (\text{PE} - \text{TI})$. The 2σ error bars are 0.14‰ .

1967; Gat, 1988). Only three storms with TE data (8/30/88, 4/9/89, and 6/5/89) had a storm large enough to fill the canopy storage capacity (≥ 0.1 cm) less than 24 hours earlier; however, the TE for these storms are no more enriched relative to PE than the other storms nor is there any correlation between the composition of the previous storm and the degree of enrichment.

Seven storms with TI data had 5 to 24 hour hiatuses between showers where water presumably remained on the canopy for extended periods of time before being washed off the leaves by a subsequent shower. The subsequent samples were never enriched relative to samples prior to the hiatus, nor did they plot along slopes in $\delta^{18}\text{O}$ - $\delta^{18}\text{O}$ space below the linear regression equation derived from the storm data. This contrasts with the 2‰ maximum overall enrichments predicted by Gat and Tzur (1967) for rain washing highly evaporated remnants of water from leaf surfaces. Therefore, there is no evidence that remnants of presumably highly evaporated water from a previous storm have any effect on subsequent throughfall samples. Perhaps if smaller fractions of water had been collected, an evaporative effect might have been observed. The first 8 bottles each collected 0.18-cm fractions of rain; this is greater than the storage capacity of the leaves.

Processes causing water loss but little kinetic fractionation:

Processes that might explain the water losses and frequent isotope enrichment of volume-weighted throughfall relative to PE without observable kinetic fractionation include: (1) evaporation followed by exchange with leaf water; (2) loss of the last isotopically light rain to canopy storage at the end of the storm; (3) simultaneous evaporation and isotopic exchange with atmospheric moisture in isotopic equilibrium with the rain; and, (4) simultaneous evaporation and exchange with atmospheric moisture dominated by evaporated-water vapor. Selective loss of depleted water in sequential samples because of collector-design problems cannot be ruled out as an explanation for the enrichments of PI relative to PE, but cannot alone explain the much greater water losses and enrichments observed in TI samples relative to PI and PE samples.

Leaf membranes are semi-permeable and water continuously passes through the walls during transpiration. Although the net isotopic composition of transpired vapor is equivalent to the isotopic composition of the water taken-up by the plant roots (Zimmermann et al., 1967), transpiration causes ^{18}O enrichments in leaf water in the range of 10 to 40‰ (Gonfiantini et al., 1965; Walker and Brunel, 1990). Leaf waters plot along lines with slopes of 1.3 to 4.4 in δD - $\delta^{18}\text{O}$ space (Cooper and DeNiro, 1989). In theory, small additions of this water to throughfall could cause significant enrichments. There have been few studies of diffusion rates of isotopic species across leaf membranes; Walker and Richardson (1991) report

incomplete equilibration of lettuce leaves and surrounding water in 12 hours. The fraction of leaf water in equilibrium with atmospheric water is inversely related to the transpiration rate and changes rapidly during active transpiration (Brunel and Walker, 1990). Since water films on leaf surfaces effectively inhibit transpiration (Dunin et al., 1988), the leaf water is probably in equilibrium with the atmosphere during storms and hence similar to the composition of the rain; thus, there should be little impetus for diffusion and exchange with leaf water is unlikely to be a dominant process.

Enrichment of throughfall relative to rain by selective storage:

The percentage of rain water lost to storage on the tree canopy ranges from 1-35% of the total PE (Table 7). Unless PE has a relatively constant composition during the storm, then the net TE composition may be affected by the selective loss of this fraction of the rain. All the storms examined show intrastorm changes in isotopic composition. It is possible that loss of the last fraction of water, which is usually depleted relative to the rest of the storm, could be the cause of the persistent isotopic enrichments seen in TE relative to PE samples. The four winter storms (Table 6) where both TI and TE data are available, were used to test this hypothesis.

All four of these storms show the typical winter intrastorm monotonic decreases in $\delta^{18}\text{O}$, with shifts in $\delta^{18}\text{O}$ in the range of 4 to 7‰. TE samples are enriched in ^{18}O by 0.19 to 0.9‰ relative to the corresponding PE samples. To cause an enrichment in ^{18}O of 0.2‰ would require the loss of

the last 6 to 9% of the PE for storms with intrastorm $\delta^{18}\text{O}$ shifts of 7 to 4‰, respectively. However, the estimated storages based on Figure 6b range from 1 to 5% of the total PE for these storms. Hence, loss to storage cannot be the cause of most of the enrichment in these winter storms (Table 7). For the other winter storms, only the enrichments under deciduous canopy for the 11/16/88 and 3/30/89 storms could be mostly explained by selective storage.

The amounts of water lost to stemflow (SE) are comparable to the amounts of water lost to storage. For these four storms, the SE yields range from half to twice the amounts in storage, with an overall combined loss of 4 to 7%. Even if all the water lost to stemflow also occurred at the end of the storm, an unlikely prospect, the combined loss is still insufficient to account for the enrichments observed.

Although conifers show little seasonal difference in storage, deciduous trees have variable storages ranging from twice as large as the storage on conifers in the winter to up to 5 times as high during the growing-season (Cappellato, 1991). Although none of the summer storms have both TE and TI data, it is reasonable to assume that the $\delta^{18}\text{O}$ ranges of about 2 to 7‰ seen in summer storms where TI samples were collected is typical. Because of the larger amounts of water stored on the deciduous canopy during the summer, most of the enrichment in ^{18}O seen under deciduous canopy for eight storms and under coniferous canopy for two storms (Table 7) could be explained by selective storage, assuming the worst-case intrastorm $\delta^{18}\text{O}$ variation of 7‰. However, there is little correlation between percent water loss to storage and degree of enrichment, with r^2 values of 0.20 and 0.23 for

deciduous and conifer trees, respectively, and no significant difference in correlation between summer and winter storms. Hence, although selective storage cannot be ruled out as an explanation for the enrichment of many storms, especially under deciduous canopy during the summer, there is no real evidence that this mechanism causes significant enrichment. In addition, if these storms had only 2 to 4‰ intrastorm variation, the amounts of water lost to storage in most of these storms is insufficient to explain the enrichments.

Enrichment or depletion of throughfall relative to rain:

The 7/21/88 storm is the only one of the storms with TE data where the δD and $\delta^{18}O$ compositions of the TE are depleted relative to PE (Table 3). This storm dropped only 0.4 cm of rain, making it the smallest storm in this study. Saxena (1986) also noted several summer storms where the throughfall was depleted relative to the rain. He developed a model which predicted whether throughfall would be enriched or depleted relative to the rain based on knowledge of the humidity, temperature, and difference between the isotopic compositions of rain and atmospheric vapor. His model correctly identified the four storms out of 24 where depletion occurred, but had two false predictions of depletions when enrichments occurred and four false predictions of either enrichments or depletions when throughfall was in fact identical to rain; hence, the model made correct predictions 75% of the time.

Saxena (1986) noted that for storms of ≤ 0.4 cm, the canopy reservoir in his field area does not saturate; hence ideally there should be no dripping from the canopy and the $\delta^{18}\text{O}$ values of any "throughfall" collected under the canopy should be identical to the rain. Because all his depleted storms were ≤ 0.25 cm in size, an alternate explanation for the depletion of his four storms and the 7/21/88 storm in this study is preferential storage of early enriched water on the canopy. This assumes that the initial fractions of rain water of Saxena's storms were enriched relative to later samples, which is probably valid based on the data in this study. The first samples from the four small (≤ 2 cm) summer storms in this study with incremental data were always enriched relative to the rest of the storm. The first samples of larger storms were also enriched relative to the rest of the storm, although several storms had waters at the middle or end of the storm as enriched as the first rain sample. However, preferential storage of enriched water does not solve the problem of why TEcon is more depleted relative to PE than TEdec for the 7/21/88 storm when the storage capacity of conifers is apparently much less than deciduous trees (0.03 cm vs 0.14 cm).

Volume-weighted TI from six summer storms (6/2/88, 6/19/88, 7/27/88, 9/4/88, 9/16/88, and 10/1/88) also are depleted in one or both isotopes relative to PE (Table 5), for one or both throughfall collectors. Because of leakage problems with the incremental samplers, these data must be interpreted cautiously, particularly for the first three of these storms where the ^{18}O depletions are small and δD values are enriched rather than depleted relative to PE. These six storms are 5 to 20 times the size of the

depleted storms studied by Saxena (1986), and several have much greater ^{18}O depletions; therefore, selective loss of initial enriched water is unlikely to be the predominant cause of the depleted TI values.

The variable isotopic fractionations of throughfall relative to rain observed for summer frontal storms could be a function of several processes. Individual showers during summer storms typically have isotopic compositions that oscillate back and forth in δD - $\delta^{18}\text{O}$ space, rather than the monotonic decreases seen in winter convective storms. This situation is ideally suited for creating significant changes in the volume-weighted average compositions by combinations of (1) erratic losses to stemflow during intense rain, (2) storage on the canopy, (3) problems during bottle-filling. During the summer, deciduous trees have more structure and greater storage areas than during the dormant season. Oscillating rain isotopic compositions implies that the isotopic composition of local atmospheric vapor is also rapidly changing because of the fast-moving fronts. Therefore, each successive tiny shower is likely to be out of isotopic equilibrium with the atmospheric vapor of the next shower. Depending on the differences between the isotopic compositions of rain and vapor, and the relative sizes of the water and vapor reservoirs, the net throughfall could be enriched or depleted relative to rain (Saxena, 1986).

Modeling the effects of canopy interception:

When rain falls onto a forested area, some rain misses the leaves completely and falls straight to the ground and some is intercepted by the tree canopy before it reaches the ground. With continued rainfall, eventually the leaf storage capacity is exceeded and the intercepted water drips to the ground too. Throughfall (T) is defined here as the combination of the rain that goes through the canopy (T_p) plus the rain that is intercepted by and later drips from the canopy (T_c). The amount of throughfall is generally less than the amount of incoming rain due to the combined effects of storage (S) of water in the canopy at the end of the storm plus evaporation (E). However, if the leaf storage was already filled with water from a previous storm, net throughfall could exceed rainfall.

In theory, the isotopic composition of rain that misses the canopy should be the same as the original rain. In contrast, the isotopic composition of rain that is intercepted by the canopy can be affected by a number of processes including: (1) evaporation; (2) mixing with evaporated water remaining on the leaf surfaces from a recent prior storm; and (3) exchange with atmospheric vapor. To distinguish among the effects of these processes, the observed data can be compared with the results of simple models incorporating only evaporation or evaporation plus exchange. Such models should shed some light on why coniferous throughfall has greater water losses and enrichments than deciduous throughfall, the relationship

between the water losses and kinetic fractionations, and why throughfall samples plot along variable slopes, mostly greater than 8, in δD - $\delta^{18}O$ space.

For the simplest case where the only process affecting the isotopic composition of throughfall is evaporation, the mass balance and isotope mass balance equations can be formulated as follows:

$$P = T + S + E$$

$$T = T_p + T_c$$

for the amounts of water in different components, with P = precipitation, T = throughfall, S = storage, E = evaporation, T_p = throughfall with the isotopic composition of precipitation that falls straight to the ground, and T_c = throughfall that intercepts the canopy and then drips to the ground after the canopy storage is exceeded (this category includes stemflow). Hence,

$$P\delta_p = T\delta_T + S\delta_s + E\delta_E = T_p\delta_p + T_c\delta_c + S\delta_s + E\delta_E.$$

If water in the canopy storage is well mixed, then

$$P\delta_p = T_p\delta_p + (T_c + S)\delta_c + E\delta_E.$$

The storage S can be approximated as the negative y-intercept of a linear regression of rain and throughfall amounts (Rutter, 1975):

$$T = C \cdot P - S$$

where C = the empirically derived multiplicative factor relating precipitation and throughfall amounts. From linear regressions of the data in Figure 6b, the C values are 0.95 for deciduous trees and 0.83 for conifers, and the values for storage on leaf surfaces range from 0.102 cm for deciduous trees to 0.026 cm for conifers. An alternate calculation method is to set $T = 0$, and solve for S : for the equations on Figure 6b, the results are almost identical.

Let's consider a series of showers being intercepted by the canopy. At the beginning of the storm, the canopy storage capacity S is completely filled by rain water of isotopic composition δ_{P_0} and amount $P_0 = S$. If this water is then partially evaporated so that only a fraction (f) of S remains, the isotopic composition of the remnant f in storage (δ_s) can be described by a Rayleigh equation (Craig and Gordon, 1965):

$$\delta_s = \delta_{P_0} - \epsilon \ln(f_0)$$

where $\epsilon = \epsilon^+ + \Delta\epsilon$. Many texts have the Rayleigh equation incorrectly written with a positive sign because of confusion about definitions for ϵ^+ and ϵ^* (see below). The equilibrium fractionation $\epsilon^+ = (1 - \alpha^+)1000 > 1$ for

$\alpha^+ = (1000 + \delta_l) / (1000 + \delta_v) > 1$, where δ_l and δ_v are the isotopic compositions of liquid and vapor, respectively, in isotopic equilibrium at some temperature. The variable $\Delta\epsilon$ is an additional diffusive (kinetic) isotope fractionation which results from the different diffusivities of the isotope water molecules in the liquid-air boundary layer. According to the Craig and Gordon model (1965), $\Delta\epsilon = (1 - h)\epsilon_k$, where the kinetic fractionation $\epsilon_k = 15\text{‰}$ for oxygen and 13‰ for hydrogen (Merlivat, 1978) and h is the relative humidity written as a fraction < 1 . Values for α^+ can be calculated from Majoube (1971).

Suppose now another shower of amount P_i and composition δ_{Pi} falls on the leaf surfaces and mixes with the evaporated remnant from the previous shower. The composition of the water on the canopy now can be described by a mixing equation:

$$\delta_{Si} = \{P_i\delta_{Pi} + f_oP_o [\delta_{Po} - \epsilon\ln(f_o)]\} / (P_i + f_oP_o) .$$

One possible scenario at this point is that this water then evaporates, leaving only a fraction f_i of $(P_i + f_oP_o)$, whose composition can be described as:

$$\delta_{Sii} = \delta_{Si} - \epsilon\ln(f_i) .$$

An alternate scenario is that, instead of evaporating, after mixing with the remnant $f_o P_o$, an additional amount of rain P_{ii} , of composition δP_{ii} , falls onto the leaf surfaces and exceeds the storage capacity so water drips off; the system can then be viewed as:

$$S\delta_{Sii} = (S - f_i X)\delta_{Pii} + f_i X\delta_{Si}$$

$$T_C\delta_C = \delta_{Pii}[P_{ii} - (S - f_i X)] + X(1 - f_i)\delta_{Si}$$

where $X = (P_i + f_o P_o)$ = the amount of mixed water on the canopy before the latest shower P_{ii} , f_i is the fraction of mixed water X that remains on the canopy after being washed off by P_{ii} , and T_C is the amount of throughfall dripping from the canopy. The remaining water on the canopy can then evaporate, be mixed with rain from another tiny shower, be washed off, etc. Obviously, attempts to model the evolving composition of throughfall during a storm as a long series of irregularly alternating steps like the above equations become complicated very fast. Therefore, let's try a few simplifications.

If the canopy storage is completely filled during each incremental shower step, partially evaporates to leave behind a remnant f which is completely displaced by the next incremental rain step (with no mixing of waters) which again fills the canopy storage, and this new rain also partially evaporates away to leave a remnant f , etc., calculations are vastly simplified. Of course, this scenario is rather unrealistic in that all the old water is

displaced at each step, instead of mixing with the new water; also, the new water probably overflows instead of mixing because the storage is already full.

Let's try an alternate approach: suppose that the tree canopy is so dense that ALL the rain is intercepted by the canopy and is consequently partially evaporated before dripping to the ground; then there is no T_p term and hence δ_c can be calculated using the equations below:

$$P = T_c + S + E$$

$$\delta_T = \delta_s = \delta_c = \delta_p - \epsilon \ln(f)$$

where $f = T_c/P-S$. The fraction f was calculated from $T_c/(P-S)$ rather than as T_c/P because the last water left on the leaves does not contribute to the isotopic composition of T_c . This equation is not valid for variable rain isotopic compositions because the Rayleigh equation is logarithmic, not linear. This model produces minimum amounts of enrichment because all the rain is assumed to intercept the canopy to form T_c and, hence, f values are larger than if there was some T_p ; more accurate models would produce greater enrichments.

The amount of the total PE that is lost as stemflow (SE) is comparable to the amounts in storage and evaporated; hence, a term for SE must be included in the water budget. Because a large component of stemflow probably occurs as overflow from the partially evaporated leaf storage capacity, I assume that $T_c = TE + SE$ for this calculation. Actual average

stemflow losses for each storm and canopy type from Cappellato (1991) were used.

Table 8 compares the actual and calculated values for the isotopic compositions of throughfall events for the 16 storms. The volume-weighted amounts and isotopic compositions from Table 3 were used for PE and TE values in the above equations. The average measured values for temperature and humidity during each storm were used in the calculations. For some storms, temperature and humidity showed considerable variation; substitution of the actual values at $\pm 1\sigma$ of the average values changes the calculated $\delta^{18}\text{O}$ values by $< 0.3\text{‰}$ and δD values by $< 0.6\text{‰}$. The value of 0.03 cm determined from Figure 6b was used for the conifer canopy storage capacity. Separate linear regressions were made to calculate the deciduous storage capacities for the growing and dormant seasons, producing values of 0.14 cm and 0.06 cm, respectively; a factor of 2 difference between winter and summer storages is typical (Rutter, 1975).

For the deciduous data there is a close match of actual and calculated δ values for TE. The calculated $\delta^{18}\text{O}$ values of TE have an average of $+0.59\text{‰}$ and range from $+4.66$ to -1.34‰ relative to actual TE. The average enrichment in D was $+4.4\text{‰}$, with a range of $+32.3$ to -6.2‰ . Four of the storms in the growing season (10/31/88, 4/9/89, 6/5/89, and 7/2/89) had estimated values of $f > 1$, meaning that all the rain could be accounted for without having to invoke evaporation (i.e., $E = \text{PE} - \text{TE} - \text{SE} - \text{S} < 0$). However, for all four of these storms, the actual TE was enriched relative to PE, suggesting evaporative fractionation. These were average-sized storms, with normal humidity, temperature, and wind speed

Table 8. Modeling Results and the Values used in the Models.*

Date	Relative Humidity	Temperature (°C)	$\Delta\delta$		Measured f		Calculated f	
			$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD
Deciduous								
10/26/87	0.87	12.2	-0.23	-0.5	0.976	0.958	0.970	
01/01/88	0.87	8.8	-0.46	-3.3	0.988	0.953	0.956	
07/21/88	0.79	25.5	4.66	32.3	0.703	1.020	1.044	
07/22/88	0.90	19.1	1.72	11.6	0.860	1.000	0.981	
08/30/88	0.86	21.6	0.70	5.2	0.922	0.979	0.980	
10/31/88	0.97	7.2	0.04	0.7	0.944	0.947	0.950	
11/16/88	0.74	13.0	1.67	10.0	0.882	0.991	0.978	
01/03/89	0.96	9.6	0.07	-0.9	0.999	1.005	0.990	
02/27/89	0.89	10.8	0.03	3.6	0.926	0.929	0.961	
03/21/89	0.90	11.6	-1.34	-6.2	0.980	0.877	0.920	
03/30/89	0.93	15.3	0.68	4.6	0.927	0.985	0.975	
04/09/89	0.94	7.0	-0.25	-0.4	0.994	0.973	0.990	
05/01/89	0.90	17.2	-0.05	-1.2	0.974	0.969	0.961	
06/05/89	0.88	19.2	0.56	3.9	0.934	0.980	0.976	
07/02/89	0.79	20.8	0.23	1.8	0.975	0.992	0.995	
07/19/89	0.85	20.6	0.62	4.1	0.951	1.001	0.997	
averages			0.59	4.4	0.933	0.972	0.977	

Date	Relative Humidity	Temperature (°C)	Δδ		Measured f	Calculated f	
			δ ¹⁸ O	δD		δ ¹⁸ O	δD
Conifers							
10/26/87	0.87	12.2	0.24	7.3	0.916	0.934	0.988
01/01/88	0.87	8.8	0.76	4.3	0.905	0.961	0.944
07/21/88	0.79	25.5	6.62	46.3	0.613	1.040	1.079
07/22/88	0.90	19.1	1.59	10.5	0.868	0.998	0.979
08/30/88	0.86	21.6	0.47	4.5	0.932	0.971	0.983
10/31/88	0.97	7.2	1.15	11.7	0.847	0.937	0.950
11/16/88	0.74	13.0	4.57	30.3	0.711	0.977	0.971
01/03/89	0.96	9.6	0.97	7.8	0.893	0.973	0.966
02/27/89	0.89	10.8	1.89	17.0	0.798	0.931	0.949
03/21/89	0.90	11.6	-0.58	2.3	0.908	0.865	0.929
03/30/89	0.93	15.3	1.66	11.5	0.836	0.969	0.948
04/09/89	0.94	7.0	1.40	13.7	0.864	0.971	0.986
05/01/89	0.90	17.2	1.56	11.9	0.836	0.958	0.954
06/05/89	0.88	19.2	3.02	20.8	0.758	0.981	0.961
07/02/89	0.79	20.8	1.08	7.6	0.915	0.995	0.998
07/19/89	0.85	20.6	2.93	20.2	0.776	0.990	0.979
averages			1.94	14.6	0.836	0.966	0.972

* f = the fraction of rain water that was NOT evaporated.

values. Two of them, 4/9/89 and 6/5/89, occurred less than 24 h after another storm, so there might have been water remnants on the leaves; addition of some antecedent moisture to the water budget could make the "true" $f < 1$. Other explanations for the high f values include nonrepresentative values for E , S , and SE . For the purpose of calculation, the lower winter storage amounts were substituted for the summer values so that $f < 1$. Of the remaining 12 storms, the calculated values for TE were enriched relative to the actual values for eight storms and depleted for four storms. The 7/21/88 storm, where the measured TE values were depleted relative to PE , had the highest calculated TE values. The storms with depleted calculated values tended to be larger in size than the average. For the coniferous data, in contrast to the deciduous results, the actual and calculated δ values for TE were significantly different, with average enrichments in ^{18}O and D of $+1.94\text{‰}$ and $+14.7\text{‰}$, respectively, and wide ranges in values. The calculated δD values for all storms were enriched relative to the actual TE values; the calculated $\delta^{18}O$ were also enriched for all but one storm. Again, the most enriched calculated TE values are for the 7/21/88 storm.

The average "measured" f value for conifers is 0.84, suggesting that about 0.16 or 16% of the PE has evaporated. In contrast, when the actual isotopic compositions of PE and TE are used to calculate f , the calculated f values for both isotopes are about 0.97, suggesting that evaporation of only about 3% of the total PE is required to account for the measured enrichment of TE relative to PE . Using the same reasoning for deciduous data, the average "measured" f value is 0.94, suggesting that about 0.06 or 6% of the

PE has evaporated. However, use of actual deciduous data to calculate evaporation produces a value of about 2.5%. Combining the above coniferous and deciduous data, there is a discrepancy of 3 to 13% between the measured and calculated percentages of PE lost to evaporation. Oddly enough, the lowest calculated percentages of evaporation occur in the summer, in general agreement with the behavior of the actual values (Figure 8).

The significantly lower values for calculated f relative to measured f are an alternate way of expressing the observation that the model shows that more water has evaporated away than can be accounted for in the magnitude of isotope enrichments of TE samples. And because this simple evaporation model underestimates the enrichment of TE, the "true" enrichments should be much higher. Therefore, some process other than evaporation has acted to decrease the kinetic evaporative fractionation. As a result, TE (and TI) samples do not fall along evaporation lines as might be expected for the amount of water lost to evaporation.

The previous models assumed that Rayleigh evaporation was occurring in isotopic equilibrium with the rain but that the evaporate was being continuously removed from the system with negligible back reaction. However, under dense tree canopy, the system is more closed than this model envisions and the local humidity increases by the processes of transpiration and evaporation. Hence, isotopic exchange between evaporating water and ambient vapor is a likely possibility. Transpiration returns water to the atmosphere unfractionated by the plants (Zimmermann et al., 1967); this vapor should be similar to the average soil-water or

ground-water composition (White et al., 1985) and, consequently, generally considerably enriched relative to vapor in equilibrium with the rain.

Evaporate, on the other hand, is considerably depleted relative to transpired water and is closer to the composition of the atmospheric vapor in equilibrium with the rain. The generally higher d-excess values of the TE and TI samples support interaction with re-evaporated water (Gat and Matsui, 1991)

According to the Craig-Gordon evaporation model (1965), the isotopic composition of the evaporate (i.e., evaporated vapor) can be formulated as:

$$\delta_E = (\alpha^* \delta_w - h \delta_a - \epsilon) / [(1-h) + \Delta\epsilon/1000] \approx (\delta_w - h \delta_a - \epsilon) / (1-h)$$

where δ_w and δ_a are the isotopic compositions of the water on the leaf surface and the atmospheric vapor, respectively, $\alpha^* = 1/\alpha^+$, $\epsilon = \epsilon^* + \Delta\epsilon$, and $\epsilon^* = (1 - \alpha^*)1000$, with all parameters in permil units; h = humidity.

If the equation is solved for both δD and $\delta^{18}O$, the isotopic compositions of E can be compared with those of PE for the 16 storms to produce evaporation lines in δD - $\delta^{18}O$ space. It was assumed that: (1) the environmental data in Table 8 were valid for conditions at the leaf surface; and (2) the atmospheric water was in isotopic equilibrium with the PE.

Probably neither of these assertions is completely correct but were made because of lack of data to the contrary. The average slope of the calculated evaporation lines for each storm is 4.2, with a range of 3.4 to 5.2. The slopes showed no correlation with season. As a group, the δ_E values fit the equation $\delta D = 6.13 \delta^{18}O + 53.4$ ($r^2 = 0.65$, $n = 16$), plotting above the

LMWL with a d-excess value of about 120. The Craig-Gordon model was developed for steady-state evaporation of open-water bodies and hence is not entirely appropriate for the physical conditions on the canopy; nevertheless, it provides a crude estimate of the composition of re-evaporated moisture being added to the local atmosphere.

The isotopic compositions of the evaporate calculated using the Craig-Gordon model plot in a much tighter band than the δ_E values calculated by mass balance from the PE and TE amounts and isotopic compositions (Figure 8). Both estimates of the isotopic composition of evaporated water have higher d-excess values than the calculated compositions of atmospheric vapor (δ_A) in equilibrium with the rain. Exchange of TE samples with this evaporate would cause the TE samples to plot along lines in δD - $\delta^{18}O$ space that are higher than any evaporation-derived slope.

The above simple models all make the assumption that the water on the leaf surfaces behaves like a well-mixed body of water. In actuality, the water on each leaf is separate and leaves may even contain several distinct evaporating raindrops. What is the effect of all this potential small-scale variability? As an example, let's suppose that two droplets of identical size each partially evaporates and loses a different fraction of its water. If the fraction of water remaining in drop A is $f = 0.75$ and in drop B is 0.5, for rain with a $\delta^{18}O$ value of 0‰ and $\epsilon = 12$ ‰, the $\delta^{18}O$ values of drops A and B are +3.45‰ and +8.32‰, respectively. If the water remnants in these two drops mix and drip from the leaves to form TE, the volume-weighted $\delta^{18}O$ value of the total TE has a $\delta^{18}O$ value of 5.40‰. However, if one calculates the net $\delta^{18}O$ value for the net loss of 37.5% of the PE ($f = .625$),

the resulting $\delta^{18}\text{O}$ is +5.64‰. These $\delta^{18}\text{O}$ values are different because the Rayleigh equation is logarithmic instead of linear. Hence, accurate a priori calculations of the expected throughfall enrichments for a given overall loss of water are not possible. The larger the fraction of water remaining on the leaves after each stage of evaporation, the smaller the difference between linear and logarithmic additions. For fractions of remaining water in the range of 0.8 to 0.95, the difference amounts to less than 0.05‰.

Slopes of evaporation lines:

The slope of an evaporation line (or a tie-line connecting the δ values of PE and TE samples in δD - $\delta^{18}\text{O}$ space) is dependent on several factors, including humidity, the isotopic compositions of liquid and vapor, and the equilibrium and kinetic fractionation factors at the observed temperature (Gat, 1971). The ambient humidity is an indication of how open the system is (i.e., how much isotopic back-reaction is possible), and is often viewed as the main control on the slope of the evaporation line. Slopes less than 8 reflect differences in the relative amounts of equilibrium and non-equilibrium evaporation taking place. Slopes greater than 8 reflect exchange with air masses of higher d-excess values (Gat and Matsui, 1991); such lines can be called "exchange lines". Hence, the range of slopes seen for the tie-lines in this study reflect a large range of environmental conditions under which throughfall enrichment may take place.

The average slope of the tie-lines between volume-weighted PE and TI or TE samples for entire events ($n=31$) is 8.5 for deciduous trees and 8.9 for conifers, and the range is very large (1 to 16 for TE samples). For the complete set of individual throughfall (TE) samples, the average slope for coniferous throughfall is 10.9 ± 9.3 ($n=101$) and for deciduous throughfall is 6.5 ± 13.1 ($n=102$). A one-sided t test indicates that the slopes for conifer samples are significantly greater, at the 99.5% level, than for deciduous samples. This level of significance is surprising considering the estimated value of 6 for the non-parametric " 2σ " analytical error associated with each slope determination. These average slopes for throughfall samples contrast with the slope of about 5 predicted by Gat and Tzur (1967) and the slopes of about 4.2 calculated using the Craig-Gordon model.

Although several factors influence slope, the best correlations are found with the $\delta^{18}\text{O}$ of PE. There is a moderate positive correlation ($r^2 = 0.45$) between slope and $\delta^{18}\text{O}$ of PE for $\text{PE} > -5\text{‰}$, and a weak negative correlation ($r^2 = 0.15$) of slope and $\delta^{18}\text{O}$ of PE for values $< -5\text{‰}$ (excluding one sample where the slope > 15) (Figure 9). This separation of slopes at -5‰ does not necessarily reflect any seasonal change; several of the winter storms are enriched relative to -5‰ and several summer storms are depleted relative to -5‰ . It is not clear why the correlation between tie-line slope and $\delta^{18}\text{O}$ changes from positive to negative at about $\delta^{18}\text{O} = -5\text{‰}$; this is approximately the volume-weighted average composition of rain at Panola.

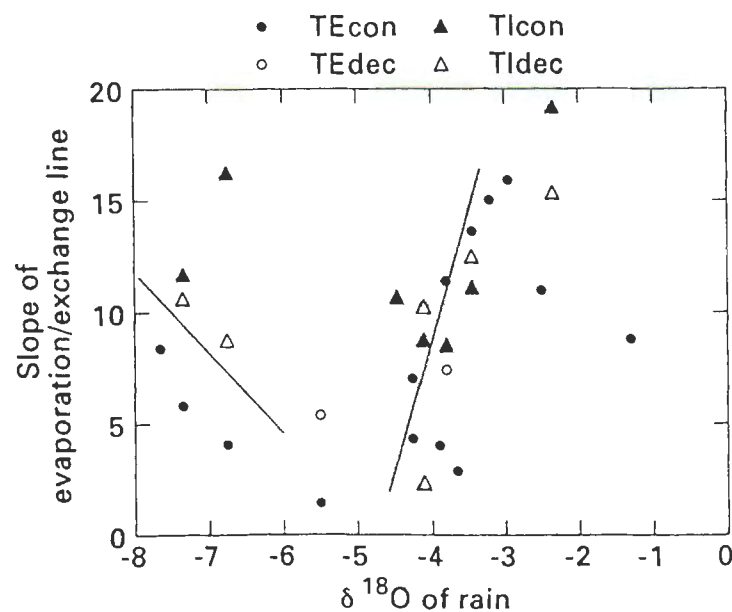


Figure 9. Relation of the slope of evaporation/exchange lines for throughfall samples relative to rain in δD - $\delta^{18}\text{O}$ space, and the $\delta^{18}\text{O}$ of event rain. The lines represent linear regressions through the data points (see text). The 2σ error bars on $\delta^{18}\text{O}$ and slope are 0.1‰ and 6, respectively.

There is a moderate positive correlation ($r^2 = 0.37$) of slope and the percent difference (ΔE) between E (determined by difference) and calculated E for the 16 storms with TE data. The value of E was calculated using the Rayleigh equation and assuming that all the enrichment was due to evaporation. This value represents the minimum amount of water loss necessary to explain the observed fractionation (see above calculations). In almost all cases, the calculated E values are less than the actual E values, indicating that there is more water lost than can be accounted for by Rayleigh evaporation alone (or that there is less enrichment and apparently more isotope exchange than would have been caused by the evaporation of the water lost). The correlation of slope and ΔE indicates that storms with higher slopes have less enrichment than expected, which supports the idea that exchange, which tends to reduce the degree of enrichment, is the mechanism responsible for the higher slopes.

So, why do the TE values as a group plot along a line with a higher slope and intercept than the PE values (Table 1)? A partial explanation might be because of seasonal and intrastorm processes that affect the enriched end of the MWL more than the depleted end. For example, the slopes of tie-lines connecting volume-weighted average rain (PE or PI) and throughfall (TE or TI) values in δD - $\delta^{18}O$ space are higher at the high (-1‰) and low (-9‰) ends of the $\delta^{18}O$ scale (Figure 9) than at mid-range values (-5‰). This pattern causes the linear regression equations derived for throughfall samples to be rotated slightly counter-clockwise relative to the

LMWL derived from rain data, producing a higher slope and y-intercept for the throughfall samples.

Examination of the TE data on Figure 9 shows that, in general, the slopes are higher for enriched storms, characteristic of the summer than for more depleted storms, characteristic of the winter. This implies that there is more exchange between canopy water and the ambient atmosphere during summer-type storms than winter-type storms, which is why the throughfall samples appear to be more evaporatively fractionated in the winter than in the summer. The slopes are also higher for storms where there has been more exchange as determined by larger differences between true TE and TE_{calc} values. The higher slopes of tie-lines in the summer is probably a result of the increased amount of re-evaporated water being added to the local atmosphere in response to the higher summer evaporation rates; because of higher summer temperatures, larger amounts of water can be stored in the atmosphere than during the winter. The local canopy environment may also be more closed to mixing with outside air during the summer when the canopy is denser; a more closed environment facilitates back reaction and reduces the kinetic fractionations.

Species effects:

Conifer throughfall is generally isotopically enriched relative to deciduous throughfall. Although the average ^{18}O enrichment for the 16 TE sites is 0.11 ‰ which is within analytical uncertainty, use of a sign test

shows that the enrichment is "real", at the 97% level for $\delta^{18}\text{O}$. The conifer sites also generally have greater water losses relative to PE than the deciduous sites, although in detail the correlation of degree of enrichment and water loss is poor. The TIcon site is unusual in that the throughfall enrichment and water loss are both less than at the TIdéc site. One explanation for this is location: the TIcon site was located at the edge of the forest where the canopy may have been much less dense than usual for the TEcon sites (personal communication, R. Cappellato, 1992), resulting in less interception than usual for conifer sites.

The greater water loss at conifer sites is somewhat unexpected. The leaf-area-index of the deciduous trees appears to be larger than for the conifers (personal communication, R. Cappellato, 1990), and the canopy storage values for deciduous trees are always greater than for conifers; hence, one would have expected greater water losses for deciduous trees. One explanation for the greater water losses under conifers might be somehow related to the way droplets get caught between needles on conifers, with their large surface areas exposed to the air. An alternate explanation is that micro-climatological conditions under the conifer canopy favor increased evaporation rates; lower ambient humidity, higher temperature, greater windspeed, and more nucleation inhibitors (or fewer nucleation sites) under conifers are all possible contributing factors. The fact that conifer TE is even more enriched relative to deciduous TE in the winter when the storages are more similar than in the summer when storages are most dissimilar, is a strong indication that relative storage capacity has little relation to degree of enrichment.

The simple model calculations suggest that deciduous TE isotopic compositions are just slightly more depleted (on average: -0.59‰ for $\delta^{18}\text{O}$ and -4.4‰ for δD) than expected for the amounts of water lost to evaporation; hence, only a small amount of isotope exchange must be invoked. In contrast, the conifer TE is depleted by -1.9‰ in $\delta^{18}\text{O}$ and -14.7‰ in δD relative to the calculated values (Table 8), suggesting large amounts of exchange. Sites where significant amounts of exchange take place should have higher slopes in δD - $\delta^{18}\text{O}$ space.

The average slopes in δD - $\delta^{18}\text{O}$ space between PE and individual TE samples for coniferous sites are higher than for deciduous sites (Figure 10). To eliminate the scatter due to analytical error, slopes were not plotted for TE samples where the $\Delta\delta^{18}\text{O} < 0.1\text{‰}$ or $\Delta\delta\text{D} < 2.0\text{‰}$ between individual pairs of PE and TE δ values because these differences were within the analytical error bars; this omitted group consisted of about 25% of the conifer samples and 40% of the deciduous samples. The remaining set of data in Figure 10 are largely derived from the five storms where almost all the samples from the 32 collectors were analyzed and may not be a good representation of any true yearly pattern. With these caveats in mind, the average slopes of the remaining samples are 9.5 (n=62) for deciduous samples and 12.6 (n=77) for conifer samples. For the 11 storms where the **volume-weighted averages** fit the same criteria for acceptable $\Delta\delta$ values, the average deciduous slope was 9.5 ± 3.8 and the average coniferous slope was 10.3 ± 3.6 . Hence, average slopes are significantly greater than the slope of 8 characteristic of equilibrium condensation or evaporation, and pairs of

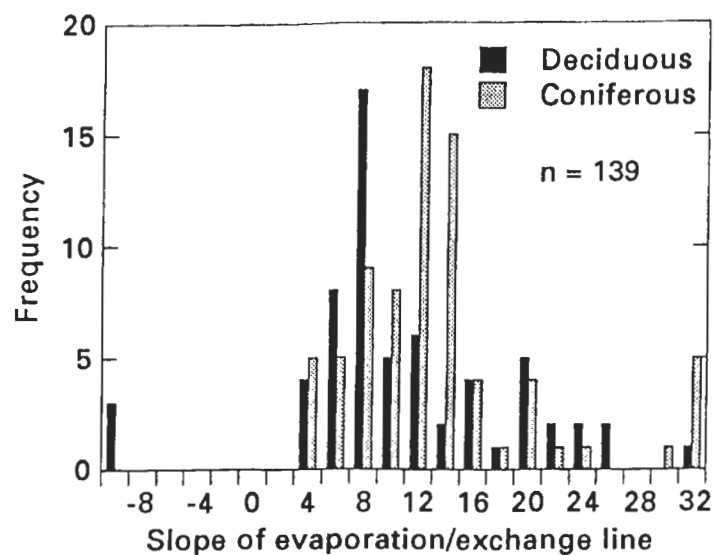


Figure 10. Frequency distribution of slopes between event rain and individual event throughfall samples for all 16 storms with spatial data. The 2σ error bar on slope calculations is about 6.

TEcon and PE samples appear to have slopes averaging 1 to 3‰ greater than pairs of TEdec and PE samples.

These several lines of evidence suggest that the differences in the isotopic compositions between deciduous and coniferous forests is largely a product of the greater extent of isotope exchange between water on the canopy and the ambient atmospheric vapor in conifer and deciduous forests. This enrichment process takes place in two steps. First, the increased evaporation rate under conifers (probably related to micro-climatological differences between canopy types) results in larger amounts of re-evaporated water being released into the local atmosphere. This water has a higher d-excess value than initial atmospheric vapor in equilibrium with the rain. Second, as evaporation continues, water on the coniferous canopy exchanges isotopically with local atmospheric vapor containing higher percentages of re-evaporated water produced from earlier fractions of rain that were probably enriched relative to the current rain. Slopes of around 8 can be explained simply by equilibrium evaporation under humidities close to 100%; slopes greater than about 8 require exchange with atmospheric moisture with a d-excess greater than the current rain (Figure 10).

The average 15% water loss by evaporation progressively adds very large amounts of isotopically depleted vapor to the canopy environment. Using the 5/1/89 storm as an example, the 0.632 cm lost to evaporation would add 6320 g of new water to each 1-m² by 20-m-high box. This compares to the 269 g already present at the measured temperature of 17.2°C and humidity of 0.90. If the canopy below 20 m were closed to the outside atmosphere, there would be 23 times more new vapor than originally

present. For smaller storms, the ratio is more like 5 or 10 to 1. Thus, there is abundant water plotting above the LMWL in δD - $\delta^{18}O$ space for the remnant water on leaves to exchange with.

The conifer-deciduous fractionations are telling us something about the relative approaches to "steady-state" of the water-vapor systems under the two canopy types. If the conifer and deciduous TE were both in equilibrium with the "new" atmospheric vapor (i.e., original vapor plus re-evaporated water), the δ values for both canopy types should not only be on the same line in δD - $\delta^{18}O$ space--which they are not--but identical in composition as well. Of course this scenario assumes that the atmospheric vapor is well-mixed between the two localities and that the local humidities are the same--which is probably the key to the whole dilemma. Therefore, it is likely that the TE formed under the two canopy types is in isotopic equilibrium with different vapor in the two areas. Mechanisms for this difference include the different ratios of intercepted versus straight-through water, the differences in the amount and composition of the evaporated vapor, the variable degree of openness of the under-canopy atmosphere to the above-canopy atmosphere, and the differences in timing of evaporation and exchange in the two canopy types. When the atmospheric systems are better mixed, or exchange times are longer, or rains are sufficiently intense--the canopy types might have the same fractionation.

Effect of interception on $\delta^{18}\text{O}$ of recharge:

The net effect of interception on the $\delta^{18}\text{O}$ of recharge can be estimated by calculating the volume-weighted isotopic compositions of total PE and TE from the 16 storms where there are spatial data (Table 9). These absolute compositions are not representative of the actual yearly mean composition of rain ($\delta^{18}\text{O} = -5.4\text{‰}$) but do illustrate the net effect of the canopy enrichment over a span of time. The differences between the calculated values of recharge for rain and throughfall are very small and are well within the 2σ range for cumulative errors of measurement and calculations for the throughfall samples, which are 0.4‰ for $\delta^{18}\text{O}$ and 8‰ for δD . An even large potential source of error is the assumption that the throughfall collected over an area of 0.07 to 0.35 m^2 (the interception area of 3 to 16 collectors) adequately represents recharge on a catchment scale. Nevertheless, recharge waters under tree canopy appear average about 0.5‰ enriched in $\delta^{18}\text{O}$ and 3‰ enriched in δD relative to total PE during the same period. There were insufficient stemflow data to incorporate the enrichments seen in stemflow in this calculation; however, the total calculated enrichments should be even a little larger to account for the stemflow. This calculated ^{18}O enrichment is identical to the value estimated by Gat and Tzur (1967) for the "probable" maximum enrichment in recharge waters intercepted by trees. However, unlike their prediction, the data do not plot along a slope of 5 in $\delta^{18}\text{O}$ - δD space. Because of exchange with atmospheric vapor during evaporation,

Table 9. Estimated Isotopic Compositions of Recharge for the 16 Storms.

Component	$\delta^{18}\text{O}$ (‰)	δD (‰)
PE	-5.04	-25.95
TEdec	-4.58	-22.98
TEcon	-4.51	-22.72

throughfall samples plot along approximately the same slope as the LMWL but have a d-excess value 2 to 3‰ greater than local rain.

CONCLUSIONS

Interception by the canopy results in an average water loss of 15% and significant fractionation of the isotopic composition of rain. On a yearly basis, throughfall at Panola appears to be enriched in ^{18}O by about 0.5‰ and enriched in D by about 3‰ relative to rain collected in the open. For almost all storms, throughfall is enriched relative to rain; the maximum enrichments seen for volume-weighted average throughfall for an event are +0.91‰ for $\delta^{18}\text{O}$ and +8.1‰ for δD . Throughfall during small summer storms is occasionally depleted in ^{18}O by up to 0.2‰ relative to rain. Many of these storms were so small that they barely exceeded the canopy storage capacity and the isotopic depletions can be partially explained by selective storage of initial enriched water on leaves. Summer storms are also frequently characterized by rapid oscillations in isotopic composition due to rapidly moving fronts; the isotopic depletions of such storms may be a result of both selective storage and exchange with atmospheric vapor of rapidly changing composition. For many storms, the amount of water evaporated on deciduous trees was very small compared with the amounts lost to storage and stemflow; hence, loss of the last isotopically light rain to storage could explain much or all the enrichment. However, the losses under conifers are too great for this explanation to "hold water".

Site-specific differences in canopy density and micro-climate result in an average $\delta^{18}\text{O}$ spread of 0.5‰ among collectors for the same storm, with a maximum range of 1.2‰. On average, there was a persistent 0.1‰ enrichment in ^{18}O of throughfall at conifer sites relative to deciduous sites, and specific sites appeared to be characterized by throughfall that was consistently enriched or depleted in ^{18}O by 0.1 to 0.2‰ relative to the average; however, on a storm by storm basis, the enrichments were erratic. Therefore, any single throughfall collector is inadequate to characterize the composition of intercepted water in forested areas. A better solution in mixed forests is to put out several collectors under different trees and combine the collected waters for isotopic analysis as is done by DeWalle et al. (1988). In semi-uniform canopy types, use of a large trough to collect throughfall may be adequate. If only one collector is to be used, I recommend putting it in the open and correcting for "average" canopy effects rather than using a single collector under a tree. This is most critical during summer storms when throughfall enrichments/depletions can be especially erratic.

The greater isotopic enrichments seen at conifer sites at Panola are related to the greater interception losses, although there is only a weak positive correlation of water loss and isotopic enrichment on a site-by-site basis during storms. The greater water losses under conifer canopy is not due to storage on the canopy but may instead be related to local differences in micro-climate. Throughfall samples typically do not plot along evaporation lines in δD - $\delta^{18}\text{O}$ space; instead the average slope of sequential intrastorm samples is about 8. Slopes of pairs of rain and throughfall

samples for individual storms range from 1 to 16, with most slopes in the range of 8 to 12. The average slopes for deciduous and coniferous trees are about 9 and 12, respectively. These high slopes suggest that exchange with atmospheric vapor containing re-evaporated water is the dominant process controlling the isotopic composition of throughfall; any kinetic evaporative effects have largely been overprinted.

Simple evaporative models have shown that coniferous throughfall, and to a much lesser extent deciduous throughfall, exhibit much less enrichment than would be expected for the amounts of water lost to evaporation. This finding underscores the importance of isotopic exchange in the canopy environment. The small enrichments observed suggest that evaporation occurred under humidities near 100%, and that the local atmospheric vapor contained large amounts of re-evaporated water with higher d-excess values than in the open atmosphere. The different enrichments seen under conifers and deciduous trees, and the different slopes of local evaporation/exchange-lines, suggest that different micro-climates developed under different canopies during storms and that these environments control the isotopic evolution of the throughfall.

It is curious that there is almost an inverse relation between amount of water lost to evaporation and the degree of kinetic fractionation seen in the δ values. Much more water is lost under conifers than deciduous trees, and conifer throughfall is often enriched relative to deciduous throughfall, but the coniferous throughfall data generally plot along higher slopes in δD - $\delta^{18}O$ space and, hence, exhibit higher degrees of exchange than is seen in the deciduous data. Also, more water is evaporated during summer storms than

winter storms, yet the winter samples appear to be more enriched relative to rain than summer samples. The connecting thread seems to be that more evaporation means more re-evaporated water and hence more exchange in the canopy environment. This mechanism results in a reduction of any kinetic fractionation signature related to the evaporation.

Summer storms tend to show smaller average enrichments of throughfall relative to rain than winter storms, despite the greater evaporation rates in the summer. This is contrary to the expectation that during the winter when deciduous trees are bare and conifer needles are more sparse, throughfall would be more similar to rain than in the summer when canopy surface area is at a maximum. This finding underscores the minimal importance of surface area in affecting the final isotopic composition of throughfall. Fractionations due to canopy interception are less predictable in the summer than in the winter because as frontal systems move through the area, each shower is out of isotopic equilibrium with the vapor of the next storm.

During intense rain in both the summer and winter, the isotopic compositions of sequential incremental rain samples show a steady monotonic decrease. In δD - $\delta^{18}O$ space, the data form broad concave-down bow-shaped curves; samples at the beginning and end of the storm typically lie on or near the local meteoric water line while mid-storm samples lie above the line. Throughfall samples show curves slightly more "bowed" than the corresponding rain samples, partially because the last throughfall sample may plot a little below the LMWL. During the winter when deciduous trees are bare, incremental deciduous throughfall samples have isotopic compositions

that are similar to rain whereas coniferous throughfall samples are enriched relative to rain throughout the storm. Throughfall samples show slightly larger enrichments relative to rain after short pauses between showers. The higher d-excess values of samples during the middle of the storms is probably due to increased exchange with re-evaporated water produced earlier in the storm.

To verify the role of re-evaporated water in determining the isotopic compositions of throughfall would require more detailed information than was available in this study, including: collection of atmospheric vapor for isotopic analysis at canopy height during each storm, for each canopy type; development of better incremental samplers for rain and throughfall; and measurement of micro-climatological information in the two types of canopy. An ISCO-type sampler with the inlet tube removed from the pump so that no rain is purged, adjusted to collect samples based on times not amounts, and connected to a tipping bucket recorder so that timings and amounts are both accurate, would probably be adequate.

The 1-2% of the intercepted rain water that falls to the ground as stemflow may be a major component of macropore flow because it is delivered directly to the tree roots where macropores are common. The few stemflow data in this study are enriched relative to both rain and throughfall, and have d-excess values around +16‰. This water may be the earliest "new" water to reach the stream. Very often streamwater at the beginning of a storm temporarily is enriched relative to either the rain or groundwater.

Plotting large amounts of data on δD - $\delta^{18}O$ plots camouflages a lot of interesting meteoric-water behavior taking place on smaller time/space

scales. The trends for individual storms are often entirely different from the trends for the entire set of storms. It is easy to get very different equations of lines whenever any process affects samples at the light and heavy end of the MWL differently -- this can cause rotations of the new lines, sometimes in a direction opposite to what occurs during an individual storm.

The average oxygen and hydrogen isotopic composition of deep homogeneous groundwater at Panola are $-5.21\text{‰} \pm 0.2\text{‰}$ and $-27.3\text{‰} \pm 1.8\text{‰}$, respectively, slightly enriched in both isotopes relative to the 3-year volume-weighted average composition of rain (-5.38‰ , -29.5‰). The groundwater values are less enriched than the $0.5\text{‰}/3\text{‰}$ enrichments predicted for canopy interception. One possible explanation is that Panola has a large unforested granite dome in the catchment that may be the main source of recharge. However, the most probable explanation is that exchange processes in the soil zone and/or selective recharge have compensated for the effects of canopy interception. But it is also possible that a study of only 31 storms is insufficient to characterize the effect of canopy interception on recharge water.

If the enrichment of throughfall seen in these storms is "real", one can expect the development of persistent isotopic differences in the recharge waters under different tree species and under areas with different ratios of intercepted to straight-through rain. These differences may affect the isotopic compositions of water taken up by trees and preserved as cellulose, the compositions of carbonates developed in the soil zone, the relative percentages of new and old water determined by isotope hydrograph separations, the compositions and calculated amounts of recharge to

groundwater, and the isotopic compositions of ambient airmasses. Because of the extent of exchange with throughfall, the d-excess value of the local airmass decreases, resulting in airmasses looking less "recycled" than expected for the amounts of water evaporated.

The average 0.5‰ enrichment of throughfall relative to rain may be of minor significance for paleoclimatic studies because the fractionation between rain and throughfall is equivalent to a 1° C change in temperature for relevant climate indicators. Many proxy indicators of climate, such as snail shells or tree cellulose, derive their water primarily from throughfall, not rain. Thus, when the $\delta^{18}\text{O}$ values of these materials are used to estimate the temperature of formation, these temperatures will be higher than for the same organisms in nearby open areas that utilize rain instead of throughfall.

Chapter 2

A LOOK INSIDE BLACK-BOX MODELS OF STORMFLOW GENERATION: ISOTOPIC, CHEMICAL, AND HYDROLOGIC MODELING AT AN ARTIFICIAL CATCHMENT

INTRODUCTION

Several approaches have been developed for the modeling of streamflow response to catchment precipitation. From a hydrogeochemical perspective, they can be divided into two basic categories of hydrograph separation methods: hydrologic response models and tracer source models. Time series models such as the instantaneous unit hydrograph (IUH) models (reviewed by Chow, 1964) separate streamwater sources by their hydrologic response; usually only two responses can be identified, one quick and the other slow. Isotope hydrograph separation (IHS) models using conservative tracers like $\delta^{18}\text{O}$, δD and tritium also generally separate streamwater into two components, new rain water and old pre-storm water (Sklash et al., 1976; Sklash and Farvolden, 1982). Chemical hydrograph separation (CHS) models using a variety of chemical tracers (Cl, SiO_2 , conductivity, etc.) also distinguish between types of old and new waters, but are more prone to interpretation problems because there is always a very real possibility that

the solute in question may be continuously reacting with matrix material along various flowpaths (Sklash et al., 1976; Bottomley et al., 1984; Kennedy et al., 1986; Wels et al., 1991) instead of behaving conservatively. In general, it is better to regard chemical tracers as indicators of water flowpaths, and only indirectly as indicators of water sources (Kennedy et al., 1986; Wels et al., 1991).

In theory, rain water which has run off the soil surface and rain which has been transported rapidly to the stream via macropores should both be chemically "new" water. Studies that compare chemical and isotopic separations often find no consistent difference between the percentages of old water calculated by the two approaches, but generally the amounts calculated using chemical tracers are higher (Wels et al., 1991). New water traveling through relatively deep macropores may not pick up much of a dissolved load, and thus the waters will isotopically and chemically resemble new water traveling along shallow flowpaths. Therefore, it has been suggested that isotope separations may only give lower limits on the amounts of water from deeper subsurface flowpaths that may contribute to streamflow (Wels et al., 1991).

All of these hydrograph separation models use a "black box" approach to understanding how catchments "work". Generally only "external" information is available--the amounts and/or compositions of the inputs: rain and baseflow, and of the output: streamwater. There usually is little direct information about "internal" functions of the box (i.e., what is going on inside the black box) such as: distribution of subsurface flowpaths, spatial variations in the amounts and/or compositions of subsurface waters, or how

these factors change during a storm. Use of black-box models requires implicit assumptions about hydrologic and geochemical behavior within the box, perhaps the most common of which is that flowpaths and other hydrologic properties are homogeneously distributed. In addition, input waters are commonly assumed to have uniform compositions. Invalid assumptions can, of course, significantly affect the interpretation of the results of the studies.

Tracer hydrograph separations are based on solutions of two simple mass- balance equations for stormflow:

$$Q_s = Q_o + Q_N$$

$$Q_s C_s = Q_o C_o + Q_N C_N$$

where Q is stream discharge, C represents the concentration of the tracer, and the subscripts s , o , and n indicate stream water, old pre-storm water, and new rain water, respectively. Several simple assumptions must be made to use these equations to solve for the new and old water contributions to stormflow. First and foremost, the old and new waters must have distinctive compositions. Other typical assumptions are that water stored in the unsaturated zone is either negligible in amount or similar in composition to groundwater, and that rain and groundwater can be adequately characterized by constant compositions (Sklash et al., 1976; Sklash and Farvolden, 1982). These simple assumptions are often adequate for general characterization of catchment response to bulk storms, but separations made using them do not have sufficient resolution to help answer questions about intrastorm changes

in flowpaths and water sources, and processes occurring along the various flowpaths. Concern about environmental problems such as acid deposition has focused attention on episodic behavior in catchments, hence creating a demand for more accurate methods of hydrograph separation.

In the last decade, the validity of the simple assumptions has been evaluated by a number of investigators, including Sklash and Farvolden (1979), Kennedy et al. (1986), McDonnell et al. (1991). Temporal variations in rain isotopic composition (McDonnell et al., 1990; Kendall and Gu, 1992) and interception of rain by the tree canopy (Kendall and Cappellato, 1993) have been found to have an appreciable effect on hydrograph separations. Several investigators have concluded that soil waters are not only an important component to storm runoff but often are isotopically or chemically distinct from groundwater (Kennedy et al., 1986; DeWalle et al., 1986; Hooper et al., 1990). A few recent studies have determined that shallow soil and groundwaters can be sufficiently inhomogeneous in composition to make their use in hydrograph separations ill-advised (McDonnell et al., 1991; Ogunkoya and Jenkins, 1991).

None of these refinements to the hydrograph separation method has caused any significant change in the basic conclusion of most isotope and chemical hydrograph studies to date--namely that most stormflow is old water (Bishop, 1991). In contrast, most hydrologic response studies find that quick-flow dominates (Rodhe, 1987; Bishop, 1991), although it is unclear what mechanism is responsible for the rapid response. One answer to the dilemma of rapid catchment response to rain when the dominant source of streamflow is pre-storm old water, is recognition of how much water is

stored in the soil zone (Kennedy et al., 1986) and how quickly this water can be delivered to the stream via macropores and other types of bypass flow as a result of infiltration of new rain water at the top of the unsaturated zone (Bishop, 1991; Stewart and McDonnell, 1991; McDonnell et al., 1991; Sklash et al., 1993).

The 490 m² Hydrohill artificial catchment was designed to be intermediate between the complexities of natural watersheds and the idealities of soil columns. The large number of wells and lysimeters for sampling subsurface waters make this catchment a very suitable location for testing some of the assumptions concerning runoff generation (Gu, 1988). This catchment is "real" or natural in the sense that it has intersecting slopes, a soil layer, and grass -- but it is artificial in that it was constructed with a homogeneous soil above a concrete aquiclude, a built-in drainage system comprised of stacked lysimeters, and impermeable retaining walls on all sides. The flow draining from different layers is separately funneled through weirs at the bottom of the catchment, making accurate determination of water balances relatively simple. Budgets in natural catchments can be very difficult or impossible to evaluate because of problems with real-time monitoring of water flow at different horizons in the unsaturated zone, lateral variations within the basin, and interactions between local and regional groundwater systems. At this experimental catchment we have the advantage of independent knowledge of the spatial and temporal variation in the amounts and compositions of waters at different depths. Hence, determinations of the relative amounts of old/new and slow/quick water using a variety of models can be compared. Furthermore, in most

catchments, accurate separations of old groundwater and old soil-water contributions to streamflow are difficult to achieve. In theory, this problem is eliminated in this experimental catchment because it drains so rapidly that generally no groundwater is present between storms and the old component of the groundwater that develops during storms is derived from soil water.

Samples collected from the experimental catchment were used to examine temporal and spatial heterogeneity of flowpaths and water compositions, to compare isotopes and different chemical species as tracers, and to illustrate the sensitivity of models to variability inside the "black box." In contrast to most other isotope hydrograph studies, at Hydrohill the dominant source of quick-flow will be shown to be new water; this was true both at the beginning of the storm when there was no groundwater and late in the storm when soils were saturated. Large amounts of old water are stored in the silty loam soils of the unsaturated zone and are delivered (displaced and/or mixed with new water) to the saturated zone during storms by various combinations of macropore and matrix flow (Kendall and Gu, 1992).

TERMINOLOGY

This paper discusses the isotopic and chemical composition and movement of subsurface waters. Because there is some variation in the literature about how to describe these waters, the definitions used in this paper are listed below:

- soil water**--non-flowing water in the unsaturated zone prior to the infiltration of new storm water.
- subsurface flow**--flowing water beneath the ground surface.
- interflow**--subsurface flow within the unsaturated zone.
- groundwater**--subsurface water occupying the saturated zone and sampled in the wells.
- saturated flow**--subsurface flow within the saturated zone that drains into the troughs.

DESCRIPTION OF THE STUDY AREA

The Hydrohill #2 catchment is an artificial catchment constructed for the purpose of studying rainfall-runoff processes in detail. The catchment is one of several instrumented catchments located in the Chuzhou Hydrology Laboratory (the field experimental base of the Nanjing Research Institute of Hydrology and Water Resources), near Nanjing China (118°12'E, 32°17'N). An entire hillslope was excavated to bedrock to create a bare catchment of 4573 m²; the Hydrohill #2 catchment with a drainage area of 490 m² was later constructed within the bare catchment. A concrete aquiclude consisting of two intersecting slopes dipping towards each other at 10° with overall downslope gradients of 14° was constructed above the bedrock (Figure 11). Impermeable concrete walls enclose the catchment on all sides to prevent any

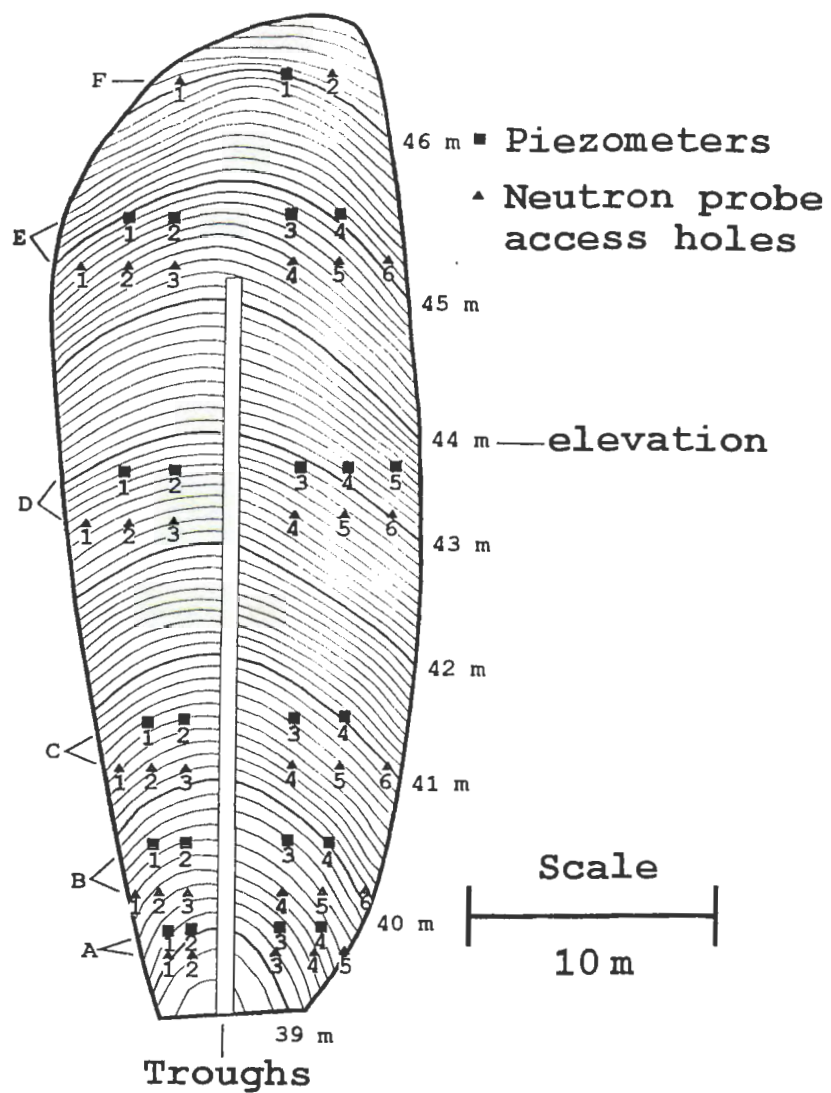


Figure 11. Plan view of the surface topography of the Hydrohill #2 experimental catchment showing the locations and numbers of wells and neutron probe access holes, and the central stacked lysimeter troughs. The numbers to the left of the map indicate the row number; eg., well number 1 of row D is well D1, etc.

flow of water between the bare and artificial catchments. A silty loam that was free of concretions was slowly piled on the aquiclude to a depth of about 1 m. During infilling, the bulk density of the soil was adjusted to approximate the natural soil profile. Grass was then planted over the surface. After letting the soil settle for 3 years, a drainage trench was dug at the intersection of the two slopes and the water-sampling instrumentation was installed.

Five troughs, each 40 cm wide and 40 m long and constructed of fiberglass, were installed longitudinally in the trench. These troughs were stacked on top of each other to create a set of long zero-tension lysimeters (Figure 12). Each trough has a 20-cm aluminum lip that extends horizontally into the soil layer to prevent leakage between layers. Waters collected in the troughs are routed through V-notch weirs located in a gaging station under the hill where discharge is continuously monitored on strip chart recorders. Water samples are collected manually above the ponding at the weirs.

As illustrated in Figure 12, the uppermost trough collects rain; the next lower trough collects surface runoff. The next three troughs collect subsurface flow from soil layers spanning the depths of, respectively, 0-30 cm, 30-60 cm, and 60-100 cm; these troughs will be referred to as the 30-cm, 60-cm, and 100-cm troughs. The source of the water in these troughs (i.e., whether the water is derived from interflow or saturated flow) varies locally and during storms. The lowermost trough collects either saturated flow or interflow, depending on the height of the water table. When the water table is high, saturated flow may be collected in both of the

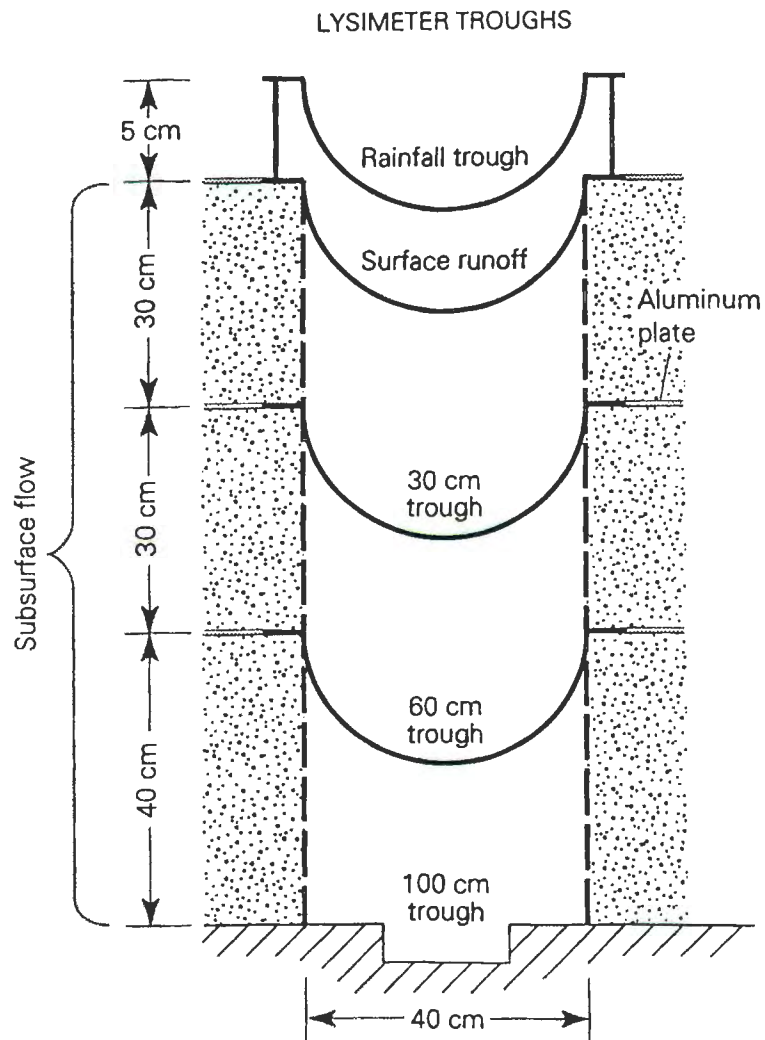


Figure 12. Schematic cross-section of rain, surface runoff, and subsurface flow collectors at the Hydrohill catchment.

lower two troughs. The troughs are analogous to throughflow gutters located in hillslope pits in that water can only pour from the free face into the trough if there is a wedge of saturated soil extending upslope from the trough (Atkinson, 1978).

Two smaller pan lysimeters were installed at 1-m depth. Lysimeter 1 and lysimeter S are constructed of 4 by 8 m and 1 by 2 m sheets, respectively, placed almost horizontally ($< 5^\circ$), that drain into the gage house under the hill. Lysimeter S was located in the bare catchment adjacent to Hydrohill.

A network of 21 access tubes for neutron moisture gages (Gu, 1987) and 22 piezometer for water-table measurements and water-sample collection were installed (Figure 11). The piezometers were drilled to the aquiclude and are slotted for the lowermost 20 cm. After installation of the piezometer pipes, the spaces around the unslotted lengths of the pipes were packed with clay balls to prevent vertical leakage along the outsides of the pipes. The neutron probe access holes were positioned adjacent to the piezometers and were numbered the same. An americium-beryllium neutron probe was used at depths of 30 and 60 cm to determine average moisture contents within a radius of about 25 cm. The uniform soil depths and relatively homogeneous soils (Table 10) made calibration of the probe by conventional gravimetric methods very simple. Water contents of surficial samples (0-5 cm) were determined by conventional gravimetric methods and the values reported in volume % water.

Rain amounts are continuously monitored using a standard WMO gauge located in the catchment, and samples are collected for analysis during

Table 10. Soil Properties.*

Depth (cm)	Bulk density (g/cc)	Porosity (%)	Grain size < 0.01 mm (%)	Organic Matter (%)
0-30	1.44	45	48.66	0.87
30-50	1.42	46	45.33	0.63
50-75	1.40	48	45.32	1.05
75-100	1.60	39	37.33	0.40

*Average values from 12 profiles across the catchment.

storms. The average yearly rainfall is 950-1000 mm. The average daily maximum temperature in July is 31.4°C.

This artificial catchment drains rapidly and a laterally continuous water table develops only for fairly large storms. Within hours after rainfall ceases, saturated conditions begin to disappear; hence, this catchment is more analogous to a hillslope than to an entire natural catchment with a perennial stream. Many deep cracks can be seen at the surface.

METHODS

Two types of rain were collected simultaneously: sequential samples from the rain gauge and grab samples from the rain trough. Subsurface samples were also collected periodically from the troughs, and suites of groundwater samples were collected three times during the storm. Because the subsurface trough samples are also grab samples, they are more analogous to the rain trough samples than to the sequential rain samples which contain the total rain collected over consecutive time periods.

Water samples were collected in 50 mL plastic bottles that were subsequently sealed with wax to prevent evaporation. Samples were analyzed for oxygen isotopic composition ($\delta^{18}\text{O}$) in the U. S. Geological Survey, Water Resources Division's stable isotope laboratory in Reston, Virginia, and for chemical composition at the Panola Mountain Research Project laboratory in Atlanta, Georgia. Water was prepared for oxygen-isotope analysis by equilibration with carbon dioxide (Epstein and

Mayeda, 1953). All isotopic compositions are expressed in ‰ relative to SMOW by laboratory calibration to V-SMOW and SLAP reference waters, with a 1σ precision of better than $\pm 0.05\text{‰}$. Chloride (Cl) concentrations were determined using a 2120A Dionex Ion Chromatograph, with 1σ precisions of $\pm 0.3\text{ }\mu\text{eq/L}$. Silica (SiO_2) concentrations were measured with an autoanalyzer with a 1σ precision of $\pm 0.8\text{ }\mu\text{m/L}$.

Determining accurate time-discharge relations was very difficult at Hydrohill because of problems the field workers had with the discharge recorders. Field engineers in China "picked" the stage values at changes in slopes on the hydrograph strip charts, made any necessary adjustments for recorder problems, and calculated discharge for each trough. The stages were later digitized from the strip charts because the picked data did not have sufficient resolution for computer modeling. The picked and digitized sets of data were interpolated to determine values at 0.1 hr intervals, and the higher resolution digitized hydrographs were normalized to the picked records to convert stage values to discharge values. A number of small adjustments were then made to correct obvious timings problems. The times of samples collected during the storm starting on July 5 are given in hours after July 5, 1989 00:00.

RESULTS

Hydrologic response:

Prior to the July 5, 1989 storm which is the subject of this study, there had been no flow from any of the troughs at Hydrohill for about four days since the last previous storm on July 1 had dropped 7 mm of rain. This tiny shower produced minute amounts of surface runoff and saturated flow from the 100-cm trough. Over a 22-hour period starting at 4 h on July 5, two storm pulses produced 115 mm of rain at Hydrohill, with 40 mm in the first three hours of the storm, gentle rain for about 10 h, and then the second pulse starting at about 21 h (Figure 13). The storm resulted in flow from the troughs starting at 6.7 h, after the first 20 mm of rain went into storage in the soil zone (Figure 13), and eventually in measurable water in all the piezometers. Because there was no saturated zone when rain started on July 5, the subsurface waters that subsequently appeared in the troughs and wells must consist of various mixtures of pre-storm soil water and new rain water. This catchment is very responsive; the hydrographs of interflow and saturated flow closely resemble the hydrograph of surface runoff (Figure 14). Arrival times for peaks are slightly later for the deeper troughs than for the shallow ones, as expected. For example, flow peaks at the 100-cm trough are 30-90 min later than at the 30-cm trough. However, because of timings problems noted above, detailed discussion of small differences in arrival

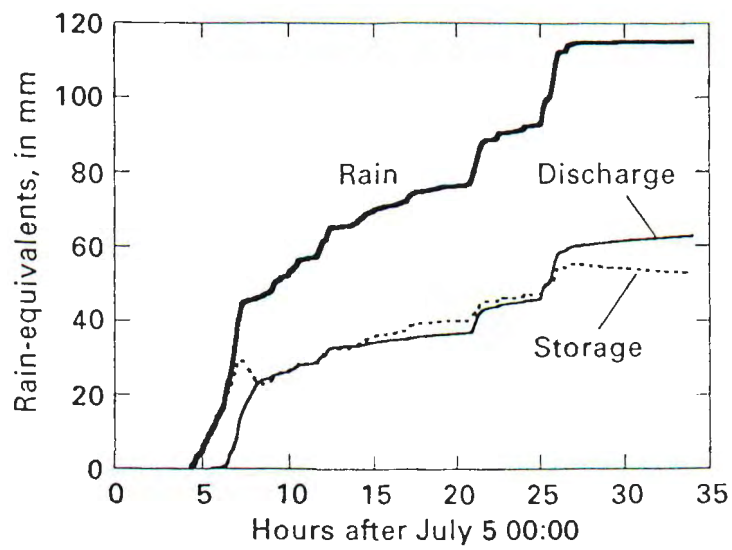


Figure 13. Cumulative rain, total discharge, and rain in storage; in mm (rain-equivalent mm).

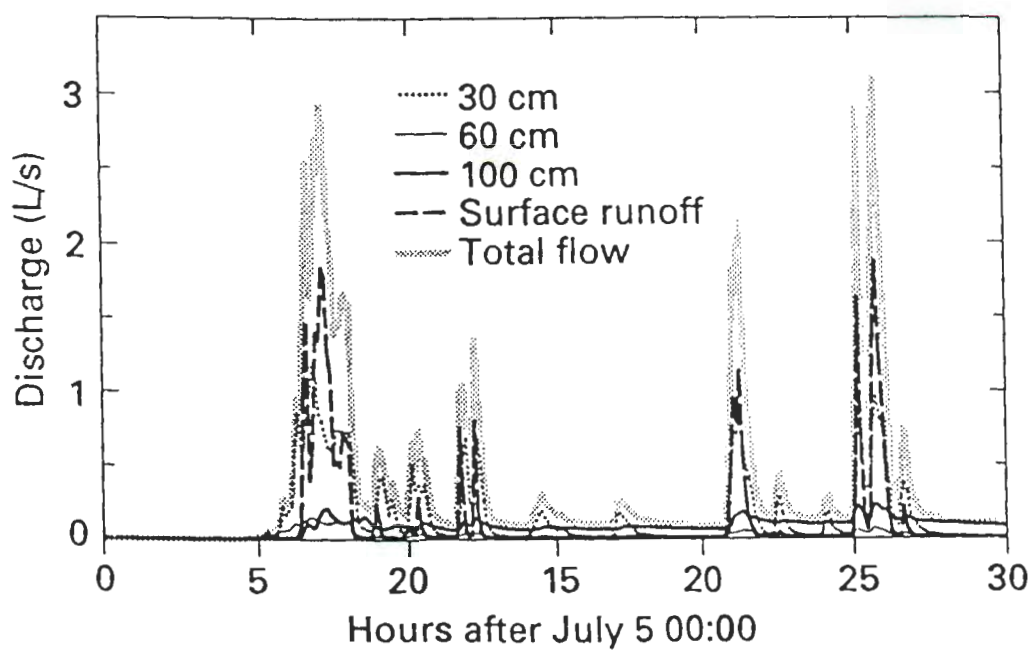


Figure 14. Discharge hydrographs for the July 5, 1989 storm.

times are probably not warranted. Tiny showers at 12 h and 17 h caused discharge increases at 30 cm, 60 cm, and 100 cm, but not surface runoff. Hence, the continuous gentle rain at a rate of about 1.7 mm/hr during this entire period (13 to 17 h) was insufficient to maintain surface saturation by offsetting water losses due to gravity draining and mid-day evaporation.

The maximum total flow from the catchment during the two major rain pulses was about 3 L/s. During rain showers, about 50-80% of the flow was surface runoff, 30-40% interflow from 30 cm, 5-10% saturated flow from 100 cm, and <5% interflow from 60 cm (Figure 14). While the catchment drained between showers, 70-90% of the total discharge was saturated flow from 100 cm. The catchment was still draining from the July 5 storm at 50 h when another storm started; at this point in time, the percentages of total discharge collected from each of the four flow troughs are (in order downward): 36%, 38%, 3%, and 23%. The discharge volume is equivalent to 57% of the total new rain.

Groundwater levels were monitored frequently during the storm. Figure 15 has contour diagrams of elevations of the water table above the aquiclude for six different monitoring times. Contouring water table elevations with so few control points necessarily involves a lot of imagination; to minimize bias, all contours were made by octagonal kriging of the 5 to 10 nearest points (depending on data density). It is unclear how to contour the water table near the center trough; as a first approximation, the elevations are plotted as dropping to zero at the elevation of the bottom trough when in fact there may have been flow into the trough from the face of a saturated wedge of water several tens of cm high. The wavy contours

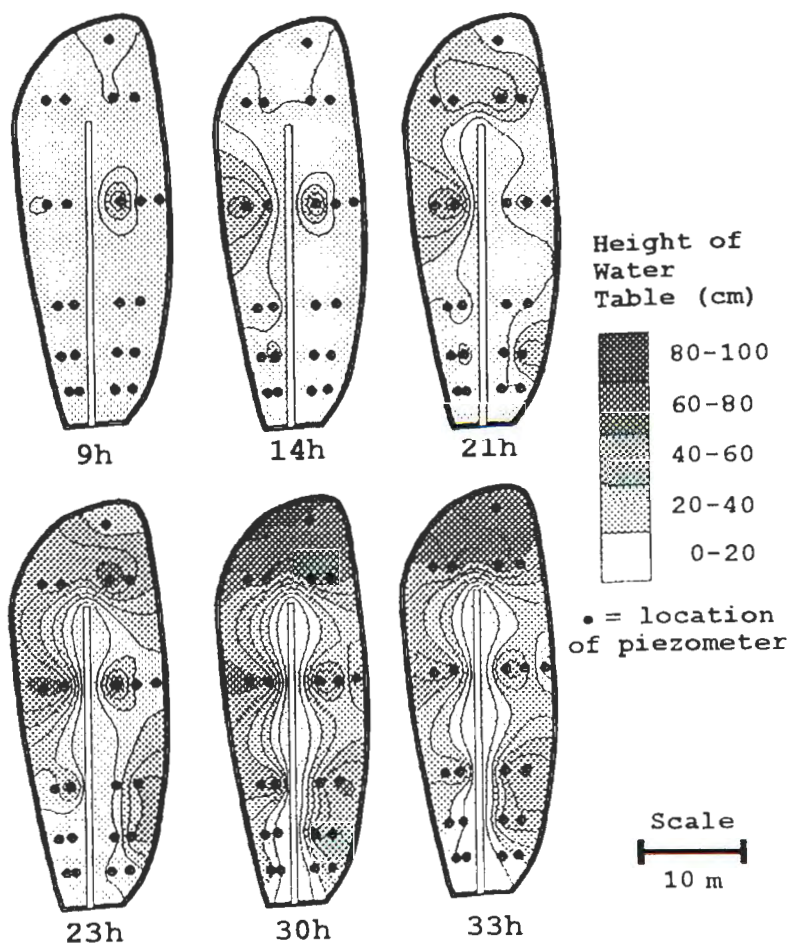


Figure 15. Contour diagrams of water table height above the aquiclude for six monitoring times after July 5, 1989 00:00. The waviness of the contours near the central troughs is an artifact of the contouring.

near the center troughs are an artifact of the data contouring; the contours adjacent to the troughs should probably parallel the troughs.

Before the storm, the entire soil layer was unsaturated; saturated zones later developed unevenly. The first well to become saturated was D3 (Figure 11) at 6 h, and the last was B1 between 23 and 30 h. Hence, a laterally continuous water table did not develop until after 23 h and water levels continued to rise in most wells until about 30 h when rain ceased. Water table elevations (above the aquiclude) ranged from 20 cm in the A and B wells on the left side of the trough to a large zone near the E and F wells where the elevations were in the range of 60-70 cm, with an average water table rise of about 35 cm. In general, upslope wells achieved saturated conditions first, and wells at the bottom of the catchment (A and B wells) last. Samples were collected at 10, 17, and 34 h (Figures 15 and 16d). The unevenness of the saturated zone is a product of the spatial and temporal variability in modes of transport of water (i.e., piston versus matrix flow) arising from permeability variations in the soil.

The water table did not develop as a wedge of water progressively rising up the catchment slopes. It is clear from the contour diagrams that steep water mounds rapidly developed at several locations very early in the storm (eg., to an elevation of 40 cm by 7 h, at well D3). Some of these mounds were transient and some were stable. For example, the water table at D3 rose during the first pulse of rain, collapsed when rain ceased and the soils drained (21 h), and rose rapidly again from 23 to 30 h during the second rain pulse, and then declined again at 33 h as the soils drained. In contrast, the water table rose steadily at mounds centered around D1 and D2,

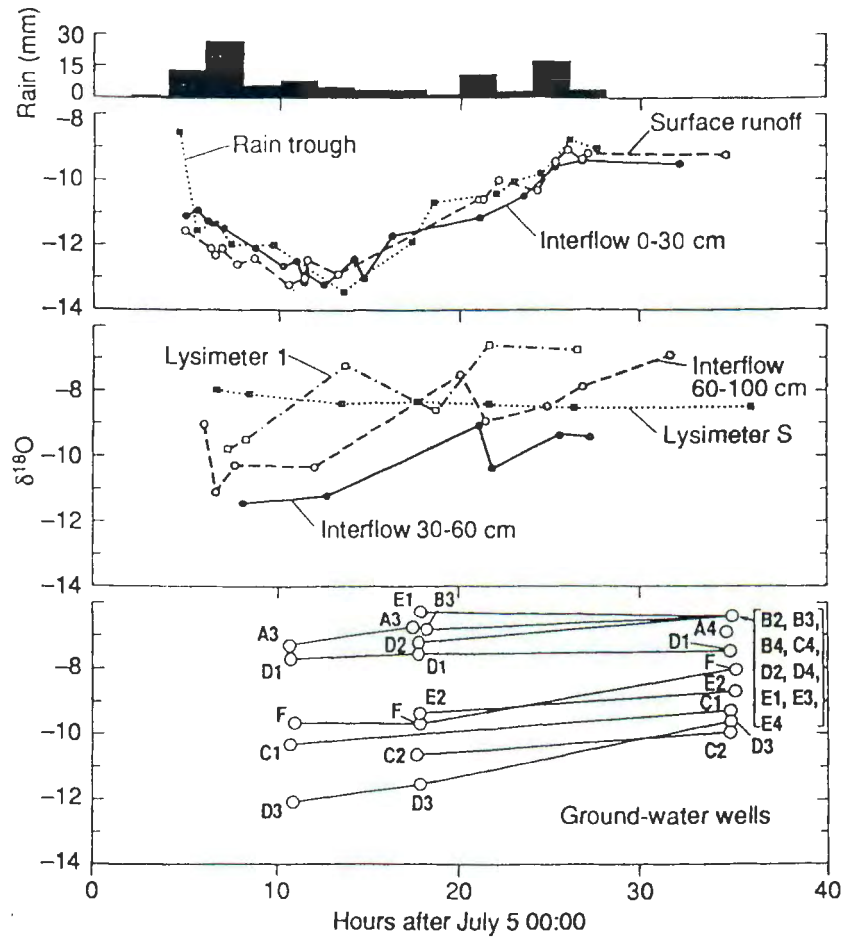


Figure 16. (a) Amounts of rain collected at the rain gage at two-hour intervals; (b) $\delta^{18}\text{O}$ values of rain, surface runoff, and 30-cm interflow; (c) $\delta^{18}\text{O}$ values of 60-cm interflow, 100-cm saturated flow, and lysimeter samples; (d) $\delta^{18}\text{O}$ values of groundwater. Data points are connected with lines to clarify the different isotopic patterns; error bars are smaller than the symbols.

and around the E and F wells, throughout both rain pulses and did not decline at either mound until 33 h. The rapid rises of the water table rises in this silty clay soil suggest that either that there was a thick capillary fringe zone (not unreasonable for clayey soils) or that bypass flow must be an important transport mechanism, or both; hence, calculation of hydraulic properties with these data is risky.

Knowledge of the water table elevations at several times during the storm allows determination of when the waters seen in the various troughs are derived solely from interflow and when saturated flow might contribute to the water seen in the troughs. Although the water table near the D and E wells is high enough by 21 to 23 h to have possibly intersected the lip of the 60-cm trough and water levels continued to rise along the length of the troughs for the rest of the storm, the low flow in the 60-cm trough (about 3% of the total flow from the catchment) suggests that little saturated flow could have drained into the trough from the soils between 30-60 cm. Discharge in the 60-cm trough was relatively constant during the entire storm, showing only minor increases when discharges increased in the other troughs. Before 21 h, the water in the 60-cm trough was all derived from interflow. The water table never rose high enough to intersect the lip of the 30-cm trough; hence interflow contributed all the water to this trough. The large amounts of flow seen in the 100-cm trough before the water table rose and saturated flow developed along the aquiclude boundary may be due to lateral flow along bedding/packing planes; for example, there is a marked change in soil characteristics at about 75 cm (Table 10), with larger grain-sizes and probably increased permeability below. Also, large cracks were

common in the clayey soil; these macropores may have allowed the creation of local saturated zones (ponding) which could have contributed saturated flow to the troughs via kinematic flow.

Water budgets:

Moisture contents were measured several times during the storm in order to calculate changes in water stored in different horizons. Volume % water contents of soils from 0-5 cm deep were determined gravimetrically (Table 11) and water contents from 5-100 cm were determined by neutron probe (Table 12). The moisture contents suggest that about 2/3 of the available porosity (Table 10) in the soils was filled with water once the catchment had wetted-up. Because the catchment soils became saturated unevenly and the neutron probe averages water contents over a large (25-cm) radius, the average moisture contents in Table 12 may hide a lot of spatial variability.

Table 13 shows water budgets calculated for three overlapping periods of time when soil-water data were available. The periods all start at about 10:00 on July 4 (a day before the storm) and end at: 12 h (high flow during a shower); 20 h (at the end of a several-hour pause between the first and second pulses of rain); and, 34 h (several hours after the end of the second rain pulse when the catchment was still draining). These three water budgets attempt to account for both the amounts of new rain water that have been added to different soil layers, and the amounts that have drained from these

Table 11. Moisture Contents of Surficial Soils (determined gravimetrically).

Depth (cm)	Moisture content (volume %)				Change in water content (%)		Rain-equivalent amounts (mm)	
	July 4	July 5 6 h	July 5 15 h	July 5 20 h	12 h ^A	20 h	12 h	20 h
0 to 1	22.5	60.4	64.5	58.7	+40.7	+36.2	+4.1	+3.6
1 to 2	22.5	36.3	64.5	58.7	+33.5	+36.2	+3.3	+3.6
2 to 5	22.5	36.3	40.2	46.7	+16.5	+24.2	+5.0 ^B	+7.3
Total:							+12.4	+14.5

^A Values interpolated from 6 h and 15 h data.

^B The change in water content for the interval 2-5 cm has been multiplied by 3.

Table 12. Soil Moisture Contents in Volume %
(determined by neutron probe).

Access Tube #	July 4 09:30		July 5 11:55		July 6 09:55	
	30 cm	60 cm	30 cm	60 cm	30 cm	60 cm
A2	28.3	31.3	32.1	32.5	32.2	32.3
C1	27.5	28.7	29.1	29.2	29.9	31.1
C6	28.0	29.7	29.6	30.6	30.2	31.3
D4	26.3	29.6	29.5	28.3	29.3	32.3
E2	30.3	33.6	30.2	32.8	32.4	33.5
E5	29.3	31.1	30.6	32.5	30.9	33.7
F2	27.6	31.2	30.7	32.7	31.3	34.2

Table 13. New-Water Budgets from July 4 10:00 to Various times after July 5 00:00 1989.

Components	Rain-equivalent amounts (mm)		
	to 12 h	to 20 h	to 34 h
Surface Runoff	13.1	14.0	23.5
Subsurface flow 0-30 cm	13.6	16.0	25.2
Subsurface flow 30-60 cm	0.8	1.1	1.7
Subsurface flow 60-100 cm	2.7	5.3	12.0
Soil water 0-5 cm	12.4	14.5	14.5*
Soil water 5-60 cm	17.1	17.7	18.3
Soil water 60-100 cm	5.1	7.5	9.9
TOTAL:	64.8	76.1	105.1
Rainfall	61.4	76.7	115.5

* Estimated amount of water lost to evapotranspiration.

soil layers into the troughs. The water budget components are given in rain-equivalent units; i.e., scaled to the amount of rain in mm over an area of 490 m² required to account for increases in the amounts of water present in or issued from each component of the catchment. Although the values for each component represent the increase in new water in the catchment, the water actually measured in each component may be a mixture of new water plus old water displaced out of the soil by the new water.

No gravimetric data for the surficial soils were available for 34 h, when the storm was over and the catchment was drying (Figure 15). Therefore, the amount of water present in the soils at 20 h, which reflects moisture conditions after several hours of draining and before much evaporation had taken place, is used as an estimate for the amount of water present at 34 h, a few hours after rain ceased at 29 h. Given the low soil-water contents seen in the soils on July 4, three days after a 7-mm storm that caused saturated flow (Table 11), it is likely that much of the water once present in the shallow soils may have evaporated by 34 h; hence, the water content given for the 0-5 cm component is probably a minimum value for the amount of new water that was evaporated from the soil.

The neutron probe data for tubes A2, C1, D4, and F2 were used to determine the water contents of soils at various distances from the troughs. Measurements from the 30-cm and 60-cm probes were used as estimates for moisture conditions in the 5-60 cm and 60-100 cm intervals, respectively. Based on several years of observations at all 21 access tubes, the moisture contents of these four tubes are believed adequate to characterize 17%, 10%, 40.6%, and 32.4% of the catchment, respectively. The volume % changes

in water contents for the four tubes are multiplied by these areal scaling factors to calculate the volume % change in water content, which is then multiplied by the total depth of the interval for which the averages are being applied (i.e., 550 mm and 400 mm for the intervals 5-60 cm and 60-100 cm, respectively) to calculate rain-equivalents in mm. The interception area of the catchment has been corrected for the area of the troughs ($\approx 3\%$) because the rain water collected in the upper trough did not contribute to flow from the catchment.

There is excellent agreement between the calculated water budgets and rain amount at 12 h and 20 h (Table 13), with 105% and 99%, respectively, of the rain water accounted for in terms of discharge or increases in water content. The agreement for the last period (to 34 h), when the evaporative water loss in shallow soils could only be estimated and the deeper soils were contributing large amounts of discharge, is good, with about 91% of the rain accounted for in the catchment components.

The amounts of new water present in the 1-m soil zone at various times (Table 13) can be estimated by a slightly different method. Instead of using the neutron probe data to estimate water contents for the entire 60-100 cm zone, the average depths of the water table as contoured in Figure 15 can be used to divide this interval into an unsaturated zone where the neutron probe data can be used and a saturated zone where the water content can be estimated using the porosity. The contoured water table elevations at 1063 evenly spaced nodes were averaged to produce the average elevations in Table 14. If the measured porosity of 39% (Table 10) is used to calculate amounts of new water in the saturated zone, the total amounts of water

Table 14. Average Height of Saturated Zone and $\delta^{18}\text{O}$ of Groundwater.*

Hours after July 5 00:00	Average height of water table (cm)	Average $\delta^{18}\text{O}$ groundwater (‰)
10 h	8.8	-9.38
17 h	16.5	-8.57
34 h	35.5	-7.30

* Depths measured at 14 h, 17 h, and 33 h used for the calculations.

stored in the soil (0-100 cm) for the three time intervals are about 50% higher than the values in Table 13. Because the total water budgets in Table 13 for 12 h and 20 h are already in such good agreement with the rain input, the validity of these new estimates seems questionable. Possible explanations for the discrepancy are that pore spaces are much less uniformly and completely filled than estimated (i.e., less than the porosity of 39%), and that the saturated zone is much less continuous than Figure 15 would suggest. If the maximum water content of 34% seen in Table 12, which may be close to the maximum volume % of water possible in the 5-100 cm soils under the kinds of saturated conditions created in this catchment, is used instead to calculate the water contents in the saturated zone, the total calculated amounts of new water for the three time periods are 107%, 101%, and 92%, almost identical to the previous estimates; hence, perhaps only 87% ($34/39 \times 100$) of the total porosity in the deep soils can be saturated.

The amount of pre-storm soil water present in the catchment on July 4 is estimated to be 290 mm (using the measured water contents in Tables 11 and 12). The maximum volume of water stored in the soil during the two storm pulses when soil data are not available can be estimated using the deep (5-100 cm) soil values at 34 h when the deeper soils were thoroughly saturated and the 0-5 cm values observed at 14 h when surface runoff and 0-30 cm flow were near their maximum discharge values, to get 315 mm. Therefore, the pre-storm water filled approximately 92% of the pore space eventually filled during the storm. If under saturated conditions the pore spaces in the interval 5-100 cm can contain 34 volume-% water, the maximum possible storage for the 1-m soil zone is 357 mm.

Isotopic compositions:

To use $\delta^{18}\text{O}$ as a tracer of intrastorm changes in water sources and flowpaths in a catchment, the new water must (1) be different from the old water, and (2) the intrastorm variation in rain and old water $\delta^{18}\text{O}$ values must either be small enough that a constant composition can reasonably be assumed, or the rain compositions must show a simple gradational pattern over time. Because there rarely is enough information to assign lag times to infiltrating fractions of rain, the oscillating isotopic compositions characteristic of frontal storms adds considerable uncertainty to the determination of the composition of rain reaching the stream during storms. Other assumptions are often listed (Sklash and Farvolden, 1979), but these are the critical ones. If the $\delta^{18}\text{O}$ values vary erratically, tracing the infiltration of this water can be extremely difficult. Fortunately, the storm on July 5, 1989, fit these criteria reasonably well.

The volume-weighted $\delta^{18}\text{O}$ of the rain storm was -11.3‰ . The isotopic composition of the 14 sequential samples of rain collected gradually change from an initial -8.3‰ , to -12.5‰ during peak rainfall, to -9.65‰ at the end of the storm. The 14 "grab" samples collected from the rain trough showed almost identical variability; for clarity, the $\delta^{18}\text{O}$ values of the rain trough samples are plotted in place of the sequential rain samples in Figure 16b.

A few samples of pre-storm waters were available. A complete set of soil samples had been collected to characterize the pre-storm soil water; unfortunately the method used to extract the water caused isotopic fractionation of the samples so they will not be discussed further. The 7-mm hour-long storm on July 1 caused a small quantity of surface runoff with a $\delta^{18}\text{O}$ value of -8.35‰ and a minute amount of saturated flow from the 100-cm trough with a composition of -5.45‰ . The surface runoff $\delta^{18}\text{O}$ value is probably representative of the composition of the July 1 rain storm, and the fact that measurable runoff occurred from such a small storm probably indicates that the surface soils were saturated at this time. From July 2 until the storm on July 5, the wells were dry, the catchment yielded no subsurface flow, and the catchment soils became progressively dryer. Saturated flow from a large storm on June 25 had a $\delta^{18}\text{O}$ value of -5.85‰ .

One way of estimating the composition of pre-storm water which takes into account possible intrastorm changes in the composition of old water is to average the compositions of baseflow prior to the storm and during hydrograph recession (Hooper and Shoemaker, 1986). The last sample of saturated flow at 31.5 h had a composition of -6.85‰ (Figure 16c); the average of this and the pre-storm flow from July 1 gives -6.15‰ . On the basis of these limited data, the soil water present in the soil prior to the July 5 storm was enriched in ^{18}O relative to the rain water, in the range of -5.5 to -8‰ . This estimation ignores the possible isotopic enrichment of very shallow soil water caused by evaporation between July 1 and July 5 because (1) any such waters are volumetrically insignificant compared to the total

water storage; and (2) exchange of the evaporated waters with atmospheric water plus contributions of water from dew can cause these shallow soil waters to be less enriched in ^{18}O than expected (Vance C. Kennedy, unpublished data).

The $\delta^{18}\text{O}$ compositions of samples collected from the three subsurface flow troughs and the two pan lysimeters provide information on the mixing of rain and pre-storm waters, and on the timing of mixing, as infiltration waters arrive at different soil horizons. Although all the hydrographs are similar (Figure 14), the isotopic compositions of waters collected in the five troughs have two different patterns as shown in Figures 16b and 16c. The rain, surface runoff, and interflow from 30 cm all have very similar $\delta^{18}\text{O}$ values during the storm (Figure 16b). The $\delta^{18}\text{O}$ values of water from 60 cm and 100 cm (Figure 16c) show no resemblance to the shallower samples. The temporal changes in $\delta^{18}\text{O}$ of 60-cm and 100-cm samples are similar, although the deeper samples are 1 to 2‰ more enriched in ^{18}O . Samples from lysimeter 1 show similar pattern, but with different lag times. Lysimeter S has an almost constant isotopic composition indicative of old water, perhaps because of drainage problems.

Samples from below 30 cm seem to show a correlation between discharge and isotopic composition. As discharge decreases from 10 to 20 h, the 60-cm and 100-cm samples show gradually increasing $\delta^{18}\text{O}$ values. An increase in discharge caused by increased rain intensity at 21 h is associated with more depleted $\delta^{18}\text{O}$ values, and then $\delta^{18}\text{O}$ values increase again as the soils drain. The final waters flowing at the 30-cm and 60-cm interflow troughs are almost identical in $\delta^{18}\text{O}$ to the last rain samples. Water continues

to flow at the 100-cm trough for several hours past the end of the rain, and the $\delta^{18}\text{O}$ values of the saturated-zone water continue to increase towards the original composition of pre-storm water. Lysimeter 1 samples also increase in $\delta^{18}\text{O}$ as discharge decreases after the first rain pulse, but then show a sudden decrease in composition about 4 h before the other deep samplers do; at the end of the storm, the waters are enriched in ^{18}O similar to those seen in the isotopically enriched wells (Figure 16d). Lysimeter S samples show much less variation than the other collectors and actually decrease slightly in isotopic composition over the storm, unlike the rest of the sampling sites.

The groundwater in this tiny catchment shows considerable spatial and temporal variability in $\delta^{18}\text{O}$, with values ranging from -12‰ to -6‰. Wells also can be divided into two categories by their isotopic response to the storm (Figure 16d): (1) wells where the initial waters have enriched compositions of -6.5 to -7.5‰ and remain approximately constant during the storm; and, (2) wells where the initial waters are considerably more depleted in ^{18}O (-10 to -12‰) and become 1 to 3‰ more enriched during the storm. To better illustrate the spatial and temporal relations among the wells, the $\delta^{18}\text{O}$ values for groundwaters collected at three times during the storm are contoured and plotted in Figure 17. The contours were also made by octagonal kriging of the 5 to 10 closest points plus a lot of poetic license because of the paucity of data points. Although the contours are drawn across the troughs, waters on either side are completely independent.

The changes in the $\delta^{18}\text{O}$ values of groundwater are not erratic but instead reflect ongoing processes affecting sizable portions of the catchment during the entire storm. At 10 h, very depleted waters (< -10‰) are found

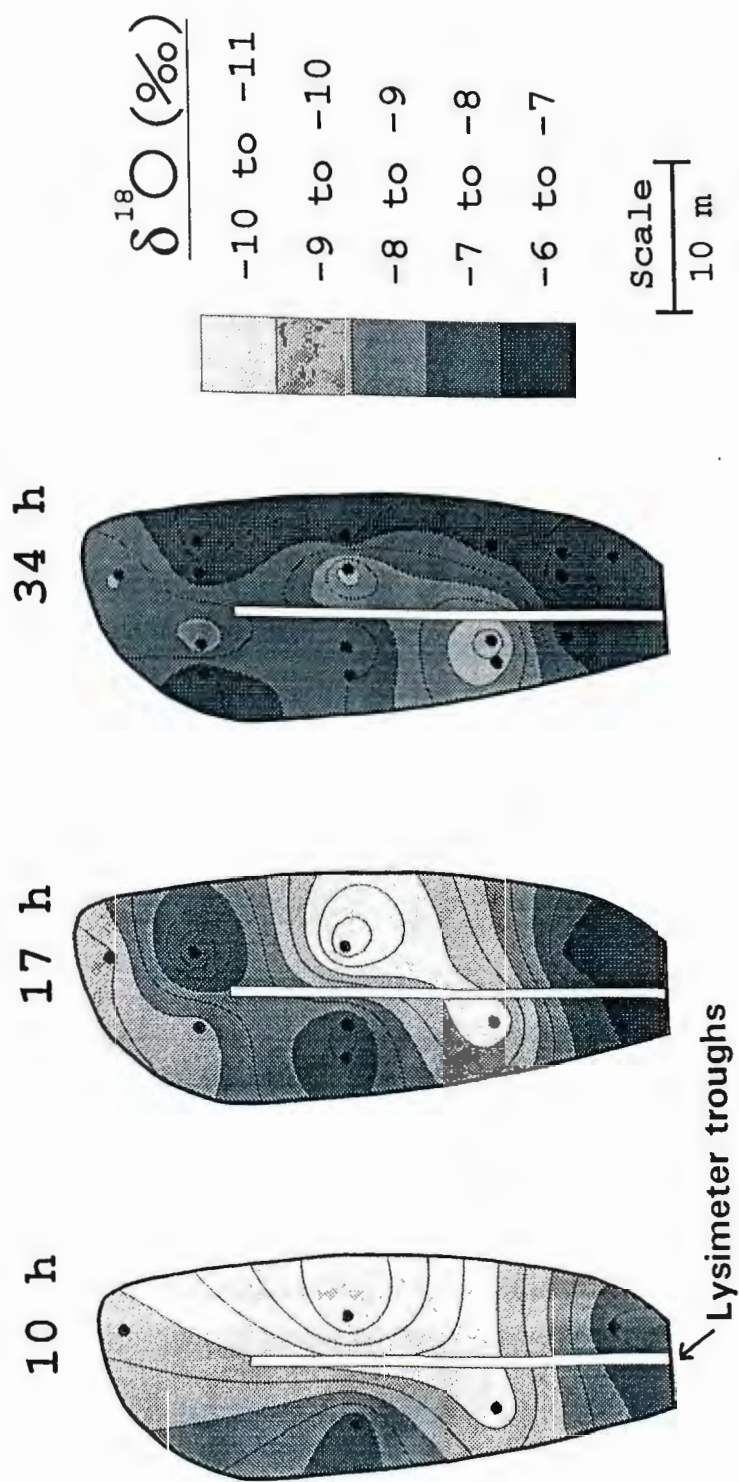


Figure 17. Contour diagrams of $\delta^{18}\text{O}$ in groundwater at three sampling times. The solid dots indicate the locations of wells where $\delta^{18}\text{O}$ values were available at these selected times.

in two areas located on either side of the central troughs. Groundwaters in these two areas are depleted relative to the rest of the catchment throughout the storm, although they gradually become more enriched at 20 h and 34 h as the water table rises. Groundwaters elsewhere also become slightly more enriched in ^{18}O from 10 to 34 h; areas that were most enriched in ^{18}O at 10 h are still enriched relative to most wells at 34 h.

There is no consistent relation between changes in water table level and changes in $\delta^{18}\text{O}$. Comparison of Figures 15 and 17 shows that although the depleted waters at D4 are associated with a transient water mound, the other depleted zone located near C2 is associated with a steadily rising water level. The zones where waters are most enriched include areas where the water table rose rapidly (E and F wells) and areas where the water table never rose very high (A and B wells).

Chemical variability:

Concentrations of Cl in rain collected in the rain gauge were 2 to 3 times higher than in rain samples collected in the rain trough; this may be a consequence of using poorly rinsed collection bottles in the gauge. Therefore, the rain trough samples were used for estimating the composition of "new" water. Although the high concentration of the first sample may be partially due to dissolution of salt deposits in the rain trough, in addition to atmospheric washout, the volume-weighted Cl and SiO_2 concentrations of rain are $7 \mu\text{eq/L}$ and $8 \mu\text{m/L}$, respectively. Concentrations of Cl and SiO_2

are low in surface runoff, which is sometimes almost as dilute as rain, and high in subsurface flow (Figures 18a and 18b), with an average of about 30 $\mu\text{eq/L}$ for Cl and 200 $\mu\text{m/L}$ for SiO_2 . Concentrations of SiO_2 in surface runoff are similar to those of subsurface samples only at times of high rain intensity and peak flow; the high concentrations at this time may result from return flow through the upper soil layers.

Groundwater samples did not have consistent chemical compositions (Figure 19a); in fact they showed considerably more variation in Cl and SiO_2 concentrations than was seen in the trough samples. The Cl and SiO_2 data weakly support the observation made with $\delta^{18}\text{O}$ that the groundwater wells can be divided into two categories. The wells with constant enriched $\delta^{18}\text{O}$ values have a wide range of Cl values, but the changes in Cl over time for any individual well are small and erratic and there is no correlation between changes in $\delta^{18}\text{O}$ and in Cl. In contrast, all the wells that became more enriched in ^{18}O during the storm also showed a strong inverse relation between Cl and $\delta^{18}\text{O}$.

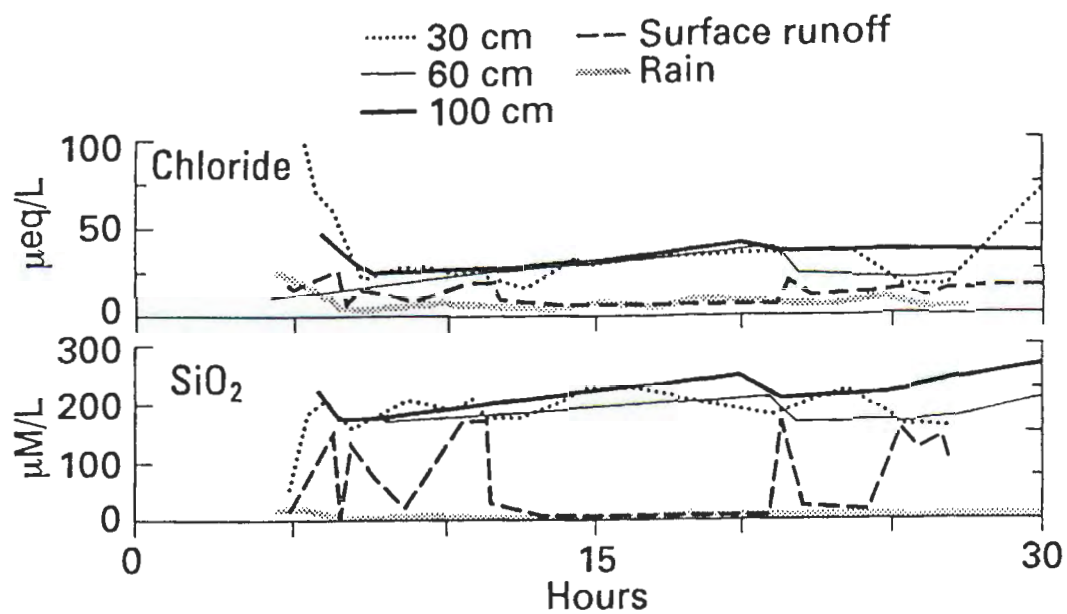


Figure 18. Chloride (a), and silica (b) concentrations in trough samples. Data points are connected with lines to clarify the different patterns.

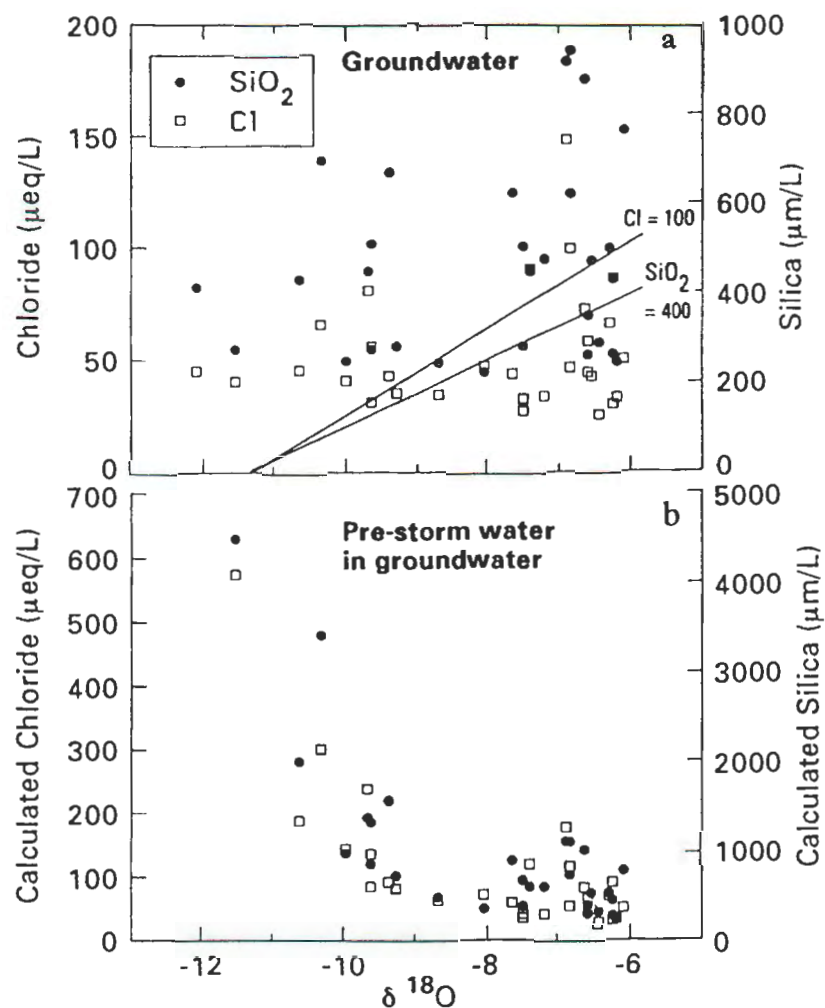


Figure 19. (a) Chloride, silica, $\delta^{18}\text{O}$ in groundwater samples; the dashed lines show what the calculated concentrations of chloride and silica (with various choices of pre-storm water compositions) in groundwater should be, assuming the amounts of new water determined with $\delta^{18}\text{O}$ are accurate and that the chemical tracers behave conservatively. (b) Calculated chloride and silica concentrations of pre-storm water in groundwater, assuming that the amounts of pre-storm water calculated using $\delta^{18}\text{O}$ (using cumulative rain) are accurate. Error bars are smaller than symbols.

DISCUSSION

Assumptions for using $\delta^{18}\text{O}$, Cl, and SiO_2 for hydrograph separations:

The amount of rain water contributing to subsurface flow at any sampling time can theoretically be calculated using simple conservative-mixing models, although such complex subsurface flow hydrographs (Figure 14) really require more frequent samples than are available. In the simplest application of the isotope hydrograph separation technique, one assumes that all subsurface water results from mixing of only two components, rain and pre-storm water, both having spatially and temporally constant $\delta^{18}\text{O}$ compositions. For these calculations, a number of other assumptions must be made about the water sources.

For isotope and chemical separations, the choice of end-member compositions (i.e., the compositions of new and pre-storm water) is critical. As discussed earlier, the meager pre-storm data suggest that the $\delta^{18}\text{O}$ value of this water was likely in the range of -5.5 to -8‰. A $\delta^{18}\text{O}$ value of -6‰ \pm 1‰ was chosen for pre-storm water because: (1) the various reasonable proxies for pre-storm water discussed earlier all had $\delta^{18}\text{O}$ values near -6‰; (2) samples from lysimeter 1, the 100 cm trough, and groundwater wells seemed to "trend" towards this value at the end of the storm; and, (3) there

was insufficient information to assign a spatially variable composition to the soil water. If a more typical value of -7‰ or -8‰ is used, the calculated percent of rain water contributing to subsurface waters exceeds 100% for many sampling times, indicating that the isotopic compositions of these subsurface waters are not intermediate in composition between the two proposed end-member compositions. Other possibilities that cannot be ruled-out include: that the true unsaturated-zone water $\delta^{18}\text{O}$ value could be even more enriched than -6‰ , that it could be vertically or horizontally stratified, or that the soil-water could be heterogeneous in composition because of poor mixing of waters from the previous storm. These different proxies for pre-storm water also had relatively constant Cl and SiO_2 values which were used for the chemical end-members.

Three possible approaches for estimating the rain-water component are: (1) the conventional approach (Sklash et al., 1976; Sklash and Farvolden, 1982), which uses the bulk composition of rain for the new-water component; (2) use of the actual, sequential rain value at the time each subsurface sample is collected (with or without a lag time); and, (3) use of the cumulative volume-weighted average of all the rain preceding each sampling time. Because of the large range of rain compositions during the storm and the existence of these same isotopic variations in the subsurface waters at 30 cm, use of the bulk rain composition is inappropriate. The two latter approaches often produce significant differences in the percentages calculated for different water sources (McDonnell et al., 1990), as will be illustrated below.

Effect of rain-estimate method on hydrograph separations:

Subsurface flow samples: The percentages of rain in discharge from the 100-cm trough were calculated using -6.5‰ for the soil water and using both sequential and cumulative values of rain as estimates of the rain-water composition. The model solutions are shown graphically on the hydrograph in Figure 20; the vertical height of any point along the two curves below the hydrograph represents the amount of the total discharge at that point derived from rain, as calculated by the two approaches.

Given the complexity of the storm hydrograph and the limited numbers of subsurface samples collected (9), the model curves on Figure 20 are highly speculative and it would be very risky to make sweeping generalizations about subsurface water sources based on this plot; nevertheless, some patterns can be seen. The main observation from this exercise is that when subsurface flow is high, the contribution of new water, probably delivered through macropores, is high; otherwise, as the soils drain, the contributions of pre-storm water increase. Not surprisingly, there appears to be more rain water present on the rising than on the falling limbs of each discharge peak. During flow peaks, the amount of rain water ranges from 50-95% of the subsurface flow; between peaks, the flow may contain

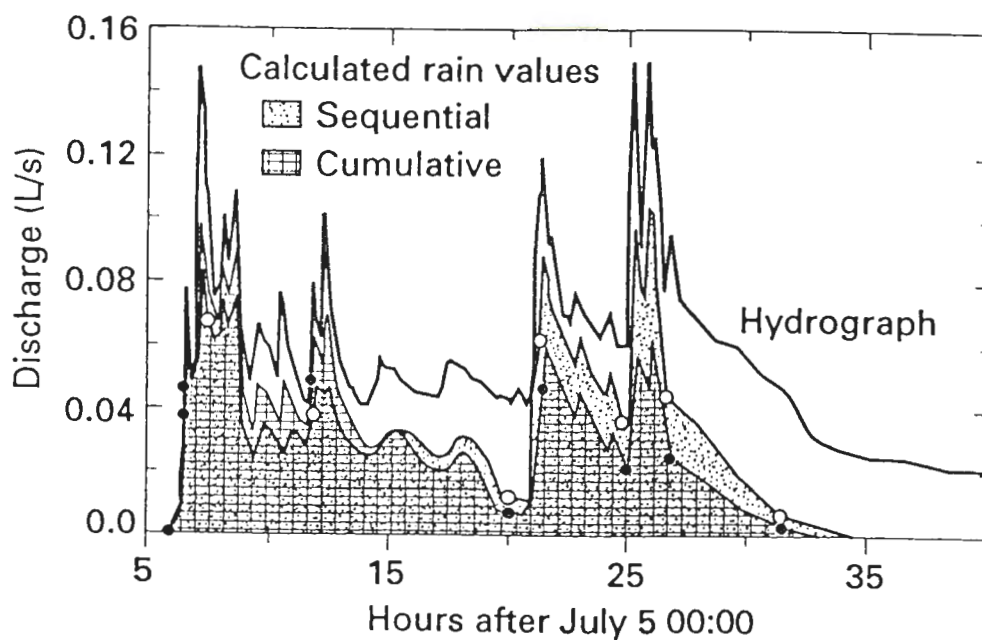


Figure 20. Estimates of the percentage of subsurface flow at the 60-100 cm collector that is derived from rain, calculated using soil water = -6.5% , and using both the sequential rain values (dots) and the volume-weighted cumulative values (circles). The shaded areas represent the amount of total discharge derived from rain.

only 20-60% rain. The longer the draining time between discharge peaks, the less rain water present in the subsequent discharge peaks.

During the first part of the storm until the increase of rain intensity at 21 hours, use of cumulative rain values produces higher (by 5-20%) estimates of the amount of subsurface water derived from this storm than use of sequential rain compositions. After this time, the cumulative rain values produce markedly lower estimates of rain contributions than the sequential rain values. This change, shown by a "cross-over" at 15 h on Figure 20, occurs during a period of low rainfall intensity (Figure 16a).

Groundwater samples: The wells with water consistently enriched in ^{18}O (Figure 16d) contained only 10-20% rain water at 10 h, decreasing to generally less than 5% rain water at 34 h; essentially the same percentages are calculated regardless of whether the sequential or the cumulative rain value is used. Because these wells contain virtually no new water, the infiltration of new water at the surface must be displacing pre-storm isotopically enriched soil water downwards to create local saturated conditions above the aquiclude. The wells that show increases in $\delta^{18}\text{O}$ with time initially (10 h) yielded groundwater containing 50-100% rain water; by 34 h, many of these wells contained only 20-50% rain water. The waters in these wells are apparently mixtures of rapidly moving, isotopically depleted rain water traveling through macropores with increasing amounts of pre-storm, isotopically enriched water flowing downwards by matrix flow.

The percentage of new water calculated for the isotopically variable wells is very sensitive to the method chosen for estimating the rain composition. Use of the cumulative rain composition at 10 h results in rain contents up to 20% higher than calculated using the sequential rain composition; at 18 h, the results are similar for the two rain compositions. At 34 h, use of the cumulative rain value produces rain amounts 2-35% lower than with the sequential rain value. In analogy to the saturated flow samples, application of sequential rain values is probably most appropriate when the water table is rising rapidly (10 and 17 h) and least appropriate when soils are draining (34 h).

Best choice: So, what is the best choice for estimating the composition of new water in this catchment? McDonnell et al. (1990) noted that use of sequential rain values may be appropriate in very responsive catchments or ones with a high proportion of overland flow, a category which includes Hydrohill. Perhaps the most critical factor in selecting a method is the percent of new water in flow from the catchment. The similarity of the surface runoff and 30-cm interflow to the rain (Figure 16b) indicate that sequential rain values must be used for the new rain composition for these troughs. Because the quick responses of the 60 and 100-cm hydrographs indicate that considerable water rapidly moves downwards and/or displaces deeper water during high flow, the sequential-rain approach probably

produces more accurate estimates of the amount of rain at the beginning of the storm or during peak discharge than the cumulative approach. Ideally, lag times should be applied for each sampling time; however, because there are insufficient data for the estimation of appropriate transit times for periods of low flow, no lag times could be assigned. When rain intensity decreases and the soils drain, water of the current rain composition may not infiltrate very rapidly and, thus, use of cumulative-rain approach is probably more realistic. By the start of the second rain pulse at 21 h, much of the early, isotopically depleted rain water may have already drained from the soils and use of sequential rain values may again be more appropriate.

Modeling of catchment response:

An instantaneous unit hydrograph (IUH) model (Jakeman et al., 1990) has been used to compare the hydrologic responses of the 490 m² Hydrohill #2 artificial catchment and the adjacent Nandadish natural catchment of 7800 m² for several consecutive storms beginning July 5, 1989 (Kendall et al., in preparation). Detailed descriptions of how the models were developed and applied are found there; in brief: The rainfall and discharge hydrographs commencing July 5 00:00 were interpolated at 0.1 h intervals to provide smoother curves. The first five hours of the storm (0 to 9 h) were not analyzed because the catchment was still wetting-up during this period;

rainfall after this is treated as excess rainfall. The time step selected for model calculations was 0.1 h and analysis continued until 33 h when discharge had almost ceased. Analyses of the excess rainfall-discharge relationship were made separately for each discharge measurement $q^{(0)}$, $q^{(30)}$, $q^{(60)}$, and $q^{(100)}$ and for various additions of these (e.g., $q^{(0+30)} = q^{(0)} + q^{(30)}$), using an obvious notation to represent discharge collected at each trough.

The model identified single storages (i.e., one flow component) for surface runoff, the 30-cm trough, and the 60-cm trough; and two storages in parallel (i.e., two flow components) for $q^{(100)}$, $q^{(60+100)}$, $q^{(0+30+60+100)}$ and $q^{(30+60+100)}$. The single component identified in the surface runoff, 30-cm trough, and 60-cm trough models cannot be distinguished from the quicker of the two components identified in the 100-cm and in the total discharge combinations. For the total flow, the time constants for quick and slow-flow are 0.13 h and 5.8 h, and the fractions of flow attributed to quick and slow-flow are 0.77 and 0.23, respectively (Jakeman and Hornberger, 1993). Only two components, compared to the five separately identified components from measurements of four individual troughs, are necessary to approximate 89% of the variance of the total discharge at the outlet. In reality, the response at any level is composed of numerous components; however, data and model errors generally prevent identification of more than a small number of them (Jakeman and Hornberger, 1993).

Comparison of hydrograph separation methods:

As the blind men learned about the elephant: when trying to identify something in the dark, the more approaches made the better. Or in other words, when using black box models like hydrograph separation models for understanding catchment response to storms, use of multiple models is advisable. As noted earlier, hydrologic, chemical, and isotopic models can provide information about catchment responses, flowpaths/residence times, and water sources, respectively. All three types of hydrograph separation models are applied to the July 5 storm.

Figures 21-24 compare the hydrograph separations made using the IUH method, the IHS method using $\delta^{18}\text{O}$, and the CHS method using Cl and SiO_2 . The values used for end-member compositions are shown in Table 15. Because of the rapid response and the dominance of new water in this catchment, the $\delta^{18}\text{O}$ values of sequential composition of rain (with no lag) were used for the new-water composition. The rain showed very little variation in Cl or SiO_2 after the first couple samples, so volume-weighted average values were used for new-water compositions.

Separations were made for surface runoff, 30-cm subsurface flow, 100-cm subsurface flow, and total flow from the catchment. Data for the 60-cm trough were not modeled separately because the flow was insignificant (3% of total) compared to the other troughs (Figure 14) and because

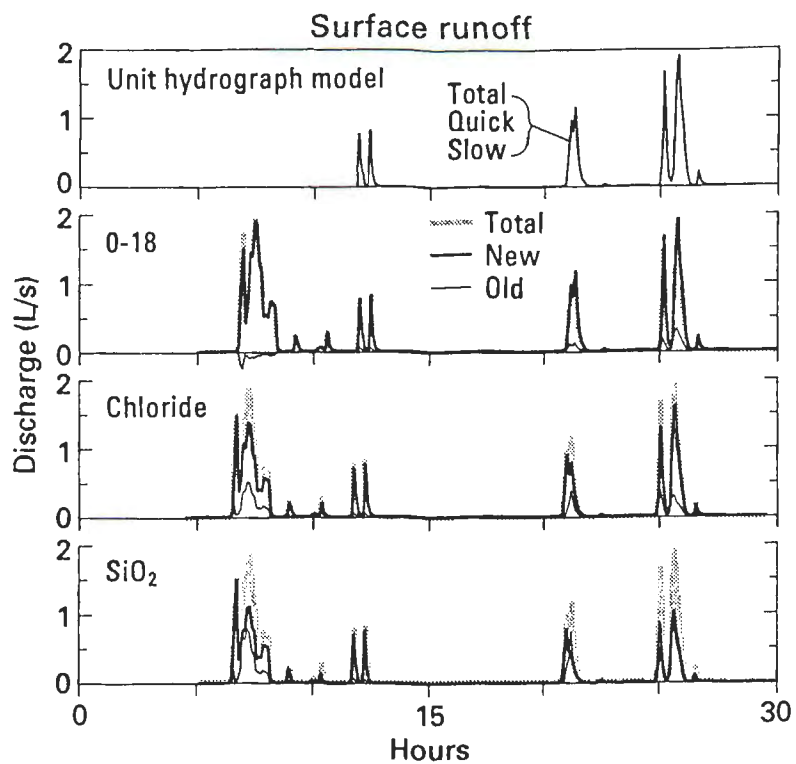


Figure 21. Hydrograph separations for surface runoff using four methods: the instantaneous unit hydrograph method, the isotope hydrograph method with $\delta^{18}\text{O}$, and the chemical hydrograph method with both chloride and silica.

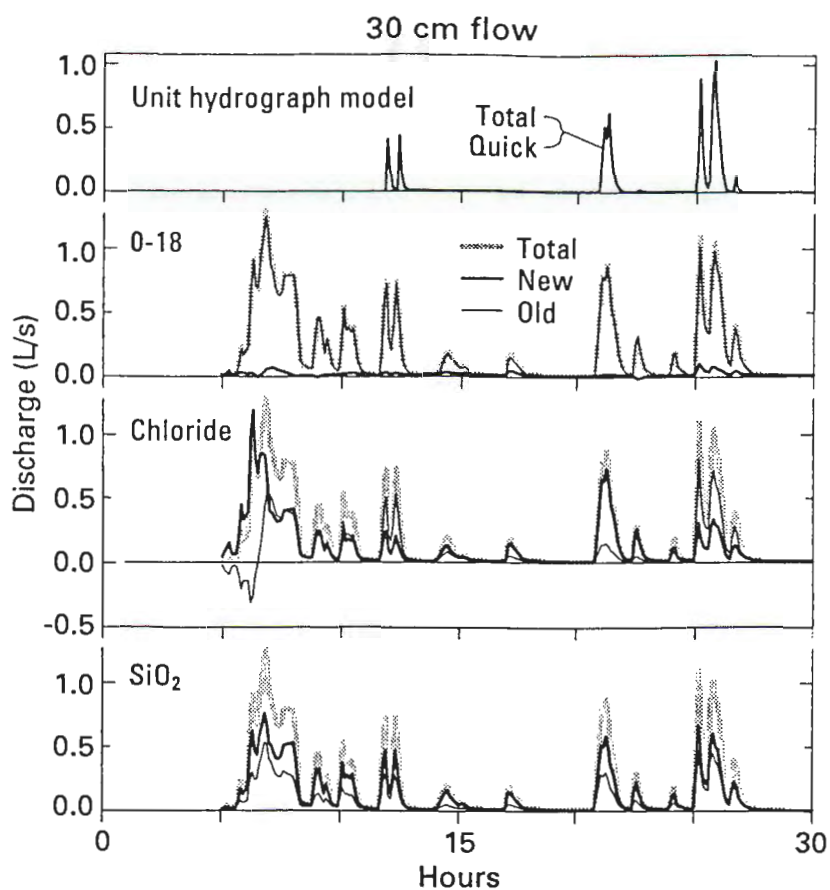


Figure 22. Hydrograph separations for subsurface flow at 0-30 cm using four methods: the instantaneous unit hydrograph method, the isotope hydrograph method with $\delta^{18}\text{O}$, and the chemical hydrograph method with both chloride and silica.

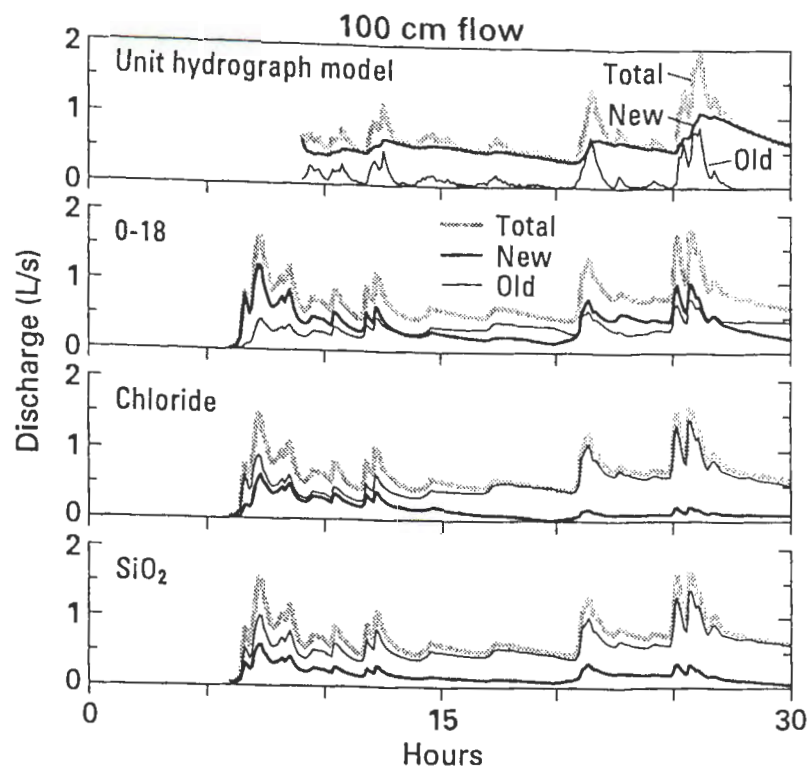


Figure 23. Hydrograph separation for subsurface flow at 60-100 cm using four methods: the instantaneous unit hydrograph method, the isotope hydrograph method with $\delta^{18}\text{O}$, and the chemical hydrograph method with both chloride and silica.

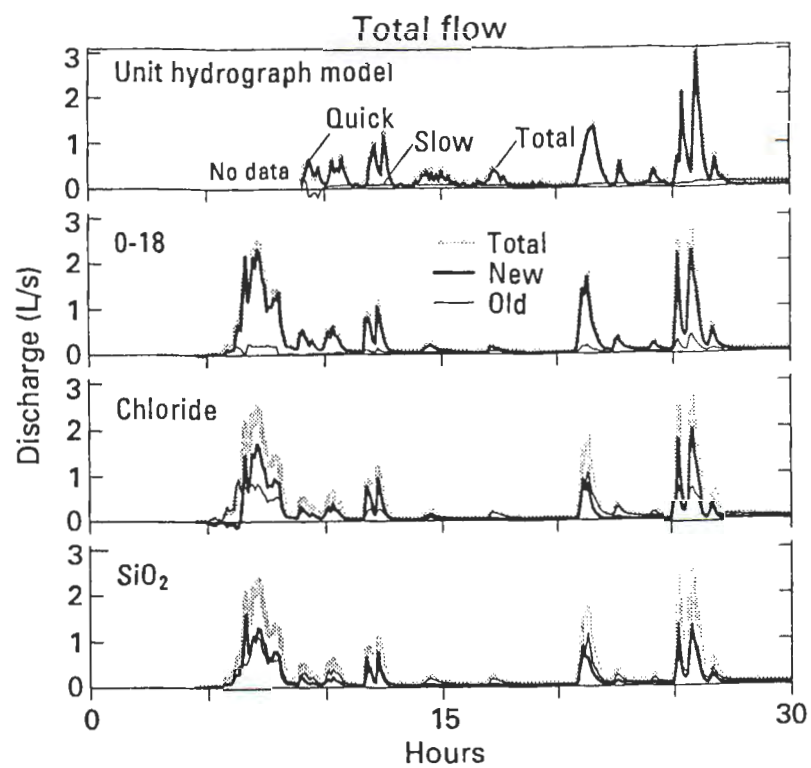


Figure 24. Hydrograph separation for total flow from Hydrohill using four methods: the instantaneous unit hydrograph method, the isotope hydrograph method with $\delta^{18}\text{O}$, and the chemical hydrograph method with both chloride and silica.

Table 15. End-Member Compositions Chosen for Hydrograph Separation Models.

End-member	$\delta^{18}\text{O}$ (‰)	Chloride ($\mu\text{eq/L}$)	Silica ($\mu\text{m/L}$)
new water	sequential rain samples	7	8
pre-storm water	-6	40	275

peak-timing problems prevented convergence of the IUH model. Each figure has four plots, all with the same discharge scale; however, the total discharge curve used for the IUH model is the "modeled" discharge curve whereas the total discharge curve used for each of the tracer separations is the actual interpolated discharge curve. The $\delta^{18}\text{O}$, Cl, and SiO_2 data were also interpolated at 0.1 h intervals to create smooth curves; actual measured values are shown in Figures 16 and 18. Tables 16 and 17 contains the calculated percentages of new water in the various troughs for the same three time periods used for calculating the water budgets in Table 13. Values greater than 100% indicate that the cumulative discharge was isotopically depleted relative to the rain.

It is no surprise that the IUH models for surface runoff (Figure 21) and 30-cm subsurface flow (Figure 22) indicate that the discharge from these zones is almost all quick-flow; the model fits have r^2 values of 0.73 and 0.88, respectively (Kendall et al., in prep). As expected, comparison with the $\delta^{18}\text{O}$ separations shows that the quick-flow here is almost entirely composed of new rain water (99%). The Cl and SiO_2 separations for these troughs suggest much more old water (20-65%) than seen with $\delta^{18}\text{O}$, and more old water in the 30-cm zone (55-65%) than in surface runoff (20-35%). The SiO_2 separations indicate about 10% more old water than is seen with Cl models. The percentages of new water calculated by each tracer is approximately constant at 12, 20, and 32 h (Table 16).

The IUH model for the 100-cm trough (Figure 23) fit the actual discharge data with an r^2 of 0.73, and indicates that most of the flow is slow-flow except at discharge peaks where the amount of quick-flow can

Table 16. Calculated Cumulative Amounts of New Water and Quick-flow for the Hydrograph Separation Models using $\delta^{18}\text{O}$, Silica, and Chloride*.

Trough	12 h					20 h					32 h				
	% New			% Quick		% New			% Quick		% New			% Quick	
	$\delta^{18}\text{O}$	SiO_2	Cl			$\delta^{18}\text{O}$	SiO_2	Cl			$\delta^{18}\text{O}$	Si	Cl		
surface runoff	112	70	79	100	100	106	72	80	100	100	98	65	80	100	100
30 cm	107	35	43	100	100	103	34	45	100	100	100	36	45	100	100
60 cm	95	80	97	--	--	84	67	80	--	--	77	68	71	--	--
100 cm	77	33	42	22	22	61	26	32	16	16	52	20	22	16	16
total flow	102	51	60	89	89	95	48	58	78	78	88	45	55	77	77

* The % quick-flow values were calculated using four different models; hence, the values are not additive.

Table 17. Calculated Cumulative Amounts of New Water, using $\delta^{18}\text{O}$ Values and Assuming the Initial 20 mm of Rain went into Storage.

Trough	% New water		
	12 h	20 h	32 h
surface runoff	103	99	95
30 cm	98	96	98
60 cm	88	78	75
100 cm	72	58	51
total flow	95	88	85

approach 50%. The $\delta^{18}\text{O}$ separation shows that the amounts of old and new waters at 32 h are approximately the same, with a general increase in the amount of old water during the storm, more new water during high discharge periods, and more old water while the catchment drains between rain pulses. Clearly the correlations between quick-flow and new water -- and slow-flow and old water -- seen in shallow samples are breaking down at depth. Although the $\delta^{18}\text{O}$ values suggest that as much as 50% of the water collected in the 100-cm trough as the soils drain is new rain water, by the response characteristics, almost all this water appears to be slow-flow. A reasonable conclusion from this is that waters from different sources are behaving hydrologically the same and hence have become well-mixed. The Cl and SiO_2 plots (Figure 23) again indicate much higher amounts of old water (70-80%) than calculated using $\delta^{18}\text{O}$ (50%). The chemical tracers suggest that there is much less new water in the flow during the second rain pulse (starting at 21 h) than in the first; the $\delta^{18}\text{O}$ separation also shows a little less new water in the second pulse. Unfortunately, the $\delta^{18}\text{O}$ of the rain during this period is in the range of -9 to -10‰, closer to the composition of the pre-storm water, making separations less precise. In addition, the saturated zone is now filled with a mixture of isotopically depleted rain and enriched pre-storm water, so that a different choice for "pre-storm" water composition might be appropriate for this second pulse of rain.

The total-flow hydrograph (Figure 24) is analogous to what might have been collected from a deeply incised stream within the catchment. The IUH model indicates that 77% of the flow is quick-flow and 23% is slow-flow. The $\delta^{18}\text{O}$ separation gives about 10% old water and the chemical

separations about 45-55% old water. These percentages are unusual; in most catchments studied to date, the quick-flow is predominantly derived from old water.

It is interesting that the two chemical separations are so similar to each other for the various troughs. In the absence of contradictory $\delta^{18}\text{O}$ data, the similarity of Cl and SiO_2 separations could have been used as confirmation that the solutes were behaving conservatively. On the contrary, the IUH model results and the $\delta^{18}\text{O}$ separation make it very clear that the new quick-flowing water is picking up sizable amounts of Cl and SiO_2 during rapid, very surficial contact with the soil before being collected as surface runoff and 30-cm interflow. The additional solutes could be derived from trapped pore waters with concentrations higher than estimated for old water, which is reasonable in surficial soils subject to evaporative concentration, or from desorption or dissolution (Kennedy, 1971; Kennedy et al., 1986).

It has been argued that some chemical tracers can provide an estimate of the amount of flow derived from overland or shallow subsurface stormflow because the limited contact time with the soil should permit little alteration of the chemical content of rain (Wels et al., 1991); this premise is not valid at Hydrohill. The Cl and SiO_2 concentrations in quick-flowing surface runoff and 30-cm interflow are 2 to 10 times the concentrations seen in rain. This very rapid uptake of solutes would tend to cause underestimation of the amounts of streamflow derived from shallow flowpaths and new water sources calculated using chemical tracers.

In natural catchment studies, the composition of baseflow is used as an indicator of pre-storm water and generally there is little information on the

chemical compositions of soil waters or groundwaters to confuse the issue. However a few recent studies (Ogunkoya and Jenkins, 1991; McDonnell et al., 1991) demonstrate that there may be considerable variability in old-water chemical or isotopic composition. So, why is baseflow so constant in composition? One possibility is that flowing from one soil environment to another changes the chemical composition of water (Christophersen and Neal, 1990); for example, passage through the hyporheic zone may homogenize or reset chemical compositions due to reaction with organics or minerals present in this zone. Another possibility is that heterogeneous conditions develop early during storms because of rapid infiltration of dilute waters through reactive soils, but these waters become relatively well-mixed as water levels rise through the soils and later drain back to baseflow conditions. The explanation could also be a simple matter of large-scale homogenization: each well may have its own site-specific variability which is damped to a relatively constant composition in aggregate.

The close match of the separations estimated using the two chemical tracers, in this study and in previous studies, may be largely fortuitous. In this catchment, there was no baseflow and other indicators of pre-storm water had to be used. Other choices could have been made for pre-storm water, resulting in different percentages of new and old water (McDonnell et al., 1991). For example, inspection of the groundwater data (Figure 19a) suggests that two types of pre-storm soil water might be present in the catchment: a more mobile water with a Cl composition of 30-40 $\mu\text{eq/L}$ and a less mobile water with a Cl concentration of 70-100 $\mu\text{eq/L}$. Using a value of 100 $\mu\text{eq/L}$ results in twice as much new water in total flow as using the

lower value for Cl. Slow-moving water has a SiO_2 concentration of about $400 \mu\text{eq/L}$; use of this value instead of the value of $275 \mu\text{eq/L}$ typical of fast-moving water produces about 50% more new water in total flow. If concentrations of $100 \mu\text{eq/L}$ and $400 \mu\text{eq/L}$ had been chosen for Cl and SiO_2 , respectively, the two chemical hydrograph separations would not have agreed and one or both solutes would have been considered to be behaving nonconservatively.

In theory, these same concentrations can also be used to estimate the percent of new water in groundwater. Although neither choice for SiO_2 is satisfactory for such calculations because the groundwater is generally more saline than either, only the value of $\text{Cl} = 100 \mu\text{eq/L}$ for the pre-storm concentrations of Cl appears to be satisfactory. If Cl and SiO_2 were behaving conservatively, there should be linear relations between the $\delta^{18}\text{O}$ and solute compositions of groundwater. Thus, the amounts of new and old water determined using $\delta^{18}\text{O}$ values can be used to calculate what the Cl and SiO_2 concentrations in groundwater SHOULD be if the solutes were conservative tracers of rain versus pre-storm water; these theoretical linear relations for groundwater are shown as dashed lines on Figure 19a. It is clear that there is no correlation of the actual and these theoretical values; the chemical compositions of pre-storm water in zones that deliver water to the troughs are apparently different from the compositions in zones that are tapped by the wells.

So what were the solute concentrations of pre-storm water in the pore-waters that were displaced by new rain to become groundwater? These concentrations can be estimated using the percentages of new water

calculated with $\delta^{18}\text{O}$ (using cumulative rain), to produce the data in Figure 19b. The wells that contained high and approximately constant amounts of old water throughout the storm (i.e., wells enriched in ^{18}O) had pre-storm water of a relatively constant chemical composition of $\text{Cl} = 100 \mu\text{eq/L}$ and $\text{SiO}_2 = 1000 \mu\text{m/L}$. The wells with $\delta^{18}\text{O}$ values that increased during the storm (i.e., had increasing amounts of pre-storm water), show a negative correlation between chemical concentration of pre-storm water and the amount of old water. The more old water there is in these wells, the lower the solute concentration in the original old water mixing with the rain water. The calculated pre-storm Cl and SiO_2 concentrations are highly correlated with an r^2 value of 0.89. The apparent higher salinities of the pre-storm waters in wells with higher concentrations of new water (i.e., $\delta^{18}\text{O} < -9\text{‰}$) could be explained by some initial flushing of salts from the walls of macropores by early infiltrating rain water. Alternatively, the pore-waters that are displaced early in the storm by rain water are more saline than the ones displaced later. In either case, the solutes are definitely not behaving conservatively.

In this catchment, we have independent knowledge of the amounts of water flowing as surface and subsurface flow and can compare these amounts with estimates calculated with the chemical hydrograph separation models (Table 16). For the total discharge up to 32 h, 38% of the discharge is surface runoff (i.e., chemically "new") and 62% is subsurface flow from the three subsurface troughs (i.e., chemically "old"). The amount of chemically "new" water in the total flow from the catchment, which should be equivalent to the amount of surface runoff (Wels et al., 1991), ranges from

36 to 45 % for calculations made with SiO_2 and Cl; these values are in excellent agreement with the discharge measurements.

However, closer inspection of the percentages of new water collected in the different troughs shows that there is a problem with this apparent agreement: 20 to 35 % of the surface runoff which should be all chemically "new" water (because of the shallow flowpath) is chemically "old", and about 35 % of the subsurface flow that should be all "old" water (because of the deeper flowpaths) is chemically "new." Therefore, the agreement between the actual amounts of discharge collected from surface runoff and subsurface flow, and the total amounts calculated by the chemical separations appears to be largely fortuitous; hence, these chemical tracers do not give accurate estimates of the amounts of water flowing along different pathways at Hydrohill. The differences in the amounts of "new" water calculated using $\delta^{18}\text{O}$ and solutes suggests that the chemically "old" water component of surface runoff is probably an artifact of the high salinity of surficial pore-water and/or dissolution of surficial salts. Comparison of the four separations for 100-cm flow (Figure 23) suggests that a part of the new-water component of subsurface flow is probably a result of large amounts of dilute rain water flowing in macropores and responding as quick-flow.

Isotope mass balances:

About $98 \pm 7\%$ of the new rain inputs to the catchment at 12 h, 20 h, and 34 h (Table 13) can be accounted for in increases in soil moisture contents or discharge; these water mass balance agreements are generally good enough that isotope mass balance calculations are feasible. For these calculations, the water mass balance is formulated in terms of the total amounts of water present in the system, instead of accounting for just the new water as was done for Table 13:

$$R + S_i = Q + S_f$$

where the inputs are: R = rain and S_i = initial amount of pre-storm soil-water stored in the catchment; and the outputs are: Q = total discharge and S_f = final amount of pore water stored in the catchment at the times the calculations were made. This formulation improves the water mass balances; the water outputs are 101%, 100%, and 97% of the water inputs for the three calculation times, respectively.

So where is the missing water at 32 h? Although the agreements of inputs and outputs are excellent, balanced water budgets are required for the subsequent isotope mass balance calculations. Discharges and rain amounts are easy to measure, so these values are probably accurate. Water contents, on the other hand, are more difficult to estimate, particularly when water contents are heterogeneously distributed; therefore, the errors probably are in

these numbers. The water budget equation above does not include a term for evaporative loss because the calculations for 0-5 cm water in Table 13 already included estimates, probably underestimates, of the amounts of water that had been present in the system prior to evaporation. To eliminate the -1 to +3 % discrepancies in the water budgets, -3.37, -0.61, and +10.34 mm of soil-water have been added to the respective S_f amounts.

The isotopic composition of water left in pore spaces in the catchment can be calculated from these data using an isotope mass balance equation:

$$R \delta_R + S_i \delta_{Si} = Q \delta_Q + S_f \delta_{Sf}$$

where δ_{Si} and δ_{Sf} are the initial and final $\delta^{18}\text{O}$ values of the stored soil pore-water. The $\delta^{18}\text{O}$ values of flow at 32 h were extrapolated to 34 h for these calculations because few samples were collected at 34 h. The $\delta^{18}\text{O}$ of pre-storm water was assumed to be $-6\text{‰} \pm 1\text{‰}$; use of values outside this range resulted in mass balance problems. The total (net) flow was calculated by summing up the 0.1-h interval interpolated discharges for each of the collectors. The net $\delta^{18}\text{O}$ of total flow was calculated by multiplying the 0.1-h interpolated $\delta^{18}\text{O}$ values by the discharges from the collectors and dividing by the net discharge. Cumulative $\delta^{18}\text{O}$ values were used instead of sequential values because the soil storage is expected to be much less "flashy" than subsurface flow to the troughs, which is mainly transported via macropores. Because much of the rain from the first rain pulse might have already drained from the soils before rain started again at 21 h, the calculations at 32 h were made using both the total cumulative $\delta^{18}\text{O}$ value at

32 h (-11.3‰) and the cumulative $\delta^{18}\text{O}$ value for only rain between 20 and 34 h (-10.2‰).

Several other assumptions were made: (1) the amount of water fractionated by evaporation was negligible compared to the amount of water stored in the soil (290 mm before the storm); (2) rain water was well-mixed in the catchment; and, (3) prior to the storm, the soils were homogeneous in isotopic composition (± 1 ‰), with mobile waters identical in $\delta^{18}\text{O}$ to immobile waters. The error bars noted in Table 18 indicate the possible spread of values calculated using the range of possible compositions discussed above. The uncertainties are greater for longer time periods because of the range of reasonable estimates for rain $\delta^{18}\text{O}$, and because water mass-balance problems become larger later in the storm when evaporative losses are more difficult to estimate.

There is some evidence of preferential storage of different time-fractions of the storm, in violation of the above assumptions. The 0.2‰ depletion of total flow relative to rain at 12 h (Table 18) is probably an example of small-scale preferential storage. Instead of rain being well-mixed in the catchment, a portion of the early enriched (-8.4‰) rain was probably preferentially retained in the shallow dry soils. This conclusion is supported by the depleted values of total surface runoff and 30-cm interflow relative to total rain. The depleted values also indicate that either there has been little or no mixing of these shallow waters with partially evaporated soil water enriched in ^{18}O , or that such evaporated waters were volumetrically insignificant. The slight depletion of surface runoff relative to 30-cm interflow at 12 h and 20 h may reflect the greater

Table 18. Isotope Mass Balance Calculations.*

Components	$\delta^{18}\text{O}$ (‰)		
	12 h	20 h	34 h*
cumulative rain (δ_R)	-11.6	-11.9	-10.8 \pm 0.6
surface runoff	-12.3	-12.3	-11.2
0-30 cm interflow	-12.0	-12.1	-11.4
30-60 cm interflow	-11.4	-11.0	-10.1
60-100 cm saturated flow	-10.4	-9.7	-8.8
total flow (δ_Q)	-11.8	-11.6	-10.7
soil water (δ_{sf})	-6.6 \pm 0.9	-6.8 \pm 0.9	-6.8 \pm 0.9
Percentages of water in catchment storages			
% of new rain stored in catchment	53.8 \pm 0.1	57 \pm 2	52 \pm 10
% of original pre-storm water stored in catchment	100 \pm 1	99 \pm 1	97 \pm 3

* Isotopic compositions at 32 h used in the calculations because none available at 34 h. Two estimates of cumulative rain $\delta^{18}\text{O}$ used.

amounts of early isotopically-enriched rain water lost to filling surficial soil storages than lost to filling soil pores at 30 cm. Table 11 shows that pore spaces in soils at 0-1 cm were filled several hours earlier than the soils at 1-2 cm, which is also consistent with the isotopic depletion of surface runoff relative to shallow interflow. An alternate explanation, that the depletion is due to the addition of pre-storm waters more depleted than $-6\text{‰} \pm 1\text{‰}$ is unlikely because the shallow waters would be expected to be more evaporatively enriched than -6‰ and because the amounts of pre-storm water in these soils is volumetrically insignificant.

The question of preferential storage of different time-fractions of rain is very important because of the large amounts of rain going into storage: 45% of the total rain by 32 h has gone into storage. The amount going into storage varies during the storm, with 100% of the rain from 4 to 6.5 h -- a total of about 20 mm of rain -- going into storage before flow starts (Figure 13). This first 20 mm of rain has a volume-weighted $\delta^{18}\text{O}$ value of -10.6‰ ; if it goes into storage and is not displaced to form discharge by later rain, the $\delta^{18}\text{O}$ values of the "residual" or mobile cumulative rain at 12 h, 20 h, and 32 h are -12.1‰ , -12.4‰ , and -11.5‰ , respectively. These values are 0.2 to 0.5‰ depleted relative to the comparable total cumulative rain $\delta^{18}\text{O}$ values in Table 18. Hence, the result of storage of initial isotopically enriched rain water is that the calculated amounts of new water in Table 17 decrease by about 7% at 12 h, 7% at 20 h, and 3% at 32 h. Only one of these new values (Table 17) is greater than 100% (103% for surface runoff at 12 h), an improvement over the original values where five values were

over 100%. Hence, assuming that the first 20 mm of rain goes into storage improves these hydrograph separations.

Although $10 \pm 5\%$ of the total flow for the three calculation times is old water (Table 15), the displacement of pre-storm water by storage of about 55% of the new rain in the catchment has had a negligible effect on the amount of pre-storm water remaining in the system ($\approx 97\%$). This is because the amount of pre-storm water stored in the soil (290 mm) was 4 to 5 times greater than the total amount of water discharged from the catchment. The $\delta^{18}\text{O}$ of the soil water at the end of the storm is only about 1‰ depleted relative to the original pre-storm water.

So what is going on inside the black box?

The isotope separations indicate that $90 \pm 10\%$ of the total flow is new rain water and the hydrologic separations show that 77% of the flow is quick-flow (Figures 21-24); hence, almost all the quick-flow must be rain but not all the rain is quick-flow. The dominant flow mechanism in this small catchment changes over the event and spatially. Immediately after the onset of intense rain, rain water reached the troughs via both surface runoff and bypass flow through soil cracks in the 0-30 cm layer. Although the contact time with the soil was short (flow-peak lag times of tens of minutes), the rain flowing along the surface and shallow flowpaths picked up concentrations of solutes approaching the concentrations seen in deeper soil waters. At several localities, deeper macropores allowed rain to rapidly penetrate to the

aquiclude where groundwater mounds largely composed of rain water progressively developed (Figure 17) and moved upwards through the soil column; chemically (but not isotopically), these waters were "old" with higher concentrations of solutes than interflow or saturated flow samples. In other localities, infiltration of new rain at the surface resulted in the downward displacement of soil water and the development of groundwater mounds with pre-storm chemical and isotopic compositions. As water table levels rise, the percentages of old water in both groundwater and saturated flow samples gradually increased; during draining of the catchment, slower matrix flow appears to be the dominant flow mechanism.

Other workers have observed transitions from macropore flow to predominantly piston (matrix) flow (Van Stiphout et al., 1987; Buttle and Sami, 1990). The uneven development of the saturated zone and variability in groundwater and saturated flow compositions supports the view that water is not necessarily infiltrating in a well-defined manner but instead may take complex routes including upward transport and several transits through the various soil horizons (Christophersen and Neal, 1990).

The ratio of new/old water at Hydrohill is much higher than in most catchments discussed in Rodhe's (1987) comprehensive review. Like the other new-water dominated storms that have been studied in other catchments (Sklash and Farvolden, 1979; Bonell et al., 1990), this storm had a higher rain intensity than "normal". One might argue that the high ratio is a consequence of Hydrohill not being a "natural" catchment. However, a catchment like Hydrohill that behaves more like a hillslope with a shallow soil over an impenetrable layer than as an entire catchment, might be

expected to have a larger amount of new water than usual. At first glance, the lack of a saturated zone prior to the storm might be deemed the cause of the high ratio of new/old water; however, the ratio in total flow from the troughs after the second pulse of rain (after 21 h) is also high (Figure 24). Inspection of Figures 21-24 shows that the surface runoff and 30-cm flow continue to be virtually all new water, and the 100-cm flow continues to be dominated by new water, regardless of antecedent moisture conditions. Hence, at least part of the reason for the high ratio of new/old water in this catchment is the large percentage of flow derived from shallow flowpaths for this 12-cm storm; the low conductivity of the clayey matrix material inhibits infiltration and encourages runoff and bypass flow.

The rapid hydrologic response of water from collectors at all depths is unusual, suggesting that flow via high conductivity zones and/or macropores must be important processes at all levels. About 20% of the rain (13.6 mm) discharges from the catchment from the 0-30 cm trough during the first 12 h of July 5. Although this rather high value invokes questions about possible leakage along the walls of the troughs, a 20-cm lip between the troughs was installed and soils along the sides of the troughs were especially packed to prevent such leakage; nevertheless, settling of soil under the lip could have caused local ponding. The similarity in the hydrologic responses and isotopic compositions of 30-cm flow and surface runoff (Figure 22) suggests that much of the water collected in the 30-cm trough may actually be derived from highly conductive shallow soils that become saturated easily (Table 11). An alternative explanation, that rain water penetrated cracks extending to 30 cm and then flowed laterally along some root-zone layer, is unlikely to have

yielded the isotopic compositions and the rapid response observed. The similarity of the $\delta^{18}\text{O}$ compositions of both troughs to rain indicates that almost all the water is new rain; however, since chemical tracers suggest almost twice as much "old" water at 30 cm as at the surface, the 30-cm flow has had considerably more contact with the soil.

For interflow to drain into a subsurface trough requires the formation of a local saturated zone extending upslope from the soil faces lining the troughs; although vertical flow through macropores can rapidly deliver large amounts of water, the slow rate of lateral flow through the silty clay soils is probably the limiting factor. The low flow at 60 cm, about 7% of the flow at 30 cm and 15% of the flow at 100 cm (Figure 14), suggests that interflow is not a major flow component below the surficial "saturated layer" that apparently discharges into the 30-cm trough; because of the lack of layering in this deeper interval, the 60-cm trough can be considered to be in the "shadow" of the 30-cm trough. Although any fractures that allow water to penetrate to 100 cm obviously give rain water access to the soils at 60 cm as well, the aquiclude-soil interface provides an ideal flowpath for lateral flow, promoting more flow into the 100-cm trough than would occur by interflow alone.

There appear to be two broad "types" of chemically different (but not truly distinctive) pre-storm water, a less-saline water characteristic of rapidly responding flowpaths that deliver water to the troughs and a more-saline water characteristic of slower matrix flow. Explanations for this dichotomy include: differences in the relative amounts of constant-composition pore waters mobilized by the different mechanisms transporting new water,

differences in the relative amounts of variable-composition pore waters of variable mobility incorporated by the different flow mechanisms, or differences in the amounts of new solute material that can be dissolved from soil surfaces (i.e., surface to pore-volume ratio) by waters traveling along different flowpaths. Unfortunately, we have no data that would allow me to distinguish among these intriguing possibilities. The more dilute waters may reflect locations where persistent macropores allow new rain water to pond at the aquiclude and rapidly create water table mounds that rise through the soil. The groundwaters thus formed in these mounds would incorporate little long-residence time water and would contribute sizable amounts of quick-flow to the troughs. On the other hand, less dilute waters would form in areas devoid of macropores where progressive displacement of old longer-residence time waters by infiltrating rain water slowly causes saturated zones to develop at the aquiclude. These more saline waters would be mainly respond as slow-flow. Bishop (1991) also finds that waters rapidly transported along "spate-specific flowpaths" at Svartberget acquire a chemical signature distinct from water moving more slowly by matrix flow.

In this conceptual model, pore waters in the unsaturated-zone and groundwaters almost always will have higher concentrations of solutes than the interflow and saturated flow that drain into the troughs and are fed primarily by zones with the shortest residence times and highest transmissivity. Between storms, immobile or less mobile waters exchange isotopically with the new mobile pore waters, and react chemically with the grain surfaces and thereby increase solute loads. By analogy, this model may explain why baseflow in natural catchments also is relatively uniform in

composition and typically more dilute than groundwaters--because baseflow is derived from the most mobile "old" water in the system.

Although this scenario appears valid when comparing the isotopic and chemical compositions of groundwater with the saturated flow samples in the troughs, it fails to explain the chemical compositions of pre-storm water in groundwater. The pre-storm water in groundwaters with more isotopically old water might be expected to be more saline than pre-storm water in groundwaters where there is little old water; however, the calculated chemical compositions of pre-storm water in groundwater show the opposite pattern (Figure 19b). Wells seeing high but decreasing proportions of rain water derive their pre-storm waters and/or salt loads from different reservoirs or flowpaths than wells that see very little new water. These calculations reinforce the point that there can be very large ranges in the chemical compositions of old pore waters in different zones or flowpaths within the catchment.

CONCLUSIONS

The Hydrohill experimental catchment provides a unique opportunity to investigate processes taking place within a catchment. Because of all the instrumentation, detailed information about spatial and temporal changes in amounts and chemical and isotopic composition of soil water, groundwater, and subsurface flow from several horizons is available. This permits

comparison of several types of hydrograph separation models with independent knowledge of the amounts and compositions of water present in different storages and flowing along different pathways, and calculation of water budgets.

The water budgets can account for $98 \pm 7\%$ of the new rain water in the catchment in terms of discharges and changes in storages, and can account for $99 \pm 2\%$ of the total "input" water. Achieving approximate closure on water budgets allows the unprecedented calculation of catchment isotope mass balances. Despite the large amount of rain that fell (12 cm) over a 24-hour period, infiltration and subsequent storage of 55% of the new water displaced only about 3-5% of the pre-storm water out of the catchment. Only 10% of the total flow is pre-storm water, mostly derived from saturated flow from deeper soils. The average composition of groundwater at the end of the storm is about 1‰ depleted in ^{18}O relative to the pre-storm water; however, it appears that the new and mixed pore-waters are very heterogeneously distributed. Thus, the remaining water in the unsaturated zone available to mix with the next storm water shows considerable ($\approx 4\%$ in groundwater) spatial and vertical variation in isotopic composition. If this much variability existed in the unsaturated zone prior to the July 5 storm, then the use of $-6\text{‰} \pm 1\text{‰}$ for the soil-water component may have resulted in erroneous calculated amounts of rain water in the subsurface samples. In addition, depending on the rate of isotopic exchange in pore waters, this heterogeneity could cause substantial difficulties for hydrograph separations of subsequent storms. Another problem is that there is evidence that isotopically enriched rain water from

the beginning of the storm is preferentially stored in shallow soils. This is a minor violation of one of the critical assumptions of isotope hydrograph separations and results in 7% change in the estimated amount of new water in runoff prior to 21 h.

Downslope transport of infiltration water via macropores, displacement of pre-storm unsaturated-zone water by matrix flow, and mixing of these two waters has caused widespread temporal and spatial variability in the isotopic and chemical compositions of interflow, saturated flow, groundwater, and post-storm unsaturated-zone water in this artificial catchment. The variability of rain and unsaturated-zone samples can pose substantial difficulties for the use of stable isotopes for tracing sources and flowpaths of water contributing to stormflow. In specific, if hillslope waters contribute much water to streams, then the conventional isotope hydrograph separation technique will need to be modified to include source components with isotopic and chemical compositions that may be temporally and spatially variable, and transit times neither constant nor instantaneous, and whose flowpaths may shift from predominantly macropore flow to matrix flow during the storm depending on rain intensity and amount of water stored in the soil zone.

Despite considerable spatial heterogeneity in the subsurface wetting up of the experimental catchment, uneven development of the saturated zone, variability in the sources of water as indicated fairly unambiguously by the $\delta^{18}\text{O}$ values, and transitions between macropore and matrix flow, the discharge response is quite linear for all four troughs. Such linearity is surprising on so small a scale--the catchment is only 490 m² in area. Only

two components can be detected among the five different responses to the storm at Hydrohill; i.e., the quick-flow component can be treated as an amalgamation of all the quick parts. The individual discharge responses at different depths become identifiable as only two single quick and slow components when discharge data are aggregated in space at the "stream" outlet.

It is remarkable how well the IUH model components matched the division of old versus new made with the $\delta^{18}\text{O}$; interestingly, the quick-flow is almost all new water, unlike at most catchments where isotope separations generally show that most stream water is derived from old quick-flow. The dominance of new water at Hydrohill is undoubtedly partly due to the lack of a saturated zone in the catchment prior to the storm event; waters in the unsaturated soil or capillary fringe require more time to mobilize than waters in the saturated zone. Saturated flow is predominantly composed of slow-flowing pre-storm water but includes some new water that has mixed with the older water. The magnitude of the storm studied is certainly a contributing factor to the new-water dominance. Another explanation for the much larger amounts of new quick-flow seen in this catchment than in others studied is that the Hydrohill soils are more clayey, less porous, and less permeable than in the others, resulting in less infiltration and more runoff of new water.

Although the relative amounts of surface runoff and subsurface flow contributing to total discharge from the catchment calculated using chemical tracers closely matches the actual measured amounts of surface runoff and subsurface flow, the agreement appears to be coincidental. Even surface

runoff and macropore flow from shallow soil responding as quick-flow and composed almost entirely of rain water are able to pick up loads of solutes similar to concentrations seen in subsurface flow. Therefore, chemical tracers are poor indicators of both water source and specific flowpaths in this catchment, yielding only qualitative information about contact time with the soil.

There appear to be two broad types of chemically old waters in the catchment--one type of water is developed by displacement of old water by new water traveling slowly downwards through the soil as matrix flow; and one type of water is derived from rapid transport of largely rain water to the aquiclude via macropores, causing mounds of groundwater that move upwards through the soil incorporating short-residence-time pore waters. The first group looks isotopically and chemically "old" and would be classified as slow-flow, whereas the second group contains more rain water and lower concentrations of salts, and contains both quick-flowing and slow-flowing components. Waters from this second group appear to be the main source of saturated flow to the troughs. Because these waters are the result of differences in local conductivity, the site-specific chemical and isotopic characteristics thus produced may persist over long time periods. The isotopic signatures of individual rain storms may be preserved in some places and rapidly blurred in others. It is clear that more information about isotopic exchange rates in pore waters is required to assess the impact of this variability on hydrograph separations.

Chapter 3

TRACING SOURCES OF CARBONATE ALKALINITY IN SMALL STREAMS USING STABLE CARBON ISOTOPES

INTRODUCTION

In recent years, the decline in alkalinity in many northeastern streams as a result of acid deposition has been a subject of much concern (Likens et al., 1979). Bicarbonate is the main component of alkalinity, and the bicarbonate/carbonic acid pair are the main buffering agents in surface waters. The concentration of bicarbonate in rivers is a measure of the "reactivity" of the watersheds and reflects the neutralization of carbonic and other acids by silicate and carbonate minerals encountered by the acidic waters during their residence in the watershed (Garrels and MacKenzie, 1971). Understanding the biogeochemical reactions controlling alkalinity in watersheds is a necessary precursor to predicting the effects of acid rain on these systems. This paper discusses the use of the stable-carbon isotopic composition ($\delta^{13}\text{C}$) of dissolved inorganic carbon (DIC) in stream water as a tracer of the sources of alkalinity in two sets of small watersheds underlain by different lithologies.

Stable-carbon isotope ratios have become a popular tool in ground-water geochemistry studies because they provide an additional constraint on geochemical mass-balance models (Wigley et al., 1978). Carbon isotopes often have been applied to help determine sources and sinks of carbon in groundwater (Pearson and Friedman, 1970; Deines et al., 1974; Reardon et al., 1979) and in surface-water bodies such as estuaries (Spiker and Schemel, 1979), lakes (Rau, 1978), and the ocean, especially for food-web studies and for determining terrestrial versus marine inputs of particulate matter (Fry et al., 1977). A few studies of calcite-precipitating springs and the streams they feed (Usdowski et al., 1979; Dandurand et al., 1982) have used $\delta^{13}\text{C}$ to examine the effects of aquatic flora and other processes on isotope equilibrium. Both ^{13}C and ^{14}C have been used to investigate cycling of dissolved organic carbon (DOC) (Schiff et al., 1990) and DIC in carbonate-free forested catchments (Aravena et al., 1992). The preliminary results of a small subset of these data (one year's worth of monthly samples for two Catoctin streams) have been reported in Mills and Kendall (1987) and Mills (1988); a brief summary of part of this study has been reported in Kendall et al. (1992c).

There have been several studies of the $\delta^{13}\text{C}$ of DIC in large rivers. Mook (1968; 1970) found that the DIC in several large rivers in the Netherlands showed a 2 to 5‰ seasonal variation in $\delta^{13}\text{C}$, with the most enriched values occurring in the summer, probably due to exchange with atmospheric CO_2 during the longer residence times of water in rivers in the summer. In the winter, when increased precipitation induces more

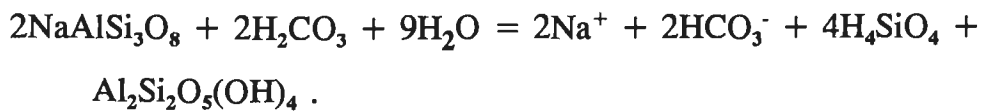
groundwater into the rivers and when river residence times are shorter, the $\delta^{13}\text{C}$ of the riverine DIC is close to that of native groundwater. Hitchon and Krouse (1972) measured the $\delta^{13}\text{C}$ of 101 surface-water samples collected from the $3 \times 10^6 \text{ km}^2$ Mackenzie drainage system in Canada and concluded that subsequent exchange of DIC with biogenic CO_2 produced in the rivers effectively masks the original $\delta^{13}\text{C}$ compositions of the DIC derived from the dissolution of bedrock carbonate by carbonic acid.

The primary types of reactions that produce carbonate alkalinity are:

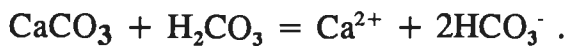
- 1) Weathering of carbonate minerals by acidic rain or other strong acids:



- 2) Weathering of silicate minerals by carbonic acid:



- 3) Weathering of carbonate minerals by carbonic acid:



The only two carbon sources in these reactions are calcite and carbonic acid produced by the dissolution of soil CO_2 by infiltrating rain water. The first and second reactions produce bicarbonate identical in $\delta^{13}\text{C}$ to the composition of either the reacting calcite or carbonic acid, and the third reaction produces bicarbonate with a composition exactly intermediate between the compositions of the carbonate and the carbonic acid. If the $\delta^{13}\text{C}$

values of the reacting carbon-bearing species are known and the $\delta^{13}\text{C}$ of the stream DIC determined, in theory we can calculate the relative contributions of these reactions to the production of carbonate alkalinity, assuming there are no other sources or sinks for carbon--that is, that we have closed-system conditions. Therefore, I propose that the $\delta^{13}\text{C}$ of stream DIC primarily reflects the mass-weighted sum of the carbon-isotopic compositions of these two sources of carbon, and that seasonal and spatial variations in stream $\delta^{13}\text{C}$ are caused by seasonal and spatial changes in the relative importance of these three biogeochemical reactions producing bicarbonate in the watershed.

Four small adjacent watersheds (Figure 25) were selected to evaluate the validity of these assumptions and the merits of this hypothesis. These watersheds consist of two pairs of watersheds, each pair underlain by different bedrock, selected to generate information on the mechanisms producing seasonal changes in water chemistry and on the causes of the differences in water chemistry between sets of headwater-streams underlain by the same and different bedrock (Katz, 1989; Bricker and Rice, 1989)

In a 2-year study of the relation between precipitation and stream-water chemistry in two of these watersheds (Hunting Creek and Hauver Branch), Katz et al. (1985) found that the observed seasonal changes in stream-water chemistry could be accounted for by the weathering of albite, actinolite, chlorite, and calcite by carbonic acid. Their reconstruction of the chemical composition of Hauver Branch stream water for 1982 showed that about 20% of the bicarbonate was derived from calcite and 80% from carbonic acid. In contrast, the isotope data presented here indicate that

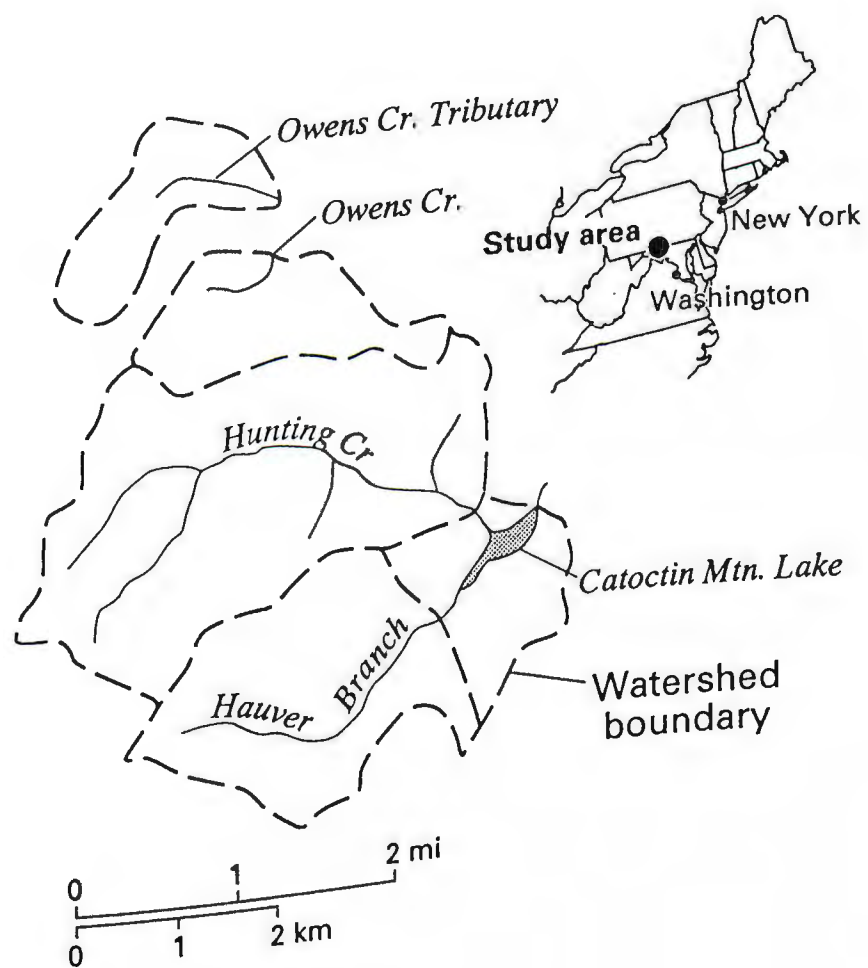


Figure 25. Locations of the study watersheds.

most of the alkalinity at Hauver Branch and the other three streams is derived from calcite instead of carbonic acid.

DESCRIPTION OF THE STUDY AREA

The Catoctin Mountain study area is located in the Blue Ridge physiographic province in central Maryland (Figure 25). The Hunting Creek and Hauver Branch paired watersheds are within Cunningham Falls State Park, with areas of 10.4 km² and 5.5 km², respectively. The Owens Creek and Owens Creek Tributary watersheds are inside Catoctin Mountain National Park, with areas of 2.62 and 2.57 km², respectively. Maximum relief is 280 m. The mean annual precipitation is 112 cm \pm 18 cm, and the mean annual temperature is 12 °C for the period 1931-80 (NOAA, 1981). Hunting Creek and Hauver Branch have been continuously monitored for water chemistry and quantity by the Acid Rain Program of the U. S. Geological Survey since 1982.

Streams in the Catoctin area are developed on meta-volcanic rocks of the Precambrian Catoctin Formation, with Hunting Creek and Hauver Branch underlain by greenstone and Owens Creek and Owens Creek Tributary underlain by interbedded greenstone and meta-rhyolite. A well-developed joint and fracture system serves as the principal pathway for the movement of water through the rocks (Katz et al., 1985). The major minerals in the greenstone bedrock are chlorite, epidote, albite, and actinolite, with minor amounts of calcite and quartz (Reed, 1964). The calcite is secondary and is

found primarily in vesicle fillings and lining fractures, comprising less than 1% of the exposed rock. This calcite is the only carbonate mineral known in the Catoctin Formation (Reed, 1964) and, thus, is the only geologic (inorganic) source of carbon in the stream. The major minerals in the meta-rhyolite are albite, microcline and quartz, with veinlets containing sericite, epidote, actinolite, and chlorite (Stose and Stose, 1946).

The soils developed on the greenstone belong to the Highfield Series, a group of medium-textured, well-developed, and generally well-drained soils (Matthews, 1956). Both the soils and the saprolitic substratum range from 0 to 1.5 m in depth in the watersheds (Katz et al., 1985); soils are thicker over the greenstone than over the more-resistant meta-rhyolite (Katz, 1989). Bedrock exposure is common on steep slopes and in streamcuts. Drainage of the lowlands is poor, resulting in saturated conditions during major storms.

At the stream gages (Figure 25), where most of the samples were collected, the streams were 1 to 3 m wide and 0.1 to 1 m deep. The stream channels within 1 km above their respective gages are significantly different. Hunting Creek has a 20-m-high waterfall, Cunningham Falls, about 0.7 km above the gage. Between the falls and the gage, the streambed consists of a single, boulder-filled channel with steep rocky slopes on both sides. Owens Creek and its tributary are similar in appearance to Hunting Creek. Hauver Branch, in contrast, is a braided stream collecting seepages from all along the soil banks. These differences in stream character provide important constraints on the stream chemistry. Discharges are given in Appendix 12.

METHODS

Stream samples:

Water samples were collected weekly from June 1986 through December 1987 for isotopic analysis at the four gage stations. Samples also were collected along four longitudinal transects of Hunting Creek and Hauver Branch, in June and August 1986 and twice in August 1987.

Water samples were collected in 1-L bottles, poisoned with a tablet of HgCl_2 to prevent biological activity, and kept chilled and in the dark until delivered to the lab where the bottle was briefly opened, 20 ml of water rapidly removed, and 20 ml of a $\text{NH}_4\text{OH-SrCl}_2$ solution (Gleason et al., 1969) added to each bottle to precipitate all the DIC as SrCO_3 . Samples were shaken and then aged for 2 days before being pressure-filtered onto glass-fiber filters using nitrogen gas to minimize atmospheric contamination. Isotopic analysis was performed on the CO_2 gas evolved by reacting one or more aliquots of homogenized SrCO_3 sample with 100% H_3PO_4 under vacuum. The weights of the precipitated material plus the yields of CO_2 were used to calculate the concentration of DIC in micromoles of carbon per liter ($\mu\text{m/L}$) of water. More than half of the samples were prepared and analyzed in duplicate for $\delta^{13}\text{C}$, and the values averaged. The average difference between replicate preparations was 0.07‰; if any pair of values

differed by more than 0.2‰, the sample was analyzed a third time and the outlier value was omitted.

DIC in surface-water samples is usually precipitated in the field (Friedman, 1970); however, some investigators have used other procedures, including precipitation within a few days in the laboratory (Hitchon and Krouse, 1972) or laboratory acidification to evolve CO₂ directly (Spiker and Schemel, 1979). Samples commonly are filtered before precipitation to remove organic and/or carbonate particles. However, because of the paucity of carbonates in the watershed and the minimal amounts of organic material in the stream, the Catoctin samples were not filtered. Mook (1968) found that poisoned river samples were unaffected by several months of storage if kept chilled and in the dark, and that total degassing of the excess CO₂ of river samples only increased the $\delta^{13}\text{C}$ of the remaining DIC by about 0.5‰.

The sampling procedure used in this study was tested for precision and accuracy by comparing the isotopic compositions of several sets of samples collected at the same time, some of which contained unusually large amounts of visible organic material and were filtered and precipitated immediately after collection, and several that were not filtered and were left for 1 week prior to addition of SrCl₂. These two sets of samples showed a 0.35‰ range in isotopic compositions but no apparent correlation with time or amount of organic matter.

The accuracy and precision of the extraction and processing procedures were checked by preparing and analyzing multiple bottles of degassed deionized water treated with known amounts of reagent-grade

sodium bicarbonate of known ^{13}C content. In the range of 50 to 500 $\mu\text{m/L}$ DIC, recoveries of DIC were within $\pm 10\%$ of the known amounts. The $\delta^{13}\text{C}$ of samples with DIC contents as low as 50 $\mu\text{m/L}$ could be enriched by as much as 1 ‰ relative to the composition of larger samples due to various sample-handling problems. For samples with DIC contents greater than 100 $\mu\text{m/L}$, the reproducibility (1σ) was about $\pm 0.2\text{‰}$.

The yields of DIC as determined from SrCO_3 -precipitation technique should be higher than the alkalinity values because about 20% of the DIC is carbonic acid at the average pH of the streams (7.0-7.5). However, the DIC contents almost always were 100-150 $\mu\text{m/L}$ lower than the alkalinity measurements, with a range of 10 to 90% of the total alkalinity. Although significant contributions of organic anions from the soil would cause increases in the non-carbonate alkalinity (Litaor and Thurman, 1988), causing less of a discrepancy between the DIC yields and the alkalinity measurements, the alkalinity of these streams is believed to be almost entirely carbonate alkalinity with only a few ppm organic anions (personal communication, Margaret M. Kennedy, 1989). The most likely explanation for the discrepancy is that a lot of DIC was being lost somewhere in the procedures, raising concern that the samples might have been isotopically fractionated by this loss.

Because adding known amounts of bicarbonate to tap water or CO_2 -free water consistently resulted in accurate DIC yields, I suspect that some constituent in Catoctin stream water, probably organic, might have been inhibiting the precipitation of SrCO_3 in the collection bottles. Several chemicals have been found to inhibit the precipitation of calcite in natural

waters (Reynolds, 1978; Turner, 1982; Matty and Tomson, 1988); these may also affect the precipitation of SrCO_3 . Filtering stream samples through 0.45μ filters prior to precipitating the carbonate slightly improved DIC yields; however, some constituent that passed through the filters formed an almost-invisible thin film on the insides of the bottles that was found to trap large amounts of fine-grained SrCO_3 . The amount of SrCO_3 on the walls ranged from 5-95% of the total DIC precipitated. The average difference in $\delta^{13}\text{C}$ between SrCO_3 collected on filters and SrCO_3 on bottle walls was less than 0.5‰, with no correlation between $\delta^{13}\text{C}$ values and amount of SrCO_3 on the walls. Although much of the discrepancy between the stream alkalinity values and the measured DIC contents was due to trapping of SrCO_3 on the walls, the average total DIC yield determined by combining the filter and wall SrCO_3 yields was still about 80% of the alkalinity. Apparently either all the carbonate was not precipitating, or the grain size was so small that it passed through the filters, or a significant part of the measured alkalinity was not carbonate.

Incomplete precipitation probably could cause significant isotopic fractionation of the samples. Experiments conducted by adding known amounts of bicarbonate of known $\delta^{13}\text{C}$ values to stream-water samples allowed independent calculation of the actual $\delta^{13}\text{C}$ of the DIC; these experiments showed that the methods used for collecting and analyzing samples used in this study could cause samples to become enriched by up to 0.5‰ relative to the true $\delta^{13}\text{C}$ of the water. Other workers have observed problems with the SrCO_3 -precipitation method (Bishop, 1990). Direct acidification of preserved water samples to evolve CO_2 probably would have

improved the accuracy of the results (Graber and Aharon, 1991). As a result of all the many analytical problems associated with using the $\text{NH}_4\text{OH-SrCl}_2$ precipitation technique in water from the Catoctin streams, the combined analytical (1σ) error is believed to be about 0.5‰.

Gas samples:

Soil gas was collected from five sites in the Hauver Branch watershed and from three sites at the Hunting Creek watershed on 10 different occasions from July 1985 through November 1986. The soil-gas probes were hollow, 1.5-cm-diameter steel tubes that were sealed at the bottom and perforated at several spots within a few cm of the base. Samples were collected by pumping with a peristaltic pump. The CO_2 in the soil gas was purified cryogenically, the amount of CO_2 measured, and the gas analyzed for $\delta^{13}\text{C}$. About 20% of the gas samples were collected in duplicate. The CO_2 yields of duplicates generally agreed within 10% and were within 10% of the yields determined by gas chromatograph. The reproducibility (1σ) of duplicate samples analyzed for $\delta^{13}\text{C}$ was 0.3‰.

$\delta^{13}\text{C}$ analyses were made at the USGS in Reston, Virginia, using a modified Dupont double-collecting mass spectrometer (Coplen, 1973) with an analytical precision (1σ) of $\pm 0.03\text{‰}$ for replicate analyses of the same gas; details of the analytical procedures are given in Appendix 1). Carbon-isotopic compositions are reported in permil relative to VPDB (Hut, 1987) on a permil scale defined by $\text{NBS-19} = +1.95\text{‰}$ and

NBS-16 = -41.66‰. The $\delta^{13}\text{C}$ values of soil gas CO_2 have not been corrected for N_2O (Mook and Van der Hoek, 1983) and probably are depleted in ^{13}C by about 0.23‰ relative to their actual composition (Mook and Jongsma, 1987).

RESULTS

Carbon dioxide in soil gas:

Carbonic acid is produced in soil waters by solution of soil CO_2 at the higher pCO_2 values typically seen in soils. CO_2 samples were collected approximately monthly (Tables 19 and 20) to determine: (1) the isotopic composition of the carbonic acid responsible for alkalinity-producing weathering reactions in the watersheds, and (2) the effect of season, location, and depth on the $\delta^{13}\text{C}$ value of the gas. Samples of soil gas collected at the eight probes show seasonal variations in CO_2 content consistent with observations at other localities (Rightmire, 1978a, 1978b; Reardon et al., 1979). Seasonal variations are most pronounced in the shallower probes (less than 1 m), where the CO_2 content of the gas ranges from 0.2 to 2.8% compared to the atmospheric content of 0.03%. The average winter CO_2 contents for all depths sampled are about half those seen in the summer. Hauver Branch pCO_2 values are consistently higher than those at Hunting Creek, with averages of 1.8% ($10^{-1.7}$) compared to 0.8% ($10^{-2.1}$).

The soil-gas $\delta^{13}\text{C}$ values range in composition from -17 to -24‰, with averages of $-22.3 \pm 1.0\text{‰}$ for Hauver Branch (Table 19) and $-21.4 \pm 1.8\text{‰}$ for Hunting Creek (Table 20). Monthly averages show that the soil gas is 1 to 2‰ more enriched in ^{13}C in the late summer and fall than in the spring. This seasonal enrichment is more pronounced at Hunting Creek than at Hauver Branch. Figure 26 shows the correlation between CO_2 content and $\delta^{13}\text{C}$ values. Most of the scatter in CO_2 content is due to the deeper samples that have a relatively consistent isotopic composition at both watershed regardless of CO_2 content. The most ^{13}C depleted values are from the two probes within 3 m of the streams where soils contain abundant organic material.

Bedrock calcite:

Empty vesicles and fissures are exposed on most weathered outcrops of greenstone in the watershed; these presumably once contained calcite that has since dissolved in the low-pH rain. Fresh samples of calcite were only found in recently blasted outcrops below the dam at Catoctin Mountain Lake (Figure 25), about 1 km below the stream gages. The six samples of amygdaloidal calcite collected had $\delta^{13}\text{C}$ values ranging from -5.75 to -3.40‰, with an average of -4.70‰. $\delta^{18}\text{O}$ values of the same samples ranged from +10.35 to +11.90‰ relative to VSMOW (Hut, 1987).

Table 19. Soil Gas Samples from Hauver Branch Watershed.

Date*	<u>Site 1^A</u>		<u>Site 2^B</u>		<u>Site 3^C</u>		<u>Site 4^D</u>		<u>Site 5^E</u>		<u>Average Values</u>	
	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂
04/16/86	-23.35	0.8	--	--	--	--	--	--	-24.05	1.2	-23.70	1.0
05/07/86	-22.60	1.4	--	--	-18.95	0.8	-23.30	1.7	-23.30	2.1	-22.05	1.5
06/20/86	-22.45	2.6	-22.85	2.8	--	--	-23.30	2.7	-22.95	2.5	-22.90	2.7
07/03/85	-22.10	2.5	-21.80	1.3	--	--	--	--	-22.70	4.9	-22.20	2.9
07/13/86	-21.90	1.9	-22.25	1.9	-22.60	0.7	-22.55	2.9	-21.60	4.4	-22.20	2.4
08/12/86	-21.75	1.9	-21.70	1.4	-22.45	2.2	-21.95	2.6	-21.95	4.7	-21.95	2.6
09/16/86	-21.40	1.3	-20.85	0.7	-22.20	1.4	-21.55	2.0	-22.00	3.5	-21.60	1.8
10/21/86	-21.75	1.0	-22.50	0.6	-23.35	0.8	-21.30	1.8	-20.75	2.2	-21.95	1.3
11/13/86	-22.65	0.9	-22.55	1.1	-24.30	0.7	-20.75	1.6	-21.75	2.8	-22.40	1.4
12/06/85	-22.25	0.7	-22.55	0.2	--	--	-21.70	0.6	-22.80	3.8	-22.35	1.3
Averages	-22.20		-22.15		-22.30		-22.05		-22.40		-22.30	1.9

* Collection dates listed in order of Julian date

^A Depth is 0.58 m

^D Depth is 1.35 m

^B Depth is 0.61 m

^E Depth is 1.40 m

^C Depth is 0.69 m

Table 20. Soil Gas Samples from Hunting Creek Watershed.

Date*	Site 1 ^A		Site 2 ^B		Site 3 ^C		Average Values	
	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂	$\delta^{13}\text{C}$	%CO ₂
04/16/86	-21.90	0.7	-23.90	0.9	--	--	-22.90	0.8
05/07/86	--	--	-22.35	0.6	--	--	-22.35	0.6
06/20/86	-21.65	2.1	-23.80	1.2	--	--	-22.75	1.7
07/03/85	-19.25	0.7	--	--	-19.80	0.4	-19.55	0.6
07/13/86	-20.70	0.9	--	--	-22.05	1.9	-21.40	1.4
08/12/86	-20.95	0.6	-23.25	1.5	-19.00	0.3	-21.05	0.8
09/16/86	-20.80	0.4	-22.85	1.0	-19.15	0.4	-20.95	0.6
10/21/86	-20.20	0.3	-23.80	0.7	-17.30	0.2	-20.45	0.4
11/13/86	-21.55	0.5	--	--	-19.60	0.4	-20.60	0.5
12/06/85	-22.35	1.0	-23.00	0.4	-20.05	0.5	-21.80	0.7
Averages	-21.05		-23.30		-19.55		-21.40	0.8

* Collection dates listed in order of Julian date

^A Depth is 0.56 m

^B Depth is 0.67 m

^C Depth is 1.24 m

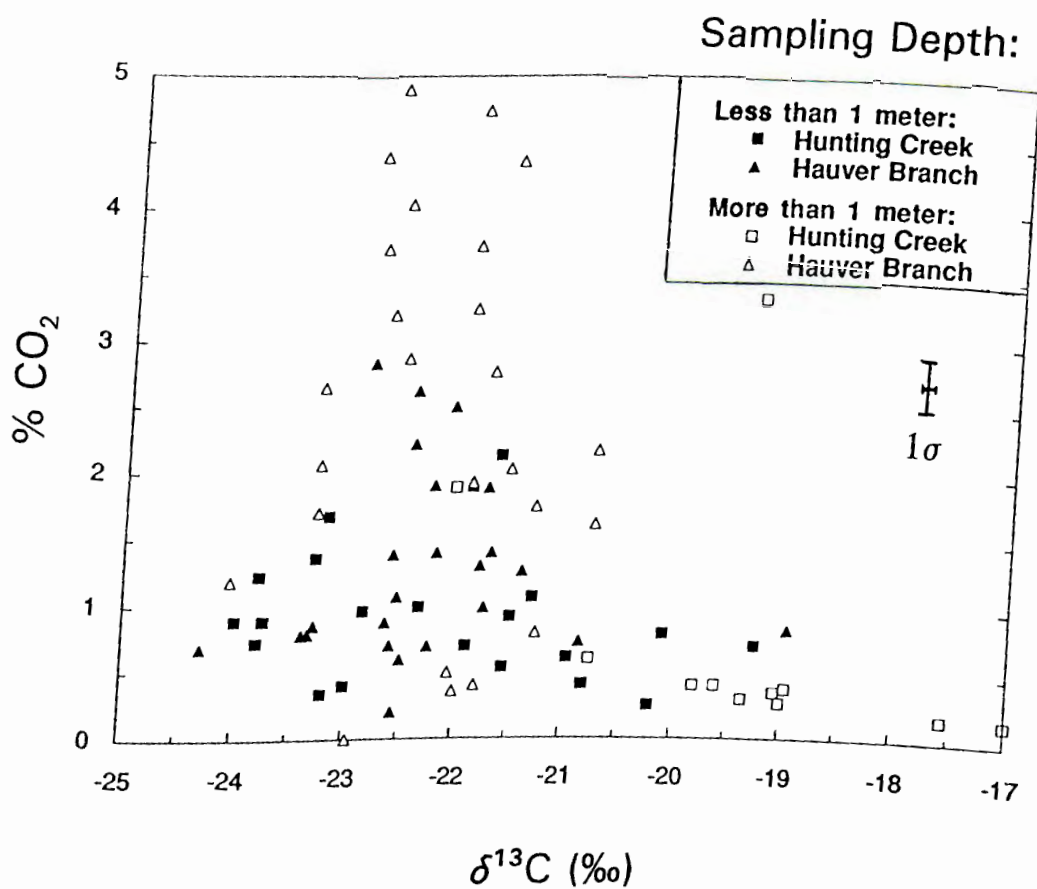


Figure 26. The relation between $\delta^{13}\text{C}$ and % CO₂ for soil gas samples collected from 8 probes at Hunting Creek and Hauver Branch watersheds.

Dissolved inorganic carbonate in stream water:

Spatial variability in water chemistry along stream transects: Figures 27a and 27b show the variation in $\delta^{13}\text{C}$ along five longitudinal transects of Hunting Creek and Hauver Branch, respectively. The sampling sites were 20 to 100 m apart, starting about 1 km upstream from the gages and ending below the gages where each stream discharges into the lake.

The first transect was collected in June 1986 at the end of the rainy season while the soils were still draining from a very large storm one week earlier. The three later transects, in August 1986 and two in August 1987, were made at successively lower streamflows. The total range in $\delta^{13}\text{C}$ of all the samples collected in the first four transects is 3‰ at Hunting Creek, compared with 11‰ at Hauver Branch. Although most profiles show considerable variation in $\delta^{13}\text{C}$, none of the profiles show any trend in $\delta^{13}\text{C}$ with distance downstream. Field notes indicate that most of the sites where the $\delta^{13}\text{C}$ values are especially low were just downstream of seeps from the soil banks. The last transect, in January 1989, was made to see if the stream response was different during the winter. Hunting Creek showed considerably more variability in $\delta^{13}\text{C}$ during this winter transect than during any of the summer ones.

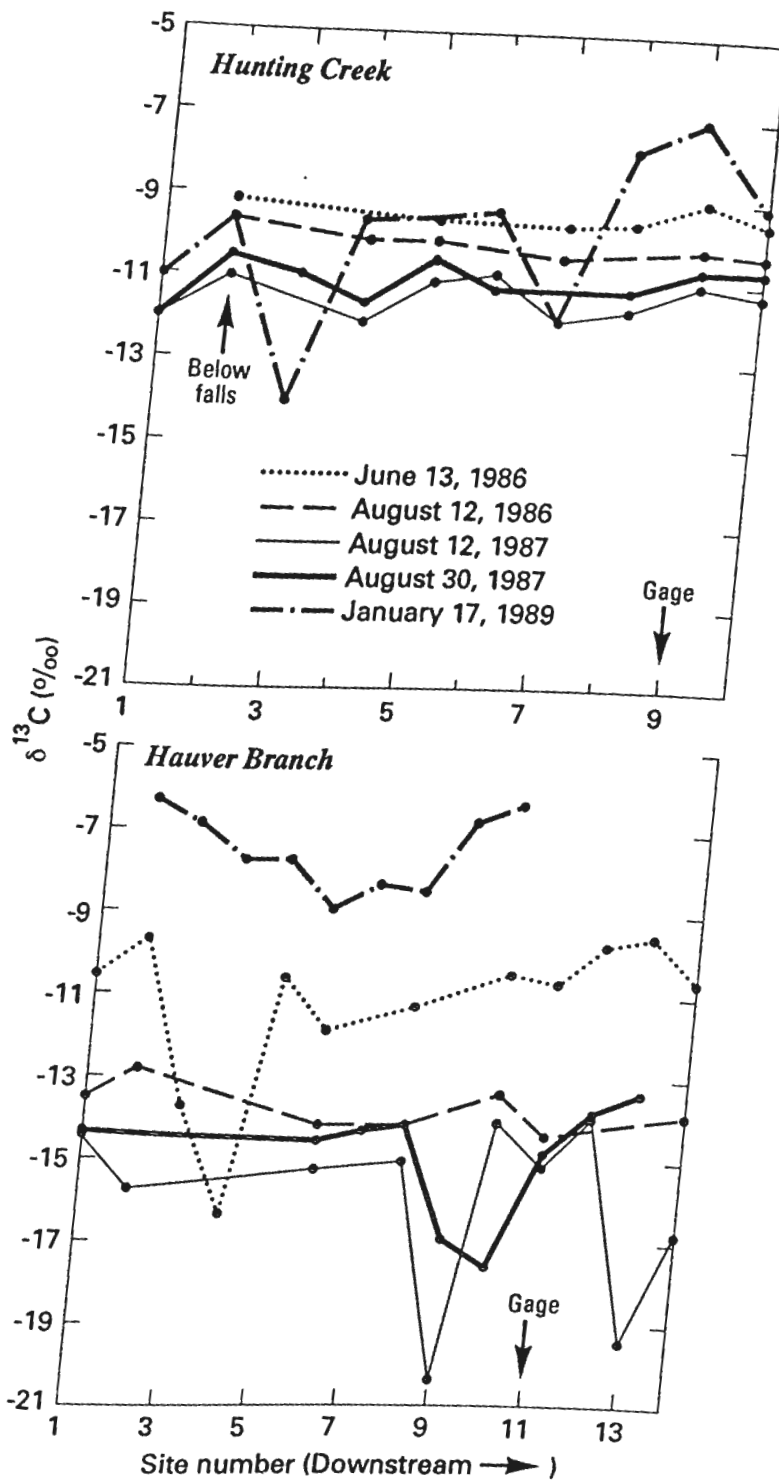


Figure 27. Variation in $\delta^{13}\text{C}$ value with distance along five transects of Hunting Creek and Hauver Branch; sample site numbers increase downstream and are 20-100 m apart. Lines connecting data points are to make comparisons among the profiles easier; $1\sigma = 0.5\text{‰}$ for $\delta^{13}\text{C}$.

Seasonal variation in stream chemistry: Both $\delta^{13}\text{C}$ and alkalinity clearly show pronounced seasonal patterns at all the watersheds (Figures 28 and 29; Appendix 13). Superimposed on the broad annual cycles are a number of smaller-scale oscillations in stream chemistry and one major fluctuation in September 1987. Alkalinity is highest during the growing season, approximately May through November, and lowest during the colder season, approximately December through April. $\delta^{13}\text{C}$ values are lower during the growing season than during the winter and are inversely related to alkalinity (Figure 30), with r^2 values of 0.49 to 0.77 depending on stream.

The $\delta^{13}\text{C}$ values of all streams seasonally fluctuate between the compositions of bedrock calcite ($-4.7 \pm 1.0\text{‰}$) and soil CO_2 ($-21.8 \pm 1.4\text{‰}$). The amplitude of the annual cycles is several permil greater at Hauver Branch, where DIC ranges in $\delta^{13}\text{C}$ from about -7 to -16‰ , than at Owens Creek where the range is about -9 to -14‰ . The two streams developed on greenstone, Hunting Creek and Hauver Branch, have winter $\delta^{13}\text{C}$ values that are significantly higher than those of the other two streams developed on interbedded greenstone and rhyolite. The average measured $\delta^{13}\text{C}$ values of DIC for water year October 1986 - September 1987 for the four streams show a 3‰ range (Table 21), with the streams underlain by greenstone enriched in ^{13}C relative to the streams underlain by meta-rhyolite.

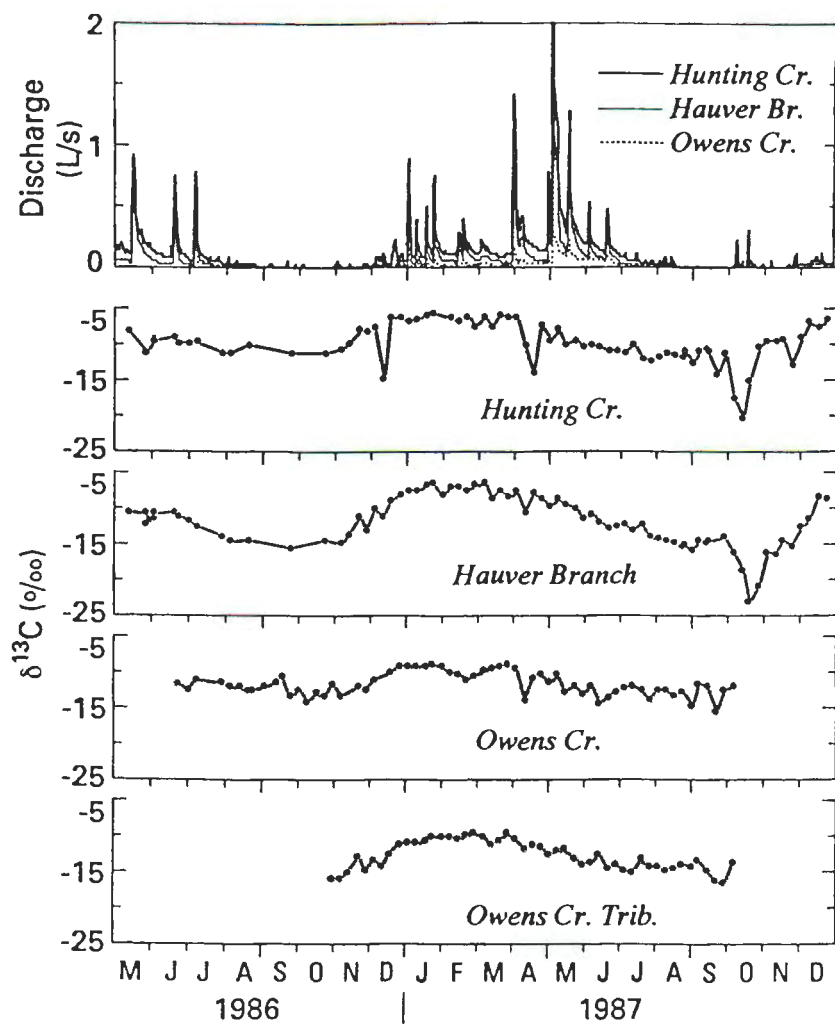


Figure 28. Variation in $\delta^{13}\text{C}$ and stream discharge of Hunting Creek, Hauver Branch, Owens Creek, and Owens Creek Tributary, 1986-87. The 1σ on $\delta^{13}\text{C}$ measurements was about 0.5‰.

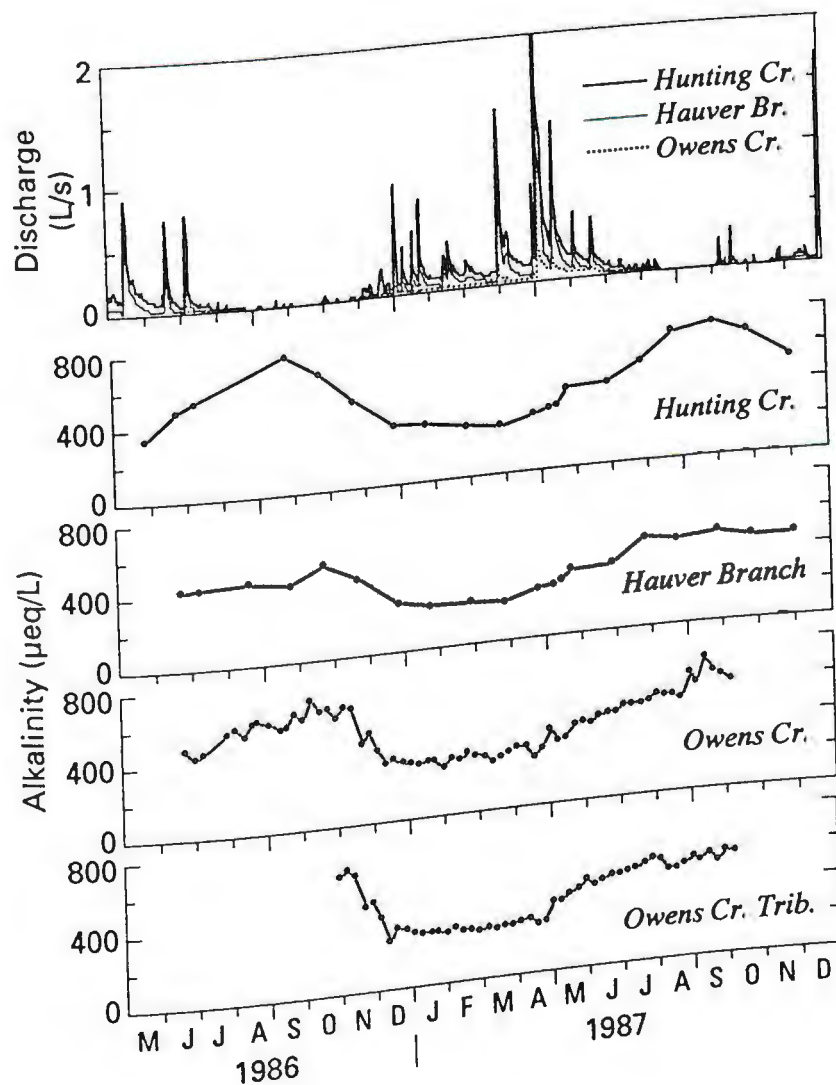


Figure 29. Variation in alkalinity and stream discharge of Hunting Creek, Hauver Branch, Owens Creek, and Owens Creek Tributary, 1986-87. The analytical uncertainties are smaller than the symbol size.

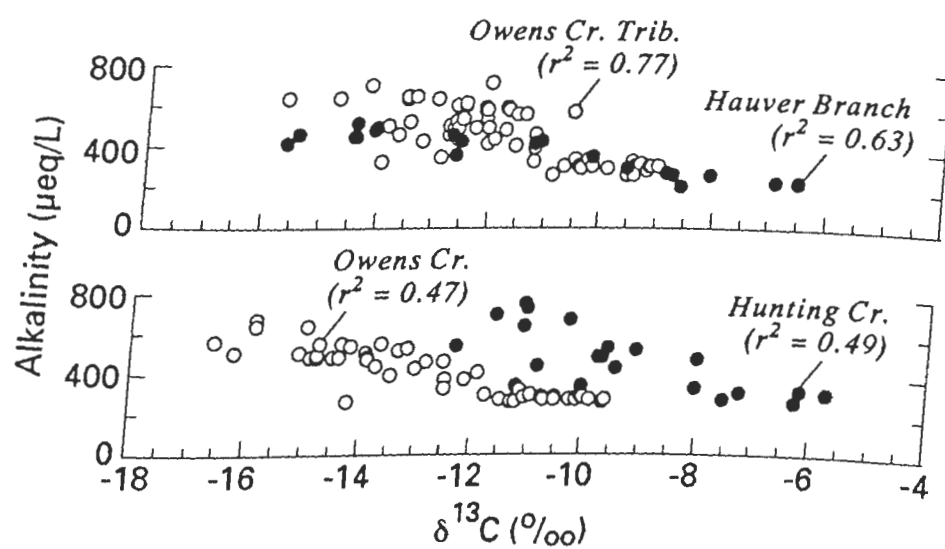


Figure 30. Correlation of $\delta^{13}\text{C}$ and alkalinity for the four streams.

Table 21. Differences among the Four Streams,
October 1986 - September 1987.

Watershed	Area (km ²)	Avg. measured $\delta^{13}\text{C}$	Avg. total* $\delta^{13}\text{C}$	% of total* DIC from calcite
Hunting Creek	10.4	-9.6	-8.95	75
Hauver Branch	5.5	-11.3	-9.55	72
Owens Creek	2.6	-11.6	-11.85	59
Owens Creek Tributary	2.6	-12.8	-12.60	54

* Discharge-weighted.

Small-scale oscillations in stream chemistry: Superimposed on the broad annual cycle of stream-water $\delta^{13}\text{C}$ values are numerous small and a few large oscillations in isotopic composition (Figure 28). These fluctuations in $\delta^{13}\text{C}$ between samples collected as close as one week apart range in magnitude from 0.5 to 9‰. A comparison of inflection points of small fluctuations at Hauver Branch and Hunting Creek shows that more than 75% of them occur in phase, indicating that the two streams may be responding in approximately the same way to some common stimulus. The correspondence of small fluctuations also indicates that most of the variation in $\delta^{13}\text{C}$ is real, not merely analytical noise. The inflection points of the two largest multi-week fluctuations, in April and September 1987, occur at slightly different times in the watersheds, suggesting that timing of the responses of the watersheds to very large scale events was slightly different.

Relation between stream chemistry and discharge: The Hunting Creek watershed is about twice the size of the Hauver Branch watershed and four times that of Owens Creek (Figure 25). The hydrographs of all streams are similar; during large storms, the peak daily flow at Hauver Branch and Owens Creek are 70% and 20%, respectively, of that at Hunting Creek (USGS, 1988). During the dry summer and fall, flow at Hauver Branch and Owens Creek are about 20% and 10%, respectively, of that at Hunting Creek. Discharge was not measured at Owens Creek Tributary, but it is

probably about the same as Owens Creek because both watersheds are the same size.

The timing of the seasonal changes in $\delta^{13}\text{C}$ (Figure 28) and the sawtooth shape of the $\delta^{13}\text{C}$ versus time curves (sharp increases in the fall, gentle decreases in the spring) closely coincides with the plant-growth cycle. During the winter, $\delta^{13}\text{C}$ values increase rapidly during the first several storms and then remain high for the rest of the winter and early spring despite periods of low rainfall. In mid-spring, $\delta^{13}\text{C}$ values decreased gradually towards the summer depleted values despite moderately high flow rates.

A few storms can be correlated with abrupt changes in the $\delta^{13}\text{C}$ of DIC. At Hunting Creek, two abrupt decreases in $\delta^{13}\text{C}$ in November 1986 and April 1987 occur within a day or so after major storms (Figure 28). Two large storms on September 8 and 18, 1987, apparently caused very depleted $\delta^{13}\text{C}$ values at both Hunting Creek and Hauver Branch in the weeks after the storm. The first storm flushed out DIC of normal summer $\delta^{13}\text{C}$ value; the second, larger storm coincides with the onset of decreasing $\delta^{13}\text{C}$ values. Over the next two weeks the stream DIC became progressively depleted in ^{13}C as the flow decreased; the stream was clogged with leaf debris and the water was greenish in some stagnant pools, suggesting that decay products could be affecting the $\delta^{13}\text{C}$ value. This isotopically depleted DIC was finally flushed out by a small storm in early October.

DISCUSSION

The primary purpose of this study was to attempt to use the $\delta^{13}\text{C}$ of stream DIC to determine the seasonal variations in the sources of alkalinity in the watersheds. A simple two-source conservative-mixing model for the production of DIC in the watersheds is shown in the two mass-balance equations below:

$$\text{DIC}_{\text{str}} = \text{DIC}_{\text{gas}} + \text{DIC}_{\text{cal}}$$
$$(\delta^{13}\text{C}_{\text{str}})(\text{DIC}_{\text{str}}) = (\delta^{13}\text{C}_{\text{gas}})(\text{DIC}_{\text{gas}}) + (\delta^{13}\text{C}_{\text{cal}})(\text{DIC}_{\text{cal}})$$

where the subscripts str, gas, and cal refer to stream, soil-gas CO_2 , and calcite, respectively. The equations are solved for the relative contributions of carbon from calcite dissolution (DIC_{cal}) and soil gas CO_2 (DIC_{gas}) to the total stream DIC (DIC_{str}). A number of assumptions have to be made to use such a simple model to describe the system.

Evaluation of assumptions:

1. Only two sources of DIC: As a first approximation, this is true; certainly the major sources of DIC are calcite and soil CO_2 . The average $\delta^{13}\text{C}$ compositions of these sources were determined to be $-4.7 \pm 1.0\text{‰}$ and $-21.8 \pm 1.4\text{‰}$, respectively. If these are the only sources and can be

assumed to mix conservatively, then the $\delta^{13}\text{C}$ of stream DIC must fall intermediate between these compositions. All $\delta^{13}\text{C}$ values (Figure 28) do fall within this range.

Another possible source of DIC is carbonic acid in precipitation. If rain water can be assumed to be in chemical and isotopic equilibrium with atmospheric CO_2 at the average rain pH of 4 (Katz et al., 1985), the calculated DIC content would be about $10\ \mu\text{m/L}$ at $25\ ^\circ\text{C}$ and $20\ \mu\text{m/L}$ at $10\ ^\circ\text{C}$ (Stumm and Morgan, 1981), and the carbonic acid would have a $\delta^{13}\text{C}$ of about -8‰ (Deines et al., 1974) for atmospheric CO_2 of -7‰ (Craig, 1953). Hydrograph separations using $\delta^{18}\text{O}$ indicate that only 10-30% of stream water during most Catoclin storms is new rain water; hence, most of the stream water has had a longer residence time in the catchment than the new rain. Additionally, because very little rain falls directly on the stream channel, as the rain flows over and through the soil during infiltration, the minor amount of DIC in rain water probably has ample opportunity to exchange carbon with soil CO_2 . Therefore, the contribution of DIC with a $\delta^{13}\text{C}$ of about -8‰ is probably much less than $10\text{-}20\ \mu\text{m/L}$. Any effect of this source of DIC would be more significant in the winter rainy season than during the summer because of lower average DIC values of the stream, lower rates of CO_2 production in the soil, and higher ratios of runoff to infiltration in the winter and spring.

Carbon-cycling reactions such as fermentation (Stevens and Rust, 1982), methane oxidation (Carothers and Kharaka, 1980), sulfate-reduction during the degradation of organic matter (Presley and Kaplan, 1968) may explain some of the small-scale variations in water chemistry; production of

small amounts of CO_2 in or below the stream by these processes cannot be ruled out as sources of DIC in these watersheds. If oxidation of methane in the soils were a major source of carbon, this would be reflected in the $\delta^{13}\text{C}$ of soil CO_2 ; however, the most depleted samples were -24.3‰ , suggesting that methane production in the soil must be minor. Oxidation of plant litter within the streambed probably is a significant source of DIC in the late summer and fall (Cleaves et al., 1970) and would produce CO_2 very similar to the composition of soil CO_2 . Because oxidation of organic matter in the soils plus respired CO_2 are the sources of soil CO_2 , for the model they need not, and cannot, be distinguished. In the model, contributions of DIC from organic oxidation are isotopically indistinguishable from contributions from the dissolution of silicates by carbonic acid.

Regional groundwater is another potential source of stream DIC, especially in the late summer when the streams are fed by baseflow (Katz et al., 1985). These watersheds are located in the recharge area for the regional ground-water system; therefore, any baseflow represents stored water that has infiltrated through watershed soil. The ultimate sources of DIC in the older, stored water are the same as for younger water: carbonic acid and calcite. Thus, contributions from groundwater do not need to be considered as a separate entity, assuming calcite has been dissolved under closed-system conditions (see below).

2. The natural ranges in $\delta^{13}\text{C}$ of the DIC sources are known and are small:

It is certainly possible, although unlikely, that there are spatial variations in

the $\delta^{13}\text{C}$ of calcite throughout the Catoctin area. It is unfortunate that so few samples of bedrock calcite could be found and those were all from the same exposed greenstone cliff. Compared to the variations in $\delta^{13}\text{C}$ seen in the streams, the observed uncertainty in the average $\delta^{13}\text{C}$ composition of calcite, $-4.7 \pm 1.0\text{‰}$, is relatively unimportant.

The isotopic compositions of soil gas CO_2 show several permil variation with depth and time, with most samples clustering around an average $\delta^{13}\text{C}$ value of $-21.8 \pm 1.4\text{‰}$. The minor variations in $\delta^{13}\text{C}$ along stream profiles suggest that local variations in soil-water chemistry may be appreciable. However, in the absence of more information and because there is a slight indication of a seasonal variation in $\delta^{13}\text{C}$, monthly averages were used for the soil- CO_2 end-member composition in modeling calculations. Given the observed areal, vertical, and temporal variations in soil CO_2 , the uncertainty in the $\delta^{13}\text{C}$ value of soil CO_2 is estimated to be $\pm 1\text{-}2\text{‰}$.

3. No sinks for carbon except DIC: Possible sinks include calcite precipitation, degassing of CO_2 within the stream, and biological uptake in the stream. Calcite precipitation can be ruled out by the stream chemistry. The calculated pCO_2 of streamwater is approximately in equilibrium with atmospheric CO_2 ; hence, degassing has probably occurred. Soil- CO_2 concentrations are as high as 5% (Table 19); the atmospheric concentration is about 0.03%. The pCO_2 in groundwater ranges from close to that in streamwater to values close to that measured in the soil zone. Thus, as water seeps into the stream bed, CO_2 is probably lost rapidly. This loss of

CO_2 can affect the $\delta^{13}\text{C}$ of the remaining DIC; the effect depends on whether the degassing is done under equilibrium or non-equilibrium conditions, which is probably a function of how rapidly the water seeps into the stream, the carbon speciation of the original and final solutions, and the amount of carbon lost. Laboratory experiments performed by Mook (1968) and repeated in our laboratory indicate that the residual DIC may become quickly enriched in ^{13}C by up to 1‰ upon total degassing, and less than 0.5‰ for exposure times less than one day. The 1 to 1.5‰ enrichments of water below the falls at Hunting Creek (Figure 27a) may be a result of degassing; because of the distance of the falls from the gage where most samples were collected, any such degassing probably has a minimal effect on the $\delta^{13}\text{C}$ values of water at the gage.

Because degassing has no effect on alkalinity, but can cause substantial enrichment in ^{13}C , the strong correlation of $\delta^{13}\text{C}$ and alkalinity observed in the streams (Figure 30) argues against degassing being the dominant process during any season. Additionally, if degassing was largely responsible for the enriched stream $\delta^{13}\text{C}$ values in the winter, one would expect to see strong correlations of discharge and $\delta^{13}\text{C}$, not the relatively constant $\delta^{13}\text{C}$ values observed regardless of discharge rate. Therefore, although there are insufficient data to truly assess the potential effect on the $\delta^{13}\text{C}$ of stream DIC, degassing appears to have a relatively minor effect in these streams.

Biological assimilation of DIC by algae produces organic material with a $\delta^{13}\text{C}$ value about 30‰ depleted relative to the composition of the carbon used (Rau, 1978), resulting in an increase in the $\delta^{13}\text{C}$ of the

remaining DIC. The streams at Catoctin are relatively fast-moving and contain only small quantities of aquatic plants. These are likely to be a significant factor only in the late summer and fall when stagnant pools are common (eg., September 1987), and may be responsible for some of the small-scale variation in $\delta^{13}\text{C}$.

4. Negligible isotopic exchange of DIC with atmospheric CO_2 : Isotopic exchange of dissolved carbon species with atmospheric CO_2 is inevitable. At equilibrium, HCO_3^- is enriched in ^{13}C relative to CO_2 by 8.5‰ at 20 °C (Mook et al., 1974). The $\delta^{13}\text{C}$ of atmospheric CO_2 is about -7‰. Therefore, at isotopic equilibrium the $\delta^{13}\text{C}$ of stream bicarbonate, the major carbonate species present at the stream pH values, would be about +1‰. Clearly, the Catoctin streams do not have this composition and hence the DIC is not in isotopic equilibrium with atmospheric CO_2 . Although partial exchange is possible, the high CO_2 pressures found year round in the soils of both watersheds, combined with the very depleted ^{13}C values of soil CO_2 , indicate insignificant exchange of soil CO_2 with atmospheric CO_2 . The estimated exposure time of stream water at Catoctin between seepage from the stream bed or banks to collection at the gage generally ranges from one to several hours, depending on discharge.

The stream transects originally were conducted to determine if there was a measurable isotope gradient downstream that could be attributed to atmospheric exchange. The effect of exchange would be to increase the $\delta^{13}\text{C}$ of the DIC. The transects (Figures 27a and 27b) show no evidence of any

systematic increase in $\delta^{13}\text{C}$ downstream even though the transects were made at a variety of flow rates during the dry season when the exposure time of stream was longest.

One could argue that the transects show no trend of increasing $\delta^{13}\text{C}$ values downstream because any enrichment in $\delta^{13}\text{C}$ produced by atmospheric exchange is masked by compensating additions of DIC depleted in ^{13}C from seepages along the channel. The Hauver Branch transects clearly demonstrate that the $\delta^{13}\text{C}$ of the stream can change by as much as 6‰ over distances of 20-100 m. Although seepages can have a significant local effect on stream chemistry, their regional impact apparently is damped by mixing with the much larger reservoir of water below and to the sides of the stream bed that is also moving down the hydrologic gradient. In contrast, the Hunting Creek transects show so little variation in $\delta^{13}\text{C}$ downstream that it is difficult to believe that fortuitous mixing of waters could camouflage any appreciable degree of atmospheric exchange.

Despite all these lines of evidence suggesting that atmospheric exchange is negligible, especially during the low-flow summer season when exposure times should be longest, partial exchange during the winter when DIC levels are lowest and the DIC derived from rain already may be in isotopic equilibrium with atmospheric CO_2 cannot be totally ruled-out. Certainly the enriched $\delta^{13}\text{C}$ values observed in the winter are within the expected $\delta^{13}\text{C}$ range for partial exchange with atmospheric CO_2 or mixing of partially-exchanged waters with waters derived from soil CO_2 . However, the high pCO_2 values and depleted $\delta^{13}\text{C}$ values observed in winter soils combined with stream DIC contents generally 10-30 times greater than rain water make

it probable that any new storm water flowing through the soils and into the streams has had ample time to exchange with soil CO_2 and little opportunity to exchange with the atmosphere. In support of this argument, in a study of dissolved CO_2 in two small watersheds in Britain, Neal (1988) found high values of excess CO_2 in the streams during periods of high flow and during the winter, indicating appreciable reaction with soil gases and lack of exchange with the atmosphere. Therefore, it appears reasonable to assume that degassing plus exchange with atmospheric CO_2 may cause, as a worst-case, about a 1‰ enrichment in $\delta^{13}\text{C}$.

5. Conservative mixing: If DIC in soil water and/or groundwater exchanges carbon with other carbon-bearing species, then the isotopic signatures could be blurred and hence conservative mixing of two distinctive end-member compositions formed via the three weathering reactions could not be assumed. The evolution of the isotopic compositions of carbon-bearing substances in simple systems where carbon is derived from only carbonate minerals plus soil CO_2 , is controlled by two limiting cases: open systems where carbonate reacts with water in contact with a gas phase with a constant $p\text{CO}_2$, and closed systems where the water is isolated from the CO_2 reservoir before carbonate dissolution (Deines et al., 1974). Hence, the conditions under which carbonate is dissolved are expected to fall between these two extremes. Under open conditions, the $\delta^{13}\text{C}$ of DIC is a function of the $\delta^{13}\text{C}$ of the CO_2 reservoir and pH; under closed conditions, the $\delta^{13}\text{C}$ is controlled by the amounts and $\delta^{13}\text{C}$ values of the carbon sources.

If the H_2CO_3 in soil water or shallow groundwater in areas where carbonic acid is the dominant carbon species is in isotopic equilibrium (i.e., an open system) with a soil CO_2 reservoir ranging in $\delta^{13}\text{C}$ from -17 to -24‰, the H_2CO_3 should have compositions ranging from -18 to -25‰. The $\delta^{13}\text{C}$ values of some 20 samples of springs and groundwater collected from various locations at Catoctin Mountain but outside the watersheds range from -16 to -26‰, similar to the compositions of soil CO_2 and similar to occasional compositions of stream water during the summer. Some of these wells may be contaminated by animal waste (Trombley and Zynjuk, 1985) which also could account for the depleted $\delta^{13}\text{C}$ values. Some of these groundwaters also have alkalinities three times as high as the maximum seen in the streams in summer when all the water comes from baseflow; clearly these waters are not major sources of baseflow.

A much more extensive sampling of shallow groundwater at Mill Run watershed in Virginia where no calcite is present in the soil zone also shows that the $\delta^{13}\text{C}$ of groundwater is approximately the same as soil CO_2 (Mills, 1988). Thus, it appears that the residence time of water in the soil zone and upper parts of ground-water reservoirs is sufficient for carbonic acid to reach approximate isotope equilibrium with the reservoir of soil CO_2 . Consequently, the $\delta^{13}\text{C}$ value chosen for the carbonic-acid end-member used in the 2-source model should probably be decreased by about 1‰ from the soil CO_2 value to reflect this exchange.

At normal ground-water pH values where bicarbonate is the major carbon species, open-system dissolution of calcite controlled by a reservoir

of soil CO₂ with a $\delta^{13}\text{C}$ value near -22‰ produces DIC with a $\delta^{13}\text{C}$ value of about -13‰. If calcite dissolution takes place under closed conditions, the DIC will have a $\delta^{13}\text{C}$ value intermediate between carbonic acid and calcite: the $\delta^{13}\text{C}$ value ranges from close to that of the initial carbonic acid if little calcite is dissolved to a maximum $\delta^{13}\text{C}$ value of about -14‰ if half of the DIC is derived from calcite. Thus, the isotopic compositions of closed systems reflect conservative mixing.

The really crucial questions at this point are: where does calcite dissolution take place and are the water residence times sufficient for significant isotope exchange with some CO₂ reservoir. Because Catoctin soils have pH values of 4.8-5.3 (Katz, 1989), there can be little or no calcite in the A or B soil horizons; thus, we can probably discount appreciable open-system dissolution in the soil zone. Calcite is present both as fracture fillings and in vesicles in the greenstone; it is apparently absent in meta-rhyolites (Katz, 1989). Empty vesicles are commonly seen in boulders in the stream channels; these presumably once contained calcite. Thus, it appears that calcite may be dissolved both in and below the streambed and as groundwater moves through fractures in the bedrock. Contributions from ground-water storage to stream discharge may be significant only in the dry summer (Katz et al., 1985); stream alkalinities are at their seasonal high during this period. The range of $\delta^{13}\text{C}$ values found in groundwaters at Catoctin Mountain are consistent with both open or closed-system dissolution of calcite. If chemical data were available for these samples, the conditions of formation of the waters could possibly be determined (Deines et al, 1974). Because baseflow is probably the oldest water in the system, reaching the

stream from the longest and slowest flowpaths, it is probably the source of water most likely to be isolated from the soil-CO₂ reservoir and hence probably evolved under relatively closed conditions.

Residence times for storm-related water in the watersheds probably are very short. Katz et al. (1985) noted that road salts applied during the winter arrived at the gage within days after a storm. The strong correlations of alkalinity and $\delta^{13}\text{C}$ fluctuations with stream discharge variations also indicate rapid movement of water through these small watersheds at all seasons. Therefore, even if significant amounts of calcite are being dissolved under semi-open conditions in bedrock joints, the residence times may not be long enough for appreciable isotope exchange. The flux of CO₂ depleted in ^{13}C out of the soil-zone also may explain the apparent lack of exchange between DIC and CO₂ in an open system; Heathcote (1985) concluded that such a continuous-flow system may appear open to changes in major-ion chemistry but closed isotopically by preventing back-diffusion of CO₂; hence, the carbonate-dissolution zone may be effectively isolated from the soil CO₂ reservoir.

From the above arguments, if calcite were dissolved under closed conditions in groundwater or in stream water, or under open conditions with long or short residence times, the $\delta^{13}\text{C}$ of DIC should be in the range -13 to -23‰ (if the CO₂ is derived from the soil). Without additional geochemical data, I cannot conclusively dismiss any of these possibilities; all I can do is argue plausibilities. The $\delta^{13}\text{C}$ of stream DIC falls within this range only during the summer low-flow season; during the winter, the average $\delta^{13}\text{C}$ is about -8‰. The strong inverse relations between alkalinity and $\delta^{13}\text{C}$

(Figure 30) suggest that the water chemistry is a product of mixing of two waters; if open-system dissolution of calcite were a major source of DIC, one would not expect to see this inverse relation between alkalinity and $\delta^{13}\text{C}$. It is noteworthy that open-system dissolution of calcite by a reservoir of soil- CO_2 would tend to decrease the $\delta^{13}\text{C}$ value of the resulting DIC, thus "camouflaging" the impact of the $\delta^{13}\text{C}$ of the dissolved calcite on the $\delta^{13}\text{C}$ of the total DIC. Only open-system dissolution of calcite in contact with atmospheric CO_2 will cause enriched $\delta^{13}\text{C}$ values.

The relations between $\delta^{13}\text{C}$ values and concentrations of weathering products such as alkalinity, Ca, and SiO_2 are similar in the four watersheds. The ratio Ca/SiO_2 shows no correlation with $\delta^{13}\text{C}$ but the ratio Ca/HCO_3 is positively correlated with $\delta^{13}\text{C}$ ($r^2 = 0.47$ for Owens Creek). The increase in Ca/HCO_3 ratios during the winter and the good positive correlation between these ratios and the $\delta^{13}\text{C}$ suggest that changes in $\delta^{13}\text{C}$ are controlled primarily by a shift from weak-acid (carbonic acid) weathering in the summer to strong-acid weathering in the winter (Figure 31). In addition, the invariance in Ca/SiO_2 ratios indicates that there is no seasonal change in the rate of silicate versus carbonate weathering, which might otherwise have affected the $\delta^{13}\text{C}$ of DIC.

Another line of evidence that supports the 2-component conservative-mixing model comes from $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of stream samples during storms (Kendall, 1990; Bullen and Kendall, 1991). During storms, both isotope tracers show large and correlated fluctuations in composition, ranging between one end-member characterized by the $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of calcite and another end-member with the $\delta^{13}\text{C}$ and

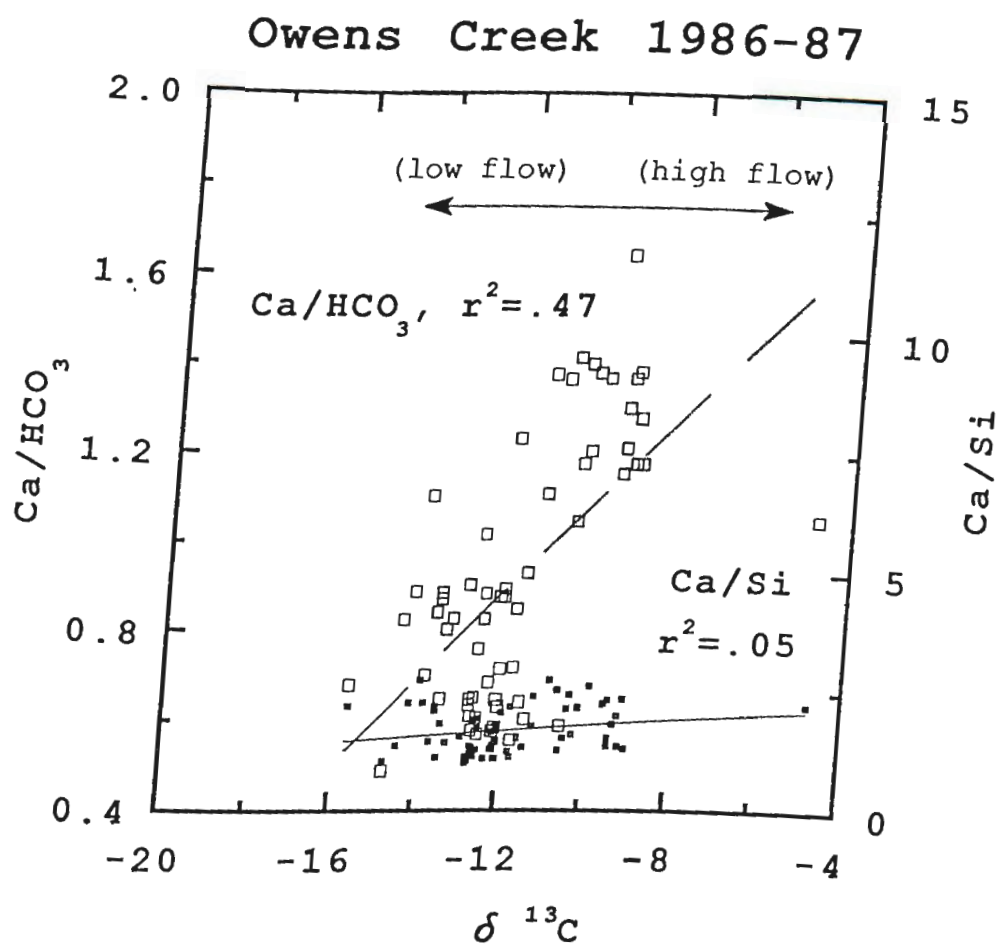


Figure 31. Correlations of stream chemistry and $\delta^{13}\text{C}$ at Owens Creek (modified from Kendall et al., 1992c). $\delta^{13}\text{C}$ values are $\pm 0.5\text{‰}$.

$^{87}\text{Sr}/^{86}\text{Sr}$ values of carbonic acid and weathered silicates, respectively. Because enriched $\delta^{13}\text{C}$ values correlate with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios typical of the calcite, the enriched $\delta^{13}\text{C}$ values observed during storms or periods of high flow (such as the winter) are consistent with large contributions of isotopically enriched carbon (and low $^{87}\text{Sr}/^{86}\text{Sr}$ values) from strong-acid dissolution of calcite. Alternate explanations such as fractionations caused by degassing or exchange would have no effect on $^{87}\text{Sr}/^{86}\text{Sr}$ and, hence, cannot be dominant processes.

Seasonal variation in the sources of DIC:

With the above caveats in mind, it is clear that few of the assumptions implicit in the simple model and explicitly addressed above are completely valid. However, with the possible exceptions of the assumption of calcite dissolution closed to atmospheric CO_2 or the assumption that degassing has a minimal effect, none of the assumptions appears to be a significant potential source of error. Hence, a simple, two-source, conservative-mixing model may be adequate for the semi-quantitative determination of the relative contributions of soil-derived carbonic acid and dissolved calcite to stream DIC.

The two mass-balance equations above can be solved for the DIC contributions from soil gas and calcite dissolution; the calculated variations in sources of alkalinity at the four streams are plotted on Figure 32. The contributions were calculated for every day when samples of stream water

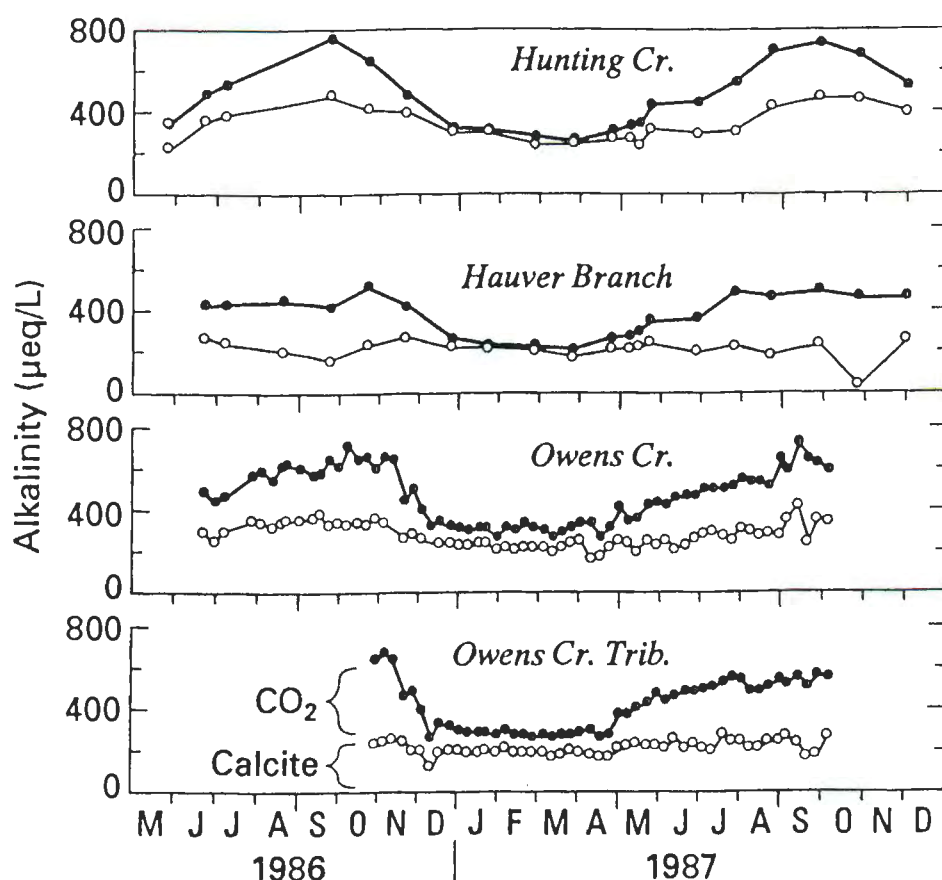


Figure 32. Seasonal variation in the sources of alkalinity at the four streams based on the 2-source conservative-mixing model. The upper dark line is the total alkalinity. The lower line is the calculated value of Alk_{cal} . The amount of alkalinity derived from calcite (Alk_{cal}) is represented by the area under this line; the amount of soil gas CO_2 (Alk_{gas}) is represented by the area between this calculated line and the measured total alkalinity. The 1σ error bars are less than the symbol size.

were analyzed for both $\delta^{13}\text{C}$ and alkalinity. The $\delta^{13}\text{C}$ value used for calcite was -4.7‰ , and the $\delta^{13}\text{C}$ values of soil CO_2 are the monthly averages. Because no soil CO_2 data are available for the Owens Creek watersheds, an average of the values at the other watersheds was used. The upper line indicates the total DIC content of the stream; the lower line separates the contributions to DIC from CO_2 and calcite.

There are strong seasonal variations in the calculated relative contributions of calcite and CO_2 in the streams. During the winter (December through April) 60-90% of the carbon in all watersheds is derived from dissolution of calcite. During the summer (May through November) approximately 40-60% of the carbon is produced from carbonic acid formed in the soil by solution of soil CO_2 . Although there are insufficient data for a rigorous evaluation of the actual impacts of other possible sources and sinks of carbon on the calculations of the relative amounts of carbon derived from calcite and CO_2 , if the effects of each of the previously discussed factors (ie., minor carbon sources and sinks, variability in compositions, etc) are calculated independently and considered to be additive, the error bars on calculations of the relative amounts of DIC derived from calcite and carbonic acid for individual samples are in the range of 10 to 50%, depending mainly on season. These uncertainties on the calculations of relative contributions are higher in the winter than in the summer because of the seasonal differences in alkalinity. Despite the size of the error bars, it is clear that there is seasonal variation in the dominant source of alkalinity: the major source of DIC in the winter is from calcite dissolution; during the rest of the year the amounts of DIC from calcite and CO_2 are approximately equal.

Figure 32 misrepresents the relative annual importance of different sources of DIC because it does not take into consideration the vastly different amounts of water flowing through the watersheds during different seasons. Both the average measured $\delta^{13}\text{C}$ values ($= \Sigma \delta^{13}\text{C} / n$, where n = the total number of measurements), and the $\delta^{13}\text{C}$ values of the total moles of carbon $[\Sigma(\text{DIC} * \delta^{13}\text{C} * \text{discharge}) / \Sigma(\text{DIC} * \text{discharge})]$ discharged from each watershed, during the water year October 1986-September 1987 are shown in Table 21. Using the simple two-source conservative-mixing model, the percentages of the total carbon derived from calcite and discharged from the streams have also been calculated (Table 21). The two streams underlain by greenstone, Hunting Creek and Hauver Branch, have significantly higher calculated contributions of carbon from calcite than the streams underlain by meta-rhyolite. The error bar on these values is about $\pm 20\%$ of the total.

Katz et al. (1985) developed a geochemical mass-balance for the watersheds based on two years of precipitation and stream-chemistry data. They modeled the system in terms of five unknowns (the amounts of albite, actinolite, chlorite, and calcite weathered plus the amount of H_2CO_3 consumed) and six mass balance equations (for H^+ , Ca^{2+} , Mg^{2+} , Na^+ , H_4SiO_4 , and HCO_3^-). For 1982, they calculated that about 80% of the bicarbonate at Hauver Branch came from carbonic acid produced in the soil and about 20% was derived from dissolution of calcite. These findings contrast with the calculations above that are based solely on carbon isotopes. So, is one of my assumptions incorrect?

If summer DIC were produced in a system open to the soil-CO₂ reservoir, then an even greater proportion of the summer DIC would be derived from calcite than in the conservative-mixing model, so this cannot explain the differences in the estimates. Large contributions of depleted carbon from oxidation of methane would also mask contributions of DIC from calcite, but there is no evidence for this. Four processes that could cause DIC to become significantly enriched in ¹³C, causing erroneously high estimates of calcite are: large amounts of calcite dissolved in a system open to atmospheric CO₂ during the winter, large amounts of carbon lost to plant uptake in the streams, extensive degassing of CO₂ under conditions that fractionated the remaining DIC, or exchange of stream DIC with atmospheric CO₂ during the winter. However, as discussed in detail above, I find that it is unlikely that significant amounts of carbon are affected by any of these processes but the possibility cannot be totally dismissed.

Such different interpretations from geochemical models based on water chemistry versus isotope ratios are not unusual in ground-water research; many workers therefore attempt to combine the approaches (Deines et al., 1974; Wigley et al., 1978). Isotopes are invaluable for providing another constraint on geochemical models and, of course, vice versa; the more constraints, the better. The analysis of DIC for ¹⁴C, although expensive, would be a valuable adjunct to such studies (Schiff et al., 1990; Aravena et al., 1992). A reinterpretation of the geochemistry of these watersheds using additional isotope and water-chemistry data is in progress. One explanation for the discrepancy is that the chemical constituents modeled

did not behave as conservatively as Katz et al. (1985) assumed (i.e., the constituents may have been incorporated in other mineral phases).

Seasonal variation in weathering reactions:

The above discussion has focused on seasonal variations in the sources of the carbon comprising the stream DIC. The next step is to investigate the reactions responsible for the production of the DIC. The three major types of geochemical reactions responsible for the production of bicarbonate (see above) involve two sources of carbon and produce DIC of three different carbon-isotopic compositions. If these are the only sources of carbon and closed-system mixing can be assumed, the system can be described by the following equations:

$$\text{DIC}_{\text{str}} = \text{DIC}_1 + \text{DIC}_2 + \text{DIC}_3$$

$$\text{DIC}_{\text{str}}(\delta^{13}\text{C}_{\text{str}}) = \text{DIC}_1(\delta^{13}\text{C}_{\text{cal}}) + \text{DIC}_2(\delta^{13}\text{C}_{\text{gas}}) + \frac{1}{2} \text{DIC}_3(\delta^{13}\text{C}_{\text{cal}} + \delta^{13}\text{C}_{\text{gas}})$$

where the subscripts str, cal, and gas refer to stream, calcite, and soil-gas CO_2 ; and the subscripts 1, 2, and 3 refer to the reaction numbers listed above. With two equations and three unknowns, a unique solution for the relative contribution each reaction makes to stream DIC is not possible. Additional geochemical constraints are required to solve for the seasonally variable contributions of these three weathering reactions. Although no

quantitative determinations can be made, the carbon isotope data can provide some upper and lower limits on the amounts of carbon contributed by these three weathering reactions.

If the DIC is derived from only two carbon sources, calcite and CO_2 , and there is no isotope exchange between carbon reservoirs, then the isotopic composition of the stream DIC is intermediate between the compositions of these two end-members. If the proportions were equal, the $\delta^{13}\text{C}$ of the stream would be $-13.3 \pm 1.2\text{‰}$. Generally, the $\delta^{13}\text{C}$ of the DIC is either: (1) more depleted than this, indicating that more of the DIC is derived from CO_2 than from calcite; or (2) more enriched, indicating that more of the DIC is derived from calcite than from CO_2 . According to the $\delta^{13}\text{C}$ values, most of the time in these watersheds there is considerably more calcite dissolved than carbonic acid consumed. Considering the enriched $\delta^{13}\text{C}$ value of the "excess DIC", one can calculate that at least 20% of the total DIC in all streams is produced by dissolution of calcite by acid rain or other strong acids. During the winter, the percent of the DIC derived from strong-acid dissolution of calcite is at least 30-75% of the total DIC, depending on stream. During most of the summer, the contributions from calcite and carbonic acid are subequal (i.e., within about 20% of each other). However, during a several week period at Hauver Branch in September 1987 when the soils were well-flushed by an unusually intense fall storm, the DIC appears to be derived almost entirely from carbonic acid, produced either by dissolution of silicates or oxidation of organics.

Biological control of weathering reactions:

All streams show higher alkalinities during the growing season; some of this is due to the large contributions of regional groundwater during this period. However, Figure 32 shows that there is a striking increase in the contributions of CO_2 relative to calcite during this period, particularly for Hauver Branch and Owens Creek Tributary.

Hauver Branch watershed appears to be more biologically active than Hunting Creek. Soil gas at Hauver Branch contains twice as much CO_2 and the soil gas is 1‰ more depleted in ^{13}C . During the summer, when $\delta^{13}\text{C}$ values at Hauver Branch are several permil depleted relative to Hunting Creek, the model indicates that 60% of the DIC at Hauver Branch is derived from CO_2 as compared to 30% at Hunting Creek and 40-50% at the Owens Creek streams (Figure 32). During the winter, Hauver Branch and Hunting Creek are similar with 10-20% of the DIC coming from CO_2 .

Hauver Branch has much more heterogeneous local soil environments than Hunting Creek. The stream profiles (Figure 32) demonstrate that different sites along the braided Hauver Branch tributaries had significant variations in $\delta^{13}\text{C}$; Hunting Creek profiles showed much less variation. Some locations at Hauver Branch maintained a distinct signature over weeks or months. The correlation of higher DIC content with more depleted $\delta^{13}\text{C}$ values suggests that the variations among locations mainly was caused by the addition of DIC with a depleted $\delta^{13}\text{C}$ value, probably due to local variations

in the amount of organic oxidation taking place in the soils and seeping into the streams.

A substantially greater amount of organic oxidation at Hauver Branch than Hunting Creek can explain their differences in $\delta^{13}\text{C}$ values. The amounts of DIC produced by strong-acid dissolution of calcite in the two watersheds are very similar except during the summer and fall (Figure 32); the proportionally higher amounts of DIC produced by silicate dissolution at Hauver Branch suggest that enhanced levels of biological oxidation of organic matter in the soils and stream at Hauver Branch may be responsible for the major differences between the two watersheds. The extra CO_2 apparently pumped into Hauver Branch soils by biological activity probably causes the observed larger seasonal variation in alkalinity and $\delta^{13}\text{C}$.

Lithologic/hydrologic control of weathering reactions:

The total annual contributions of DIC from calcite from Hunting Creek and Hauver Branch are similar to each other and substantially greater than at the Owens Creek streams (Table 21). Although calcite is a minor mineral in the greenstone, it is not seen in veinlets in the meta-rhyolite (Katz, 1989); hence, because Owens Creek and Owens Creek Tributary are underlain by interbedded flows of greenstone and meta-rhyolite, subsurface waters in these watersheds could be expected to have less contact with calcite than at Hunting Creek and Hauver Branch.

Meta-rhyolite is more resistant to weathering than greenstone, so any contribution to alkalinity derived solely from silicate weathering should be lower at the Owens Creek streams than at Hunting Creek or Hauver Branch. Additionally, the smaller amount of calcite in the interbedded volcanics should result in a corresponding decrease in calcite-derived alkalinity. Yet this is not the case; the alkalinities in all four streams are similar. Of course, on an annual basis, because the Hunting Creek and Hauver Branch watersheds are much larger, a significantly larger amount of carbon is discharged from them than the Owens Creek streams. The explanation for the similar alkalinities despite different susceptibilities to weathering may be related to the relative sizes of the two sets of paired watersheds and their depths of weathering; alternatively, perhaps only a small amount of contact with the meta-basalt is required to change the chemical "signature" of stream water.

The correlations of discharge with $\delta^{13}\text{C}$ for the summer low-flow period are consistent with mixing of baseflow of semi-constant $\delta^{13}\text{C}$ composition with small amounts of newer storm-related waters (Kendall et al., 1992c). Only minor amounts of water flushed from shallower flowpaths by rain pulses may reach the stream at this time due to high evapotranspiration rates. During storms, although stream $\delta^{13}\text{C}$ values show considerable oscillations caused by rapid changes in sources of water (Kendall, 1990), in general $\delta^{13}\text{C}$ values become temporarily depleted, presumably due to flushing of calcite-free soil zones where silicate weathering by carbonic acid is the dominant source of alkalinity. In

contrast, significant amounts of younger waters are probably flushed into the stream during periodic winter storms. In addition, the rise of the water table during the winter causes saturation of different and more acidic parts of the soil profile than are normally accessed during the dry summer.

CONCLUSIONS

The $\delta^{13}\text{C}$ value of DIC in stream water appears to be a useful tracer of the seasonal changes in the sources of carbon contributing to stream alkalinity, the relative seasonal importance of different weathering reactions affecting stream chemistry, and the seasonal and discharge-related contributions of different hydrologic flowpaths to stream flow. In the Catoctin streams, there are two main sources of carbon contributing to stream DIC, soil CO_2 and calcite, and three major alkalinity producing weathering reactions, each with a distinct $\delta^{13}\text{C}$ value. The $\delta^{13}\text{C}$ of each stream sample can be interpreted in terms of the relative amounts of these two sources of carbon and these three reactions. Based on the conservative-mixing model, about 60-70% of the DIC discharged from the Catoctin Mountain watersheds was derived from calcite; at least 20% of the DIC was derived from dissolution of calcite by acid rain or other strong acids. At present, my best estimate of the error bars on these yearly estimates is about $\pm 20\%$.

More precise calculations of the relative contributions of carbon from soil CO_2 and calcite will require more information regarding other minor

sources and sinks for carbon. The impact of other sources of carbon is more significant during the winter than the summer because of the lower DIC contents in stream water in the winter. In particular, the question of whether appreciable calcite dissolution may be occurring under open-system conditions needs to be resolved. Stream $\delta^{13}\text{C}$ values in the range of -13 to -22‰ can be explained by dissolution of calcite by soil CO_2 under either open- or closed-system conditions. The high pCO_2 values in the soil zone and the depleted $\delta^{13}\text{C}$ values of soil CO_2 indicate that exchange of subsurface waters with atmospheric CO_2 is minimal. However, because any such exchange during the winter as the water moves through the soil towards the stream could produce enriched ^{13}C values, further investigation is indicated. There is no evidence of exchange of stream DIC with atmospheric CO_2 , probably because stream residence times are short. In addition, although degassing of soil waters could cause significant isotope fractionation, the good correlations of $\delta^{13}\text{C}$ and alkalinity suggest that any effect is minor.

If significant isotopic exchange takes place in these catchments, the 2-source model can greatly overestimate the contributions of carbon from calcite dissolution to winter DIC and, hence, the $\delta^{13}\text{C}$ of DIC cannot easily be used to calculate the contributions from different carbon sources. In this case, however, the $\delta^{13}\text{C}$ values still uniquely label waters derived from different flowpaths and hence can be useful for explaining seasonal variations in sources of water and chemical constituents. The strong correlations between $\delta^{13}\text{C}$, alkalinity, and other chemical species in these streams suggest mixing of waters of distinct $\delta^{13}\text{C}$ values; such correlations would not occur if

much of the variation in $\delta^{13}\text{C}$ were a consequence of degree of isotopic exchange with soil or atmospheric CO_2 .

The seasonal variations in stream $\delta^{13}\text{C}$ values and the differences between the watersheds appear to be controlled primarily by seasonal and spatial variations in soil CO_2 production rates and relative amounts of calcite in the bedrock. Because carbon isotopes behave more conservatively than most chemical species, they provide less-ambiguous information about the relative contributions of different weathering reactions than is possible with chemical data alone (Kendall et al., 1992c). Analysis of the $\delta^{13}\text{C}$ of stream DIC provides a way to model stream water in terms of contributions from two or more ground waters -- each with its own $\delta^{13}\text{C}$ value and distinct water chemistry reflecting the weathering reactions taking place along the flowpath -- that add together to form stream water.

SUMMARY

A major uncertainty in hydrologic and geochemical modeling of stormflow generation in watersheds has been quantification of the contributions of water and solutes from different sources and hydrologic pathways to stream water. Although hydrologic models exist that can reproduce the hydrograph, when chemical data are coupled to most of these physical models they do not accurately reflect the stream-water chemistry. It has therefore been concluded that the hydrologic pathways are inaccurately represented in most models, or that the processes affecting the water chemistry are not well understood. Isotopic techniques have recently gained widespread acceptance as useful tools in the investigation of sources of stream flow, but the assumptions implicit to their application have yet to be thoroughly addressed. Considerable debate still surrounds the question of whether spatial and temporal variations in the isotopic and chemical compositions of water components are negligible, and whether simple mass balance models realistically portray catchment hydrology.

Although most isotope hydrology studies use the $\delta^{18}\text{O}$ and δD of rain samples collected in open areas as the indicator of the composition of recharge water, much of the earth's land surface is forested and rain is intercepted by the tree canopy prior to infiltration. At Panola Mountain, Georgia, a 2-year study of temporal and spatial variability in rain and throughfall has determined that, on average, throughfall is enriched by 0.5‰

in $\delta^{18}\text{O}$ and 3.0‰ in δD relative to rain. Site-specific differences in canopy type, density, and micro-climate result in an average $\delta^{18}\text{O}$ spread of 0.5‰ among collectors for the same storm, with a maximum range of 1.2‰. Sets of sequential rain and throughfall samples indicate that throughfall enrichment takes place throughout the storm, not just at the beginning when rain falls onto dry leaves. During the middle portions of convective storms, both rain and throughfall samples generally plot considerably above the local meteoric water line in δD - $\delta^{18}\text{O}$ space, suggesting more exchange with re-evaporated water during the middle of the storms than at the beginning or end. Evaporative losses are greater and throughfall is slightly enriched in ^{18}O and D in conifer forests relative to deciduous forests. However, throughfall shows little evidence of evaporative (kinetic) fractionation; instead, the high d-excess values suggest considerable exchange with re-evaporated waters under semi-closed conditions.

The spatial and temporal variability in rain and throughfall isotopic composition seen at Panola will have a greater effect on hydrograph separations in catchments where rain water is a major contributor to stormflow (like Hydrohill), than in more typical catchments dominated by old groundwater. The effects of site and species-specific isotope fractionations, and of open versus canopy isotope fractionations, will be more significant in watersheds with mixed forests and large open areas. In such catchments, a 1‰ range in the $\delta^{18}\text{O}$ of infiltrating rain water at any point during the storm is probably typical. Depending on the difference between the compositions of rain and groundwater (among other factors), a 1‰ range in rain composition could produce large differences in the

calculated intrastorm amounts of rain in stream water; for calculations of the total rain input to stormflow, the effect of rain variability is less. More exact predictions of the effect this intrastorm variability might have on the use of isotopes in natural systems is hampered by our current lack of understanding of the details of the infiltration process.

Several approaches have been developed for the modeling of streamflow response to rain, including hydrologic, chemical, and isotope models. Most of these hydrograph separation models are essentially "black box" models where only external information is available -- the amounts and/or compositions of the inputs (rain and baseflow) and of the output (stream water). Such models allow quantification of catchment response to storm events but do not reveal how the catchment "works". The existence of spatial and temporal variability inside the black box during storms can pose substantial difficulties for the use of such models for tracing sources and flowpaths of water contributing to stormflow. At the well-instrumented Hydrohill artificial catchment near Nanjing China, hydrologic response models and isotopic and chemical hydrograph separation models provide detailed information about the heterogeneous nature of the shallow soil system.

For a 12-cm storm at Hydrohill, 90% of the total flow was derived from new rain water. Surface runoff and shallow interflow dominate the total hydrograph which is composed of 77% quick-flow and 23% slowflow. The shallow flow is all quick-flow and the $\delta^{18}\text{O}$ values indicate that the flow is virtually all new water; solute tracers (Cl and SiO_2) greatly underestimated the component derived from rain and/or shallow flowpaths because of rapid

incorporation of solutes from the soil. In contrast, the deeper flow is composed of mixtures of new water mainly transported via macropores and old water that is being displaced from the soils by recharge, that change rapidly in response to fluctuations in rain intensity. The rain storm had a 5‰ range in $\delta^{18}\text{O}$; selective storage of the first enriched fraction of the storm causes the remaining water discharging as surface runoff and shallow interflow to become depleted in ^{18}O relative to both the rain and pre-storm water. In response to temporal and spatial differences in flowpaths, groundwater throughout the storm exhibited remarkable variability in $\delta^{18}\text{O}$ and chemical composition for such a small catchment; at the end of the storm, the groundwaters showed a 4‰ range in $\delta^{18}\text{O}$. Because of selective storage of rain fractions and variations in transport mechanisms, the pre-storm waters for the next storm cannot be characterized by a single composition, making future hydrograph separations less quantitative.

The Panola and Hydrohill studies illustrate the kinds of isotopic variability present in natural hydrologic systems. The Hydrohill study discusses the kinds of information about catchment response to storms than can be generated with different types of hydrograph separation models. The spatial and temporal heterogeneity in isotopic composition of pre-storm waters can significantly increase the already large error bars on determinations of the relative amounts of new and old water, and shallow and deep flowpaths, contributing to stream water. This hampers our ability to use isotopes to gain understanding of how catchments "work" in terms of hydrology and geochemistry. One solution to the realization that δD and $\delta^{18}\text{O}$ variability in natural waters makes them increasingly difficult to use for

quantitative hydrograph separations, is to try some new isotope tools. The Catoctin study is a preliminary investigation of the applicability of using the $\delta^{13}\text{C}$ of stream DIC for tracing flowpaths and sources of water in catchments. In specific, the study investigates the seasonal and lithologic constraints on $\delta^{13}\text{C}$ variability in shallow systems.

There appear to be two major sources of carbon that control the $\delta^{13}\text{C}$ value of stream DIC at the four Catoctin streams studied: calcite and carbonic acid. The $\delta^{13}\text{C}$ value of each stream sample can be interpreted in several ways: in terms of the relative amounts these two sources contribute to the total alkalinity; as an indicator of the relative amounts of carbon produced by three different weathering reactions; or in terms of the relative amounts of water contributed from flowpaths with distinct chemical and isotopic signatures. During the summer, the streams are dominated by baseflow with a relatively constant $\delta^{13}\text{C}$ value. Minor amounts of water flushed from shallower flowpaths where calcite is absent may reach the stream during storms. In contrast, the rise of the water table during the winter, especially during storms, causes saturation of different parts of the weathering zone or bedrock fractures higher on the hillslopes. Flow from these hillslope areas, which presumably contain calcite in less weathered locations, is chemically and isotopically distinct from the flowpaths that generate most of the flow in the summer.

The Catoctin study focuses on the assumptions required for application of $\delta^{13}\text{C}$ for tracing sources of alkalinity and flowpaths in watersheds, and uses data from the four streams to discuss the merits of each assumption. Although none of the simple assumptions is shown to be entirely correct,

none of the assumptions has been shown to be seriously in error either. Hence, it appears that the $\delta^{13}\text{C}$ value of stream DIC is suitable as a semi-conservative tracer of alkalinity sources in these watersheds. In larger watersheds where residence times are longer or in systems with more biological activity in the streams, the $\delta^{13}\text{C}$ signatures of weathering reactions may be overprinted by atmospheric exchange and in situ productivity.

The usefulness of $\delta^{13}\text{C}$ of DIC a geochemical tool, in addition to the more conventional $\delta^{18}\text{O}$ and δD of water, for understanding catchment hydrology/geochemistry remains to be seen. I am currently testing the applicability of an integrated isotope approach ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$) at four watersheds (Catoclin, MD; Shelter Run, VA; Sleepers River, VT; and Trout Lake, WI).

The results of these three studies suggest several topics where more research is indicated. To summarize some of the more important items:

**** The Panola study is one of only two studies of throughfall $\delta^{18}\text{O}$ variability and the only one to include both $\delta^{18}\text{O}$ and δD . The finding that throughfall samples are not kinetically fractionated despite about 15% water losses, and that they generally plot along slopes greater than 8 in δD - $\delta^{18}\text{O}$ space, has some important implications about the recycling of atmospheric vapor in forested areas. Throughfall needs to be investigated at several other sites to determine the magnitude of possible regional or local fractionation effects.**

****** If throughfall elsewhere is generally enriched in ^{18}O by about 0.5‰, then investigators will have to modify their models of the isotopic compositions of recharge. Although this is not a large difference, it is enough to cause a 1°C increase in the estimated temperature used for paleoclimatic reconstructions.

****** The bow-shaped nature of the isotopic compositions of intrastorm rain and throughfall samples in δD - $\delta^{18}\text{O}$ space during convective storms and heavy rainfall during frontal storms has not previously been observed. It may be an artifact of sampling in and around forested areas where recycled atmospheric moisture is abundant. Further work is indicated.

****** Because of the spatial variability of throughfall at Panola, single collectors are inadequate for characterizing the isotopic composition of the throughfall. I recommend either putting out several collectors and homogenizing the bulk waters or perhaps using a very large single trough. Otherwise, it would be better to just collect bulk rain and apply a correction factor. More work is needed to establish if this kind of variability is typical and whether an empirically derived correction factor is feasible.

****** I speculate that micro-climate differences under conifers and deciduous trees are responsible for the different water losses and isotopic compositions of the throughfall. This could be verified by careful monitoring of temperature, humidity, wind speed, and isotopic compositions of atmospheric vapor during one or several storms, at several locations under each canopy type.

**** Selective storage of different time fractions of rain violates one of the important implicit assumptions of isotope hydrograph separations. It is likely to be most important in catchments such as Hydrohill where surface runoff, shallow interflow, and macropore flow of rain dominate the hydrograph. In systems dominated by old-water where the new rain water is transported mostly as piston-flow, any selective storage will be seen as variable lag times for the new water. This phenomena needs to be investigated in other catchments.**

**** Hydrohill demonstrates how soil waters and groundwaters can become isotopically and chemically heterogeneous. If such waters are major contributors to streamflow, then this finding poses substantial difficulties for the isotope hydrograph separation technique. More workers need to concentrate on sampling wells and lysimeters that have good connections to the stream to see how variable these waters are, and whether these variations persist between storms or for longer time periods.**

**** There has been almost no work on isotopic exchange between mobile pore waters and less mobile pore waters, or between variably-mobile water and soil vapor. It is possible that natural exchange mechanisms in the soil will tend to reduce isotopic variability in soil waters between storms, thus reducing the problem posed by heterogeneous flowpaths.**

**** Investigators need to be much more cautious about trying to use chemical tracers as tracers of water sources; the Hydrohill data provide some interesting insights on how fortuitous agreement with $\delta^{18}\text{O}$ can be achieved.**

It is too easy for a variety of solutes to be dissolved by waters making very brief contact with different soil horizons. It would be interesting to find some common denominator for previous studies where solute hydrograph separations have appeared to "agree" with the results of $\delta^{18}\text{O}$ separations.

** The discrepancy between the relative amounts of calcite and carbonic acid contributing to stream alkalinity as calculated by geochemical mass balance models and the carbon isotope mixing model is a matter of considerable concern. One way of attacking the problem is to try to derive a combined isotope-chemical model for the stream water. A problem with this approach is that if one or both models is built upon flawed assumptions of conservative behavior, then a combined approach may not identify the problem. An alternative approach is to identify the possible weak assumptions in each model, and then try to devise experiments to invalidate the assumptions. Obvious candidates for further investigation include ^{14}C analyses of stream water to see if the carbon that the $\delta^{13}\text{C}$ values indicate is mostly derived from calcite is "dead", continued investigations of the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of stream water, and consideration of possible reactive phases in the hyporheic zones of the streams that may be "resetting" the chemical signatures of subsurface flow.

** The $\delta^{13}\text{C}$ composition of water, even if it proves to be only a semi-conservative tracer of carbon sources, may still useably label waters flowing along different flowpaths. From the data thus far, shallow flowpaths appear to have more lower $\delta^{13}\text{C}$ values than deeper groundwater, and new water has a negligible DIC content. Hence, the $\delta^{13}\text{C}$ may be a useful method for

distinguishing between different types of "old" water. The Hydrohill study has shown how complicated it can be to use $\delta^{18}\text{O}$ to trace old waters; combining $\delta^{18}\text{O}$ with $\delta^{13}\text{C}$ (and $^{87}\text{Sr}/^{86}\text{Sr}$) may be a way to improve the accuracy of the isotope hydrograph separation technique.

Appendix 1. Description of methods used to analyze samples for isotopic composition.

$\delta^{18}\text{O}$ of water samples:

Almost all water samples were analyzed on an automated $\text{CO}_2\text{-H}_2\text{O}$ equilibration device, connected an automated mass spectrometer. The procedure used is a modification of Epstein and Mayeda (1953) as follows: Two-ml aliquots of water were introduced into each of 24 vessels (15 cc volume). Two standard waters and one random repeat were added to each batch of 24 samples. These vessels were attached to the automated preparation system and were evacuated for about 30 minutes. The vessels were then filled with about 0.3 atm. of dry CO_2 . The closed vessels were then left to shake and equilibrate for at least five hours at 25.0°C . After this time, each sample is automatically introduced into the mass spectrometer, one by one, for analysis.

δD of water samples:

The procedures used are exactly as are stated in Kendall and Coplen (1985) and Coplen et al. (1991).

$\delta^{13}\text{C}$ of gas samples:

Field collection: I used custom made 250-cc glass vessels with stopcocks at either end to collect gas samples. To collect a gas sample from a soil probe: remove the cap on the soil probe, attach one end of the vessel using a Tygon hose, and attach the other end of an evacuated vessel to a peristaltic pump

with another length of Tygon hose. Then open the stopcocks, turn on the pump at a low speed and pump out stagnant air for about 1-2 minutes (depending on the depth of the probe). Then turn off the pump and let soil gas expand into the vessel for about 2 minutes. Close stopcocks, put the cap back on the soil probe, and return the vessel to the lab for analysis.

Analysis: Attach vessel to a vacuum line with Tygon hose. Attach an evacuated sample tube to another port. Evacuate the line for about 5 minutes. Put a dewar of LN_2 on a Horibe-type U-trap between the vessel and the diffusion pump. Slowly open the upper stopcock of the vessel so that the soil gas very gradually is pumped through the trap and out the diffusion pump (thus trapping all the CO_2 and H_2O in the U-trap). This should take about 15 minutes. When the vacuum is good, close the vessel, close the line to vacuum, replace the dewar of LN_2 with a dewar containing a dry ice-methanol slush, put the dewar of LN_2 on the sample tube, and open the stopcock of the tube. After about 15 minutes all the water should be trapped in the U-trap and all the CO_2 in the tube; close the tube. Remove the dewar from the U-trap; if there is a lot of water frozen here, pump it away, and then transfer the CO_2 from the tube back into the U-trap to purify the CO_2 again. When the CO_2 appears to be dry, measure the yield on a manometer and then attach to the automated inlet system of the mass spectrometer for analysis.

$\delta^{13}\text{C}$ of rock samples:

Collect carbonate-bearing rock, crush and sieve, then treat the sample like SrCO_3 powder (see below).

$\delta^{13}\text{C}$ of DIC samples:

The field collection methods are described in Chapter 3. The preparation method is a modification of Gleason et al. (1969). Water samples are precipitated with about 30 ml of SrCl_2 . After letting the solution age for at least 2 days the samples are filtered through a 0.4μ glass-fiber filter under dry N_2 and rinsed thoroughly with DI water. Filters are dried at about 80°C overnight and then the powder is scraped off the filter paper, homogenized, and weighed. About 50 mg of powder are put into one arm of a carbonate reaction vessel; about 3 cc of 100% H_3PO_4 is added to the other arm. The vessels are attached to a vacuum line and evacuated for about 15 minutes. At this point the vessels are closed, removed from the line, tilted so that the acid mixes with the powder, and then returned to the vacuum line which is evacuated. After reaction has ceased or 30 minutes has passed, the stopcock between the vacuum line and the diffusion pump is closed, a dewar of LN_2 is put on the U-trap, and the vessel is opened and the CO_2 and H_2O frozen into the U-trap. After 10 minutes non-condensibles are pumped away, the vessel closed, and the CO_2 transferred into a sample tube by replacing the dewar on the U-trap with a dry-ice slush and putting the dewar of LN_2 on the sample tube. The amount of CO_2 can be measured in a manometer. The sample tube is then attached to the inlet system of the mass spectrometer for analysis.

Mass spectrometer analysis:

The mass spectrometers automatically analyze the samples and custom software calculates the δ values relative to the appropriate international standard (VSMOW for waters and VPDB for carbonates). Correction factors for working standard drift (among other possible problems) are determined from the set of standards analyzed everyday along with the samples. These values are entered into the lab database and the software corrects the isotopic compositions for the samples. The laboratory standards analyzed everyday include both gaseous materials and either waters or carbonates (depending on what types of samples are being run).

Reproducibility and precision of analyses:

The 2σ analytical precisions for multiple analyses of the same gas for isotopic composition are about 0.07‰ for $\delta^{18}\text{O}$, 0.06‰ for $\delta^{13}\text{C}$, and 1.0 for δD . The 2σ analytical precision for complete replicate preparations of the same pure sample are about 0.07‰ for $\delta^{18}\text{O}$, 0.10‰ for $\delta^{13}\text{C}$, and 2.0‰ for δD ; these values are the same for samples run on the same day and for samples run over spans of months.

Appendix 2. Isotopic compositions, dates, and water amounts of all samples from Panola.

Lab ID	Type	Site	Code	Date	Time	Volume (cm)	δD (‰)	$\delta^{18}O$ (‰)
3963	PI	1	A	01/01/88	0.3826	0.193	13.5	-0.75
3964	PI	1	B	01/01/88	0.6549	0.196	8.5	-1.90
3965	PI	1	C	01/01/88	0.7722	0.191	11.5	-1.80
3966	PI	1	D	01/01/88	0.8347	0.193	-10.5	-4.30
3967	PI	1	E	01/01/88	0.9875	0.193	-18.0	-4.85
3968	PI	1	F	01/02/88	0.1382	0.193	-33.0	-6.15
3969	PI	1	G	01/02/88	0.1757	0.193	-53.5	-7.50
3970	PI	1	H	01/03/88	0.1847	0.196	-74.5	-10.65
3971	PI	1	I	01/03/88	0.2736	0.361	-91.5	-13.15
3972	PI	1	J	01/03/88	0.3333	0.297	-101.0	-14.00
3973	PI	1	K	01/03/88	0.7931	0.663	-97.0	-13.85
5595	PI	1	A	05/10/88	0.1882	0.153	-10.5	-0.85
5596	PI	1	B	05/10/88	0.2931	0.167	-6.5	-2.10
5597	PI	1	C	05/10/88	0.3125	0.145	-16.5	-3.25
5598	PI	1	D	05/10/88	0.3299	0.164	-25.5	-4.15
5599	PI	1	E	05/10/88	0.3549	0.182	-27.5	-4.20
5600	PI	1	F	05/10/88	0.3792	0.164	-33.5	-4.55
5601	PI	1	G	05/10/88	0.4118	0.182	-53.0	-6.50
5637	PI	1	A	05/15/88	0.7139	0.165	-9.5	-2.20
5638	PI	1	B	05/15/88	0.7222	0.168	-37.0	-5.55
5639	PI	1	C	05/15/88	0.7268	0.151	-28.0	-5.25
5640	PI	1	D	05/15/88	0.7313	0.173	-24.5	-4.55
5641	PI	1	E	05/15/88	0.7326	0.185	-27.5	-5.20
5642	PI	1	F	05/15/88	0.7340	0.163	-43.5	-6.75
5643	PI	1	G	05/15/88	0.7354	0.184	-42.0	-6.25
5644	PI	1	H	05/15/88	0.7368	0.162	-49.0	-7.40
5645	PI	1	I	05/15/88	0.7375	0.141	-53.5	-7.65
5646	PI	1	J	05/15/88	0.7424	0.307	-51.0	-7.85

5762	PI	1	A	06/02/88	0.7951	0.158	29.5	3.00
5763	PI	1	B	06/02/88	0.7958	0.179	23.5	1.05
5764	PI	1	C	06/02/88	0.7986	0.154	21.5	0.75
5765	PI	1	D	06/02/88	0.8007	0.170	26.0	1.20
5766	PI	1	E	06/02/88	0.8250	0.149	29.0	2.35
5792	PI	1	A	06/09/88	0.6330	0.161	4.0	-0.75
5793	PI	1	B	06/09/88	0.6340	0.163	-6.5	-2.30
5794	PI	1	C	06/09/88	0.6347	0.140	-7.5	-2.40
5795	PI	1	D	06/09/88	0.7319	0.131	-8.0	-2.30
5885	PI	1	A	06/18/88	0.8285	0.184	16.5	1.75
5886	PI	1	B	06/19/88	0.7581	0.161	13.0	0.35
5887	PI	1	C	06/19/88	0.7601	0.146	5.0	-1.40
5888	PI	1	D	06/19/88	0.7615	0.171	4.0	-1.65
5889	PI	1	E	06/19/88	0.7636	0.183	2.5	-1.75
5890	PI	1	F	06/19/88	0.7650	0.173	1.5	-1.75
5891	PI	1	G	06/19/88	0.7706	0.166	2.5	-1.50
5892	PI	1	H	06/19/88	0.7719	0.154	2.0	-1.25
5893	PI	1	I	06/19/88	0.7733	0.297	2.5	-1.25
5894	PI	1	J	06/19/88	0.7754	0.341	-2.5	-1.30
5895	PI	1	K	06/19/88	0.7761	0.191	-7.0	-1.70
6205	PI	1	A	07/27/88	0.5604	0.158	-14.5	-3.55
6206	PI	1	B	07/27/88	0.5611	0.123	-18.0	-4.00
6207	PI	1	C	07/27/88	0.5618	0.171	-19.0	-4.25
6208	PI	1	D	07/27/88	0.5625	0.157	-20.5	-3.30
6209	PI	1	E	07/27/88	0.5632	0.058	-16.5	-2.65
6644	PI	1	A	09/03/88	0.7757	0.163	-18.5	-4.30
6645	PI	1	B	09/03/88	0.7771	0.166	-19.5	-4.40
6646	PI	1	C	09/03/88	0.7785	0.178	-24.0	-4.80
6647	PI	1	D	09/03/88	0.7799	0.197	-26.0	-4.85
6648	PI	1	E	09/03/88	0.7819	0.166	-28.0	-5.20
6649	PI	1	F	09/03/88	0.7853	0.174	-32.5	-5.65

6650	PI	1	G	09/03/88	0.7917	0.170	-40.0	-6.10
6651	PI	1	H	09/03/88	0.8021	0.182	-38.5	-6.40
6652	PI	1	I	09/03/88	0.8090	0.308	-30.0	-5.40
6653	PI	1	J	09/03/88	0.8264	0.337	-19.5	-4.55
6654	PI	1	K	09/03/88	0.8854	0.525	-22.5	-4.60
6655	PI	1	L	09/03/88	0.9063	0.707	-32.0	-5.65
6656	PI	1	M	09/04/88	0.6979	3.865	-47.5	-7.40
6748	PI	1	A	09/04/88	0.7347	0.176	-90.0	-12.05
6749	PI	1	B	09/04/88	0.7500	0.197	-97.5	-13.05
6750	PI	1	C	09/04/88	0.7792	0.176	-100.5	-13.50
6751	PI	1	D	09/04/88	0.8056	0.170	-97.5	-13.20
6752	PI	1	E	09/04/88	0.8236	0.176	-98.0	-13.60
6753	PI	1	F	09/04/88	0.8333	0.179	-97.5	-13.45
6754	PI	1	G	09/04/88	0.8507	0.156	-98.5	-13.55
6755	PI	1	H	09/04/88	0.8576	0.159	-99.0	-13.70
6756	PI	1	I	09/04/88	0.8646	0.329	-97.5	-12.95
6757	PI	1	J	09/04/88	0.8854	0.333	-53.0	-9.90
6758	PI	1	K	09/04/88	0.9063	0.123	-103.5	-14.35
6972	PI	1	A	09/16/88	0.6826	0.169	-6.5	-3.10
6973	PI	1	B	09/16/88	0.7361	0.178	-10.0	-3.10
6974	PI	1	C	09/16/88	0.7465	0.194	-18.5	-4.60
6975	PI	1	D	09/16/88	0.7708	0.180	-13.0	-3.90
6976	PI	1	E	09/16/88	0.8194	0.173	-15.0	-4.45
6977	PI	1	F	09/16/88	0.9132	0.186	-11.5	-4.00
6978	PI	1	G	09/17/88	0.1007	0.153	-9.0	-3.70
6979	PI	1	H	09/17/88	0.1319	0.163	-8.5	-3.85
6980	PI	1	I	09/17/88	0.1806	0.351	-9.5	-3.85
6981	PI	1	J	09/17/88	0.1910	0.336	-13.5	-4.25
6982	PI	1	K	09/17/88	0.2083	0.311	-11.5	-3.95
7110	PI	1	A	10/01/88	0.9458	0.161	-2.5	-2.50
7111	PI	1	B	10/01/88	0.9507	0.152	-8.0	-3.50

7112	PI	1	C	10/01/88	0.9549	0.166	-11.0	-3.65
7113	PI	1	D	10/01/88	0.9583	0.161	-21.0	-4.80
7114	PI	1	E	10/01/88	0.9632	0.189	-21.5	-4.75
7115	PI	1	F	10/01/88	0.9646	0.156	-17.0	-4.35
7116	PI	1	G	10/01/88	0.9653	0.160	-16.5	-4.05
7117	PI	1	H	10/01/88	0.9674	0.188	-18.5	-4.10
7118	PI	1	I	10/01/88	0.9875	0.306	-18.5	-4.60
7119	PI	1	J	10/02/88	0.0181	0.342	-20.0	-4.65
7120	PI	1	K	10/02/88	0.3903	0.511	-9.0	-3.55
7121	PI	1	L	10/02/88	0.4063	0.704	-19.5	-4.60
7596	PI	1	A	01/03/89	0.3132	0.168	16.5	0.70
7597	PI	1	B	01/03/89	0.3299	0.172	9.0	-1.10
7598	PI	1	C	01/03/89	0.3382	0.185	-3.0	-2.75
7599	PI	1	D	01/03/89	0.3479	0.171	-12.5	-3.25
7600	PI	1	E	01/03/89	0.3639	0.167	-15.0	-3.60
7601	PI	1	F	01/03/89	0.3854	0.186	-12.0	-3.20
7602	PI	1	G	01/03/89	0.5847	0.194	-17.0	-3.60
7886	PI	1	A	02/28/89	0.1458	0.196	-4.5	-3.35
7887	PI	1	B	02/28/89	0.1528	0.196	-9.5	-4.35
7888	PI	1	C	02/28/89	0.1590	0.194	-24.0	-6.25
7889	PI	1	D	02/28/89	0.1632	0.172	-21.0	-6.05
7890	PI	1	E	02/28/89	0.1875	0.169	-28.0	-7.05
7891	PI	1	F	02/28/89	0.2153	0.184	-28.5	-6.70
7892	PI	1	G	02/28/89	0.2326	0.154	-38.5	-7.50
7893	PI	1	H	02/28/89	0.2569	0.156	-53.0	-8.90
7894	PI	1	I	02/28/89	0.2813	0.320	-63.0	-9.40
8059	PI	1	A	03/30/89	0.0986	0.152	1.5	-1.20
8060	PI	1	B	03/30/89	0.1118	0.163	-12.5	-3.35
8061	PI	1	C	03/30/89	0.1354	0.150	-9.5	-3.85
8062	PI	1	D	03/30/89	0.1667	0.175	-12.5	-3.45
8063	PI	1	E	03/30/89	0.1806	0.160	-21.5	-3.70

8064	PI	1	F	03/30/89	0.1979	0.156	-28.5	-4.25
8065	PI	1	G	03/30/89	0.2188	0.075	-38.5	-5.50
4018	SE	11.1		01/02/88			-3.5	-2.85
4019	SE	11.2		01/02/88			-0.5	-2.65
4020	SE	11.3		01/02/88			-6.5	-3.00
4021	SE	11.4		01/02/88			-5.5	-3.20
4022	SE	11.5		01/02/88			-5.5	-2.85
4023	SE	11.6		01/02/88			-1.5	-2.65
4024	SE	22.1		01/02/88			-5.5	-3.00
4025	SE	22.2		01/02/88			2.0	-2.15
4026	SE	22.3		01/02/88			-9.5	-3.20
4027	SE	22.4		01/02/88			-2.5	-2.50
4028	SE	22.5		01/02/88			0.0	-2.60
4029	SE	22.6		01/02/88			-6.0	-3.25
4030	SE	33.1		01/02/88			3.0	-2.60
4031	SE	33.2		01/02/88			0.5	-2.40
4032	SE	33.3		01/02/88			-1.5	-2.65
4033	SE	33.4		01/02/88			-7.0	-3.20
7580	SE	11.1		01/03/89			-6.0	-2.40
7581	SE	11.2		01/03/89			-6.5	-2.50
7582	SE	11.3		01/03/89			-8.5	-2.60
7583	SE	11.4		01/03/89			-7.5	-2.50
7584	SE	11.5		01/03/89			-8.5	-2.45
7585	SE	11.6		01/03/89			-7.0	-2.50
7586	SE	22.1		01/03/89			-8.0	-2.70
7588	SE	22.3		01/03/89			-5.5	-2.30
7589	SE	22.4		01/03/89			-7.0	-2.40
7590	SE	22.5		01/03/89			-3.5	-2.20
7591	SE	22.6		01/03/89			-4.5	-2.30
7592	SE	33.1		01/03/89			-4.5	-2.25
7593	SE	33.2		01/03/89			-6.0	-2.30

7594	SE	33.3		01/03/89			-5.5	-2.35
7595	SE	33.4		01/03/89			-5.5	-2.40
8857	SE	11.1		07/02/89			-11.0	-3.45
8858	SE	11.2		07/02/89			-13.5	-3.55
8859	SE	11.3		07/02/89			-11.0	-3.50
8860	SE	11.4		07/02/89			-12.0	-3.40
8861	SE	11.5		07/02/89			-10.5	-3.50
8862	SE	11.6		07/02/89			-14.0	-3.70
8863	SE	22.1		07/02/89			-13.5	-3.55
8864	SE	22.2		07/02/89			-11.5	-3.50
8865	SE	22.3		07/02/89			-12.5	-3.50
8866	SE	22.4		07/02/89			-11.5	-3.45
8867	SE	22.5		07/02/89			-13.0	-3.50
8868	SE	22.6		07/02/89			-13.5	-3.55
8869	SE	33.1		07/02/89			-12.5	-3.50
8870	SE	33.2		07/02/89			-11.0	-3.50
8871	SE	33.3		07/02/89			-12.5	-3.50
8872	SE	33.4		07/02/89			-12.5	-3.55
3366	TE	2.2		10/27/87		0.767	-24.0	-5.00
3370	TE	3.2		10/27/87		0.950	-25.0	-5.00
3374	TE	4.3		10/27/87		1.103	-23.5	-4.90
3376	TE	5.2		10/27/87		0.935	-27.0	-4.80
3377	TE	6.3		10/27/87		0.888	-24.5	-4.50
3986	TE	1.1		01/02/88		1.671	-3.5	-2.95
3987	TE	1.2		01/02/88		1.488	-9.0	-3.40
3988	TE	1.3		01/02/88		1.520	-9.0	-3.40
3989	TE	1.4		01/02/88		1.626	-9.0	-3.45
3990	TE	2.1		01/02/88		1.416	-7.0	-3.40
3991	TE	2.2		01/02/88		1.317	-5.0	-3.30
3992	TE	2.3		01/02/88		1.697	-7.0	-3.15
3993	TE	2.4		01/02/88		1.509	-7.5	-3.40

3994	TE	3.1		01/02/88		1.522	-9.5	-3.50
3995	TE	3.2		01/02/88		1.514	-9.0	-2.65
3996	TE	3.3		01/02/88		1.386	-8.0	-3.25
3997	TE	3.4		01/02/88		1.704	-5.5	-3.00
3998	TE	4.1		01/02/88		1.656	-8.0	-3.35
3999	TE	4.2		01/02/88		1.440	-6.5	-3.45
4000	TE	4.3		01/02/88		1.618	-2.5	-2.15
4001	TE	4.4		01/02/88		1.563	-5.5	-3.20
4002	TE	5.1		01/02/88		1.288	-7.0	-3.60
4003	TE	5.2		01/02/88		1.141	-5.0	-3.25
4004	TE	5.3		01/02/88		1.159	-3.5	-2.85
4005	TE	5.4		01/02/88		1.206	-8.5	-3.50
4006	TE	6.1		01/02/88		1.589	-4.5	-3.15
4007	TE	6.2		01/02/88		1.263	-8.0	-3.30
4008	TE	6.3		01/02/88		1.372	-4.0	-3.25
4009	TE	6.4		01/02/88		1.484	-5.0	-3.30
4010	TE	7.1		01/02/88		1.505	-5.0	-3.25
4011	TE	7.2		01/02/88		1.256	-6.5	-3.40
4012	TE	7.3		01/02/88		1.643	-5.5	-3.50
4013	TE	7.4		01/02/88		1.636	-8.5	-3.50
4014	TE	8.1		01/02/88		1.429	-7.5	-3.50
4015	TE	8.2		01/02/88		1.030	-3.5	-3.05
4016	TE	8.3		01/02/88		1.536	-4.0	-2.95
4017	TE	8.4		01/02/88		1.420	-5.0	-3.25
6057	TE	3.1		07/22/88	0.4167	0.188	-10.5	-2.35
6062	TE	4.3		07/22/88	0.4167	0.289	-14.0	-3.00
6063	TE	4.4		07/22/88	0.4167	0.261	-11.0	-2.75
6066	TE	5.3		07/22/88	0.4167	0.274	-13.0	-3.00
6068	TE	6.1		07/22/88	0.4167	0.366	-13.0	-3.10
6077	TE	8.2		07/22/88	0.4167	0.135	-11.0	-2.65
6104	TE	3.1		07/23/88	0.4167	1.395	-48.0	-8.20

6105	TE	3.2		07/23/88	0.4167	1.378	-47.5	-8.20
6110	TE	4.3		07/23/88	0.4167	0.972	-48.0	-8.20
6114	TE	5.3		07/23/88	0.4167	1.268	-47.5	-8.20
6116	TE	6.1		07/23/88	0.4167	1.278	-48.0	-8.15
6122	TE	7.3		07/23/88	0.4167	1.216	-48.0	-8.20
6602	TE	3.1		08/30/88	0.8750	2.456	-15.5	-3.50
6603	TE	3.2		08/30/88	0.8750	2.497	-18.0	-4.25
6607	TE	4.2		08/30/88	0.8750	2.855	-17.0	-4.20
6612	TE	5.3		08/30/88	0.8750	2.509	-15.5	-3.70
6614	TE	6.1		08/30/88	0.8750	2.464	-17.0	-3.85
6620	TE	7.3		08/30/88	0.8750	2.526	-18.5	-4.15
7250	TE	3.2		11/01/88	0.5000	1.202	-6.0	-3.45
7252	TE	3.4		11/01/88	0.5000	1.141	-7.0	-3.75
7255	TE	4.3		11/01/88	0.5000	1.217	-9.0	-3.70
7259	TE	5.3		11/01/88	0.5000	1.060	-7.0	-3.55
7261	TE	6.1		11/01/88	0.5000	1.188	-8.5	-3.65
7270	TE	8.2		11/01/88	0.5000	0.776	-6.0	-3.25
7355	TE	1.1		11/16/88	0.5000	0.477	3.0	-1.05
7356	TE	1.2		11/16/88	0.5000	0.352	1.5	-1.25
7357	TE	1.3		11/16/88	0.5000	0.398	2.5	-0.95
7358	TE	1.4		11/16/88	0.5000	0.369	3.0	-1.20
7359	TE	2.1		11/16/88	0.5000	0.331	3.5	-1.15
7360	TE	2.2		11/16/88	0.5000	0.307	1.5	-1.25
7361	TE	2.3		11/16/88	0.5000	0.366	2.0	-1.10
7362	TE	2.4		11/16/88	0.5000	0.471	2.0	-1.20
7363	TE	3.1		11/16/88	0.5000	0.411	2.0	-1.35
7364	TE	3.2		11/16/88	0.5000	0.460	1.5	-1.40
7365	TE	3.3		11/16/88	0.5000	0.343	3.0	-1.15
7366	TE	3.4		11/16/88	0.5000	0.391	2.0	-0.95
7367	TE	4.1		11/16/88	0.5000	0.363	2.5	-1.05
7368	TE	4.2		11/16/88	0.5000	0.286	2.0	-1.05

7369	TE	4.3		11/16/88	0.5000	0.409	1.0	-1.30
7370	TE	4.4		11/16/88	0.5000	0.463	2.5	-1.20
7372	TE	5.2		11/16/88	0.5000	0.295	3.0	-1.00
7373	TE	5.3		11/16/88	0.5000	0.242	5.0	-0.80
7374	TE	5.4		11/16/88	0.5000	0.275	6.0	0.25
7375	TE	6.1		11/16/88	0.5000	0.454	4.0	-1.20
7376	TE	6.2		11/16/88	0.5000	0.358	2.0	-1.10
7377	TE	6.3		11/16/88	0.5000	0.184	4.5	-0.55
7378	TE	6.4		11/16/88	0.5000	0.378	2.0	-1.10
7379	TE	7.1		11/16/88	0.5000	0.420	1.0	-1.05
7380	TE	7.2		11/16/88	0.5000	0.341	6.0	-1.10
7381	TE	7.3		11/16/88	0.5000	0.407	1.5	-1.00
7382	TE	7.4		11/16/88	0.5000	0.348	2.0	-1.10
7384	TE	8.2		11/16/88	0.5000	0.345	0.5	-1.20
7386	TE	8.4		11/01/88	0.5000	0.264	3.0	-1.05
7548	TE	1.1		01/03/89	0.6250	1.496	-6.0	-2.65
7549	TE	1.2		01/03/89	0.6250	1.505	-7.5	-2.70
7550	TE	1.3		01/03/89	0.6250	1.496	-6.0	-2.20
7551	TE	1.4		01/03/89	0.6250	1.555	-7.0	-2.65
7552	TE	2.1		01/03/89	0.6250	1.456	-9.5	-2.70
7553	TE	2.2		01/03/89	0.6250	1.277	-7.0	-2.25
7554	TE	2.3		01/03/89	0.6250	1.607	-5.5	-2.60
7555	TE	2.4		01/03/89	0.6250	1.453	-9.5	-2.60
7556	TE	3.1		01/03/89	0.6250	1.491	-7.0	-2.70
7557	TE	3.2		01/03/89	0.6250	1.481	-6.5	-2.55
7558	TE	3.3		01/03/89	0.6250	1.421	-7.0	-2.45
7559	TE	3.4		01/03/89	0.6250	1.642	-6.5	-2.55
7560	TE	4.1		01/03/89	0.6250	1.535	-6.5	-2.65
7561	TE	4.2		01/03/89	0.6250	1.357	-7.5	-2.45
7562	TE	4.3		01/03/89	0.6250	1.648	-7.0	-2.65
7563	TE	4.4		01/03/89	0.6250	1.599	-7.0	-2.55

7564	TE	5.1		01/03/89	0.6250	1.059	-5.0	-2.40
7565	TE	5.2		01/03/89	0.6250	1.178	-4.5	-2.40
7566	TE	5.3		01/03/89	0.6250	1.281	-2.0	-2.05
7567	TE	5.4		01/03/89	0.6250	1.162	-7.5	-2.30
7568	TE	6.1		01/03/89	0.6250	1.473	-3.5	-1.95
7569	TE	6.2		01/03/89	0.6250	1.286	-7.0	-2.45
7570	TE	6.3		01/03/89	0.6250	1.517	-5.0	-2.15
7571	TE	6.4		01/03/89	0.6250	1.501	-5.0	-2.30
7572	TE	7.1		01/03/89	0.6250	1.425	-4.0	-2.00
7573	TE	7.2		01/03/89	0.6250	1.316	-8.0	-2.50
7574	TE	7.3		01/03/89	0.6250	1.436	-3.0	-2.00
7575	TE	7.4		01/03/89	0.6250	1.581	-6.0	-2.35
7577	TE	8.2		01/03/89	0.6250	1.303	-3.0	-2.15
7578	TE	8.3		01/03/89	0.6250	1.471	-2.5	-1.80
7579	TE	8.4		01/03/89	0.6250	1.267	-3.5	-2.25
7840	TE	1.4		02/28/89	0.4167	1.484	-36.0	-6.30
7843	TE	2.3		02/28/89	0.4167	1.887	-35.0	-6.50
7850	TE	4.2		02/28/89	0.4167	1.545	-34.5	-6.50
7855	TE	5.3		02/28/89	0.4167	1.546	-35.5	-6.50
7862	TE	7.2		02/28/89	0.4167	1.418	-32.0	-6.50
7866	TE	8.2		02/28/89	0.4167	1.156	-34.0	-6.40
7936	TE	1.3		03/22/89	0.4167	3.687	-28.5	-5.20
7939	TE	2.2		03/22/89	0.4167	3.014	-32.0	-5.20
7944	TE	3.3		03/22/89	0.4167	3.250	-31.0	-5.10
7951	TE	5.2		03/22/89	0.4167	2.757	-31.0	-4.80
7960	TE	7.3		03/22/89	0.4167	4.080	-30.5	-5.00
7965	TE	8.4		03/22/89	0.4167	2.881	-33.0	-5.20
8011	TE	1.1		03/30/89	0.4167	0.892	-14.5	-3.10
8012	TE	1.2		03/30/89	0.4167	0.988	-14.0	-3.25
8013	TE	1.3		03/30/89	0.4167	1.006	-17.5	-3.30
8014	TE	1.4		03/30/89	0.4167	0.984	-15.0	-3.25

8015	TE	2.1		03/30/89	0.4167	0.892	-16.5	-3.35
8016	TE	2.2		03/30/89	0.4167	0.867	-14.0	-3.25
8017	TE	2.3		03/30/89	0.4167	1.042	-14.5	-3.30
8018	TE	2.4		03/30/89	0.4167	0.979	-16.0	-3.40
8019	TE	3.1		03/30/89	0.4167	1.108	-15.0	-3.30
8020	TE	3.2		03/30/89	0.4167	0.979	-15.0	-3.25
8021	TE	3.3		03/30/89	0.4167	0.943	-16.5	-3.20
8022	TE	3.4		03/30/89	0.4167	1.088	-17.0	-3.30
8023	TE	4.1		03/30/89	0.4167	0.999	-16.0	-3.20
8024	TE	4.2		03/30/89	0.4167	0.879	-16.0	-3.35
8025	TE	4.3		03/30/89	0.4167	1.092	-17.5	-3.35
8026	TE	4.4		03/30/89	0.4167	1.032	-15.5	-3.35
8027	TE	5.1		03/30/89	0.4167	0.847	-13.0	-3.05
8028	TE	5.2		03/30/89	0.4167	0.710	-12.5	-3.05
8029	TE	5.3		03/30/89	0.4167	0.823	-12.0	-3.00
8030	TE	5.4		03/30/89	0.4167	0.713	-14.0	-3.15
8031	TE	6.1		03/30/89	0.4167	0.913	-12.0	-3.00
8032	TE	6.2		03/30/89	0.4167	0.868	-13.0	-3.20
8033	TE	6.3		03/30/89	0.4167	0.944	-13.0	-3.20
8034	TE	6.4		03/30/89	0.4167	0.932	-14.0	-3.15
8035	TE	7.1		03/30/89	0.4167	1.316	-12.5	-3.15
8036	TE	7.2		03/30/89	0.4167	0.805	-12.5	-3.10
8037	TE	7.3		03/30/89	0.4167	1.019	-11.5	-3.00
8038	TE	7.4		03/30/89	0.4167	1.117	-15.0	-3.20
8039	TE	8.1		03/30/89	0.4167	0.848	-12.5	-3.05
8040	TE	8.2		03/30/89	0.4167	0.872	-13.5	-3.00
8041	TE	8.3		03/30/89	0.4167	1.103	-13.0	-3.00
8042	TE	8.4		03/30/89	0.4167	1.030	-16.0	-3.15
8134	TE	2.2		04/11/89	0.4167	0.785	-23.5	-3.50
8137	TE	3.1		04/11/89	0.4167	1.698	-25.0	-3.60
8143	TE	4.3		04/11/89	0.4167	1.463	-26.0	-3.60

8145	TE	5.1		04/11/89	0.4167	0.826	-23.5	-3.00
8148	TE	5.4		04/11/89	0.4167	1.195	-26.5	-3.80
8159	TE	8.3		04/11/89	0.4167	1.188	-23.5	-3.70
8217	TE	3.1		05/02/89	0.4167	2.958	-45.0	-7.25
8218	TE	3.2		05/02/89	0.4167	4.302	-47.5	-7.40
8223	TE	4.3		05/02/89	0.4167	4.339	-43.5	-7.20
8227	TE	5.3		05/02/89	0.4167	2.773	-44.5	-7.25
8229	TE	6.1		05/02/89	0.4167	3.133	-45.0	-7.05
8235	TE	7.3		05/02/89	0.4167	2.909	-45.0	-7.15
8631	TE	3.1		06/06/89	0.4167	0.823	-12.0	-2.95
8632	TE	3.2		06/06/89	0.4167	0.797	-11.0	-2.60
8637	TE	4.3		06/06/89	0.4167	0.664	-11.0	-2.55
8641	TE	5.3		06/06/89	0.4167	0.510	-10.5	-2.70
8643	TE	6.1		06/06/89	0.4167	0.687	-10.0	-2.85
8649	TE	7.3		06/06/89	0.4167	0.488	-9.5	-2.60
8690	TE	1.1		06/21/89	0.4167	4.401	-21.0	-3.70
8694	TE	2.1		06/21/89	0.4167	4.368	-46.0	-6.50
8696	TE	2.3		06/21/89	0.4167	4.374	-50.0	-7.00
8698	TE	3.1		06/21/89	0.4167	4.373	-45.0	-6.80
8699	TE	3.2		06/21/89	0.4167	4.359	-44.5	-6.90
8703	TE	4.2		06/21/89	0.4167	5.728	-17.0	-2.80
8704	TE	4.3		06/21/89	0.4167	4.373	-47.0	-7.25
8708	TE	5.3		06/21/89	0.4167	4.382	-46.0	-7.10
8709	TE	5.4		06/21/89	0.4167	5.502	-13.5	-2.20
8710	TE	6.1		06/21/89	0.4167	4.389	-46.0	-6.95
8711	TE	6.2		06/21/89	0.4167	7.394	-41.5	-6.10
8715	TE	7.2		06/21/89	0.4167	5.513	-38.5	-6.00
8716	TE	7.3		06/21/89	0.4167	5.285	-36.0	-5.65
8720	TE	8.3		06/21/89	0.4167	4.504	-46.0	-6.70
8826	TE	1.2		07/03/89	0.5417	2.029	-13.5	-3.55
8827	TE	1.3		07/03/89	0.5417	1.789	-11.5	-3.55

8828	TE	1.4		07/03/89	0.5417	2.141	-13.0	-3.65
8829	TE	2.1		07/03/89	0.5417	3.648	-12.0	-3.50
8830	TE	2.2		07/03/89	0.5417	1.450	-14.0	-3.60
8831	TE	2.3		07/03/89	0.5417	2.526	-13.0	-3.60
8832	TE	2.4		07/03/89	0.5417	2.943	-14.0	-3.60
8833	TE	3.1		07/03/89	0.5417	1.809	-14.0	-3.65
8834	TE	3.2		07/03/89	0.5417	2.756	-12.5	-3.50
8835	TE	3.3		07/03/89	0.5417	1.758	-12.0	-3.50
8836	TE	3.4		07/03/89	0.5417	2.495	-13.5	-3.50
8837	TE	4.1		07/03/89	0.5417	2.417	-13.0	-3.55
8838	TE	4.2		07/03/89	0.5417	3.336	-13.5	-3.55
8839	TE	4.3		07/03/89	0.5417	2.287	-14.5	-3.55
8840	TE	4.4		07/03/89	0.5417	3.118	-13.0	-3.50
8841	TE	5.1		07/03/89	0.5417	1.764	-13.5	-3.60
8842	TE	5.2		07/03/89	0.5417	1.782	-13.0	-3.50
8843	TE	5.3		07/03/89	0.5417	2.571	-14.5	-3.60
8844	TE	5.4		07/03/89	0.5417	1.659	-14.0	-3.50
8845	TE	6.1		07/03/89	0.5417	2.246	-13.0	-3.60
8846	TE	6.2		07/03/89	0.5417	2.116	-13.5	-3.45
8847	TE	6.3		07/03/89	0.5417	2.343	-14.0	-3.60
8848	TE	6.4		07/03/89	0.5417	2.255	-12.5	-3.55
8849	TE	7.1		07/03/89	0.5417	2.159	-13.5	-3.50
8850	TE	7.2		07/03/89	0.5417	1.935	-12.5	-3.60
8851	TE	7.3		07/03/89	0.5417	2.075	-13.0	-3.65
8852	TE	7.4		07/03/89	0.5417	2.529	-13.5	-3.60
8853	TE	8.1		07/03/89	0.5417	2.661	-12.5	-3.65
8854	TE	8.2		07/03/89	0.5417	2.102	-13.5	-3.65
8855	TE	8.3		07/03/89	0.5417	2.679	-13.0	-3.55
8856	TE	8.4		07/03/89	0.5417	2.299	-13.0	-3.65
8919	TE	3.1		07/20/89	0.5000	2.471	-12.5	-3.20
8920	TE	3.2		07/20/89	0.5000	3.135	-13.0	-3.20

8925	TE	4.3		07/20/89	0.5000	2.281	-12.5	-3.25
8927	TE	5.1		07/20/89	0.5000	2.330	-10.0	-3.05
8931	TE	6.1		07/20/89	0.5000	2.322	-12.5	-3.05
8937	TE	7.3		07/20/89	0.5000	1.950	-11.0	-3.15
5608	TI	110	A	05/10/88	0.1847	0.145	-5.0	-0.95
5609	TI	110	B	05/10/88	0.2896	0.163	-6.0	-1.60
5610	TI	110	C	05/10/88	0.3125	0.156	-14.0	-2.45
5611	TI	110	D	05/10/88	0.3299	0.157	-19.0	-3.30
5612	TI	110	E	05/10/88	0.3521	0.153	-21.0	-3.55
5613	TI	110	F	05/10/88	0.3757	0.164	-26.0	-3.75
5614	TI	110	G	05/10/88	0.3889	0.146	-36.5	-4.65
5615	TI	110	H	05/10/88	0.4118	0.133	-40.0	-5.10
5647	TI	110	A	05/15/88	0.7153	0.147	-18.5	-3.30
5648	TI	110	B	05/15/88	0.7222	0.151	-31.5	-5.60
5649	TI	110	C	05/15/88	0.7257	0.155	-37.0	-6.60
5650	TI	110	D	05/15/88	0.7306	0.152	-39.0	-6.80
5651	TI	110	E	05/15/88	0.7319	0.150	-38.0	-6.60
5652	TI	110	F	05/15/88	0.7326	0.160	-41.0	-6.85
5653	TI	110	G	05/15/88	0.7340	0.150	-42.5	-7.05
5654	TI	110	H	05/15/88	0.7361	0.175	-42.5	-6.90
5655	TI	110	I	05/15/88	0.7396	0.342	-43.5	-6.90
5656	TI	110	J	05/15/88	0.7431	0.280	-48.5	-7.50
5657	TI	110	K	05/15/88	0.7500	0.242	-49.5	-7.55
5767	TI	110	A	06/02/88	0.7951	0.160	25.0	1.60
5768	TI	110	B	06/02/88	0.7972	0.164	25.5	1.35
5769	TI	110	C	06/02/88	0.7993	0.162	26.5	0.75
5770	TI	110	D	06/02/88	0.8021	0.150	27.5	0.85
5771	TI	110	E	06/02/88	0.8125	0.125	27.5	1.60
5796	TI	110	A	06/09/88	0.6333	0.170	-1.0	-1.60
5797	TI	110	B	06/09/88	0.6340	0.159	-8.0	-2.40
5798	TI	110	C	06/09/88	0.6347	0.147	-5.5	-2.25

5799	TI	110	D	06/09/88	0.6361	0.164	-4.5	-2.20
5896	TI	110	A	06/18/88	0.8424	0.164	10.0	-0.20
5897	TI	110	B	06/19/88	0.7667	0.165	5.5	-1.35
5898	TI	110	C	06/19/88	0.7681	0.148	6.5	-1.35
5899	TI	110	D	06/19/88	0.7701	0.157	6.5	-1.05
5900	TI	110	E	06/19/88	0.7715	0.160	7.5	-0.60
5901	TI	110	F	06/19/88	0.7722	0.165	6.5	-1.10
5902	TI	110	G	06/19/88	0.7729	0.166	0.5	-1.55
5903	TI	110	H	06/19/88	0.7743	0.181	-3.5	-1.25
5904	TI	110	I	06/19/88	0.7750	0.138	-1.0	-1.15
6210	TI	110	A	07/27/88	0.5597	0.159	-13.0	-3.00
6211	TI	110	B	07/27/88	0.5604	0.158	-13.5	-3.45
6212	TI	110	C	07/27/88	0.5611	0.164	-15.0	-3.70
6213	TI	110	D	07/27/88	0.5618	0.164	-17.0	-4.00
6214	TI	110	E	07/27/88	0.5625	0.156	-19.0	-4.10
6215	TI	110	F	07/27/88	0.5632	0.152	-19.5	-4.15
6216	TI	110	G	07/27/88	0.5681	0.146	-19.5	-3.85
6217	TI	110	H	07/27/88	0.5694	0.160	-16.0	-3.25
6218	TI	110	I	07/27/88	0.5806	0.291	-16.0	-3.15
6219	TI	110	J	07/27/88	0.5903	0.309	-15.0	-2.90
6220	TI	110	K	07/27/88	0.6521	0.709	-16.5	-3.15
6221	TI	110	L	07/27/88	0.7139	0.676	-20.0	-3.50
6657	TI	110	A	09/03/88	0.7757	0.176		-3.60
6658	TI	110	B	09/03/88	0.7771	0.185		-4.33
6659	TI	110	C	09/03/88	0.7778	0.187		-4.58
6660	TI	110	D	09/03/88	0.7785	0.166		-5.29
6661	TI	110	E	09/03/88	0.7792	0.184		-5.66
6662	TI	110	F	09/03/88	0.7799	0.169		-5.98
6663	TI	110	G	09/03/88	0.7813	0.185		-5.33
6664	TI	110	H	09/03/88	0.7840	0.170		-4.68
6666	TI	110	I	09/03/88	0.7986	0.313		-4.61

6665	TI	110	J	09/03/88	0.8056	0.343		-3.96
6667	TI	110	K	09/03/88	0.8542	0.714		-4.75
6759	TI	110	A	09/04/88	0.7361	0.195	-88.0	-11.00
6760	TI	110	B	09/04/88	0.7535	0.182	-96.0	-13.30
6761	TI	110	C	09/04/88	0.7708	0.187	-96.0	-13.30
6762	TI	110	D	09/04/88	0.7917	0.190	-96.5	-13.40
6763	TI	110	E	09/04/88	0.8125	0.163	-97.0	-13.70
6764	TI	110	F	09/04/88	0.8229	0.168	-96.0	-13.25
6765	TI	110	G	09/04/88	0.8333	0.183	-96.5	-13.80
6766	TI	110	H	09/04/88	0.8472	0.142	-77.5	-8.75
6767	TI	110	I	09/04/88	0.8576	0.275	-98.5	-13.70
6768	TI	110	J	09/04/88	0.8750	0.334	-102.5	-14.55
6769	TI	110	K	09/04/88	0.9063	0.220	-104.5	-14.75
6983	TI	110	A	09/16/88	0.7083	0.188	-9.0	-3.60
6984	TI	110	B	09/16/88	0.7431	0.194	-14.5	-4.15
6985	TI	110	C	09/16/88	0.7708	0.190	-11.5	-3.95
6986	TI	110	D	09/16/88	0.9097	0.194	-13.0	-4.15
6987	TI	110	E	09/17/88	0.1042	0.179	-8.0	-3.55
6988	TI	110	F	09/17/88	0.1458	0.179	-9.0	-3.85
6989	TI	110	G	09/17/88	0.1771	0.190	-6.5	-3.75
6990	TI	110	H	09/17/88	0.1924	0.141	-8.0	-3.80
6991	TI	110	I	09/17/88	0.1979	0.281	-9.5	-3.95
6992	TI	110	J	09/17/88	0.2604	0.336	-11.5	-4.05
6993	TI	110	K	09/17/88	0.3750	0.093	-11.0	-3.85
7122	TI	110	A	10/01/88	0.9479	0.191	-6.5	-3.30
7123	TI	110	B	10/01/88	0.9549	0.183	-8.0	-3.35
7124	TI	110	C	10/01/88	0.9576	0.196	-10.0	-3.60
7125	TI	110	D	10/01/88	0.9618	0.163	-11.5	-3.80
7126	TI	110	E	10/01/88	0.9646	0.171	-16.0	-4.15
7127	TI	110	F	10/01/88	0.9667	0.161	-15.5	-4.20
7128	TI	110	G	10/01/88	0.9688	0.174	-20.0	-4.85

7129	TI	110	H	10/01/88	0.9931	0.174	-18.0	-4.50
7130	TI	110	I	10/02/88	0.0174	0.346	-6.5	-3.25
7131	TI	110	J	10/02/88	0.3819	0.317	-6.5	-3.20
7132	TI	110	K	10/02/88	0.3993	0.698	-30.5	-6.20
7133	TI	110	L	10/02/88	0.4375	0.323	-48.5	-8.35
7604	TI	110	A	01/03/89	0.3132	0.173	8.5	-0.55
7605	TI	110	B	01/03/89	0.3299	0.173	9.0	-1.10
7606	TI	110	C	01/03/89	0.3382	0.174	1.5	-1.95
7607	TI	110	D	01/03/89	0.3479	0.174	-6.5	-2.65
7608	TI	110	E	01/03/89	0.3639	0.169	-6.5	-2.75
7609	TI	110	F	01/03/89	0.3854	0.162	-13.0	-3.05
7610	TI	110	G	01/03/89	0.5847	0.180	-8.0	-2.75
7611	TI	110	H	01/03/89	0.5868	0.163	-9.0	-3.15
7612	TI	110	I	01/03/89	0.5972	0.129	-15.5	-3.45
7895	TI	110	A	02/28/89	0.1528	0.167	-9.5	-4.10
7896	TI	110	B	02/28/89	0.1590	0.164	-20.0	-5.70
7897	TI	110	C	02/28/89	0.1632	0.163	-24.0	-6.30
7898	TI	110	D	02/28/89	0.1875	0.164	-23.0	-6.35
7899	TI	110	E	02/28/89	0.2153	0.174	-30.5	-6.65
7900	TI	110	F	02/28/89	0.2326	0.161	-43.0	-8.00
7901	TI	110	G	02/28/89	0.2569	0.193	-48.5	-8.15
7902	TI	110	H	02/28/89	0.2813	0.133	-55.0	-8.50
8066	TI	110	A	03/30/89	0.1111	0.170	-3.0	-1.75
8067	TI	110	B	03/30/89	0.1146	0.162	-10.5	-3.00
8068	TI	110	C	03/30/89	0.1458	0.144	-10.5	-3.05
8069	TI	110	D	03/30/89	0.1736	0.148	-13.5	-3.00
8070	TI	110	E	03/30/89	0.1875	0.143	-17.5	-3.35
8071	TI	110	F	03/30/89	0.2188	0.112	-21.0	-3.70
3974	TI	610	A	01/01/88	0.3799	0.170	6.0	-1.55
3975	TI	610	B	01/01/88	0.6208	0.157	13.5	-0.90
3976	TI	610	C	01/01/88	0.7056	0.165	18.5	-0.70

3977	TI	610	D	01/01/88	0.7722	0.157	5.5	-2.35
3978	TI	610	E	01/01/88	0.8368	0.188	-10.5	-4.35
3979	TI	610	F	01/01/88	0.8597	0.155	-14.5	-4.50
3980	TI	610	G	01/02/88	0.0618	0.183	-19.0	-4.65
3981	TI	610	H	01/02/88	0.1847	0.165	-36.5	-5.75
3982	TI	610	I	01/03/88	0.1861	0.193	-54.0	-7.85
3983	TI	610	J	01/03/88	0.2625	0.351	-79.5	-11.65
3984	TI	610	K	01/03/88	0.4542	0.673	-96.0	-13.60
3985	TI	610	L	01/03/88	0.8542	0.699	-84.0	-12.55
5602	TI	610	A	05/10/88	0.1882	0.168	-3.5	-1.35
5603	TI	610	B	05/10/88	0.2958	0.188	-9.5	-2.30
5604	TI	610	C	05/10/88	0.3139	0.159	-19.5	-3.50
5605	TI	610	D	05/10/88	0.3319	0.166	-25.0	-3.65
5606	TI	610	E	05/10/88	0.3358	0.171	-32.5	-4.40
5607	TI	610	F	05/10/88	0.3396	0.069	-44.0	-5.40
5608	TI	610	A	05/15/88	0.7188	0.185	-13.5	-2.75
5658	TI	610	B	05/15/88	0.7243	0.183	-25.5	-5.05
5659	TI	610	C	05/15/88	0.7285	0.153	-36.0	-6.55
5660	TI	610	D	05/15/88	0.7306	0.163	-44.0	-7.05
5661	TI	610	E	05/15/88	0.7326	0.167	-48.0	-7.40
5662	TI	610	F	05/15/88	0.7361	0.163	-51.0	-7.80
5663	TI	610	G	05/15/88	0.7396	0.159	-52.0	-8.05
5664	TI	610	H	05/15/88	0.7576	0.040	-53.5	-8.05
5665	TI	610	A	06/02/88	0.7951	0.156	24.5	1.85
5772	TI	610	B	06/02/88	0.7972	0.176	27.5	1.40
5773	TI	610	C	06/02/88	0.8007	0.193	23.5	0.95
5774	TI	610	A	06/09/88	0.6333	0.133	3.5	-0.75
5801	TI	610	B	06/09/88	0.6347	0.169	-6.5	-2.55
5802	TI	610	C	06/09/88	0.6375	0.071	-8.0	-2.70
5803	TI	610	A	06/18/88	0.8424	0.179	6.5	-0.90
5905	TI	610	B	06/19/88	0.7667	0.183	5.5	-1.25
5906	TI	610						

5907	TI	610	C	06/19/88	0.7688	0.183	5.5	-1.30
5908	TI	610	D	06/19/88	0.7708	0.180	2.0	-1.40
5909	TI	610	E	06/19/88	0.7715	0.184	2.0	-1.60
5910	TI	610	F	06/19/88	0.7722	0.178	2.0	-1.25
5911	TI	610	G	06/19/88	0.7729	0.183	1.0	-1.60
5912	TI	610	H	06/19/88	0.7750	0.162	-5.0	-2.05
6222	TI	610	A	07/27/88	0.5590	0.184	-13.5	-3.50
6223	TI	610	B	07/27/88	0.5604	0.168	-21.5	-4.30
6224	TI	610	C	07/27/88	0.5611	0.128	-15.5	-3.35
6225	TI	610	D	07/27/88	0.5618	0.177	-18.0	-3.95
6226	TI	610	E	07/27/88	0.5625	0.119	-19.5	-3.95
6227	TI	610	F	07/27/88	0.5646	0.163	-21.0	-4.35
6228	TI	610	G	07/27/88	0.5681	0.184	-19.0	-4.15
6229	TI	610	H	07/27/88	0.5701	0.182	-15.0	-3.65
6230	TI	610	I	07/27/88	0.5743	0.310	-16.5	-3.55
6231	TI	610	J	07/27/88	0.6465	0.320	-17.0	-3.45
6232	TI	610	K	07/27/88	0.6549	0.624	-16.5	-3.25
6233	TI	610	L	07/27/88	0.7111	0.710	-20.5	-3.90
6669	TI	610	A	09/03/88	0.7757	0.187		-1.80
6670	TI	610	B	09/03/88	0.7771	0.191		-4.55
6671	TI	610	C	09/03/88	0.7778	0.148		-2.39
6672	TI	610	D	09/03/88	0.7785	0.191		-3.65
6673	TI	610	E	09/03/88	0.7792	0.169		-3.94
6674	TI	610	F	09/03/88	0.7799	0.183		-4.16
6675	TI	610	G	09/03/88	0.7813	0.178		-3.93
6676	TI	610	H	09/03/88	0.7840	0.199		-4.08
6677	TI	610	I	09/03/88	0.7986	0.353		-4.74
6678	TI	610	J	09/03/88	0.8125	0.325		-4.70
6679	TI	610	K	09/03/88	0.8646	0.614		-3.99
6680	TI	610	L	09/03/88	0.8958	0.720		-6.07
6681	TI	610	M	09/03/88	0.9236	0.363		-7.61

6770	TI	610	A	09/04/88	0.7396	0.152	-77.0	-10.25
6771	TI	610	B	09/04/88	0.7569	0.179	-87.5	-10.80
6772	TI	610	C	09/04/88	0.7778	0.168	-93.5	-12.30
6773	TI	610	D	09/04/88	0.7986	0.137	-93.5	-12.3
6774	TI	610	E	09/04/88	0.8194	0.185	-95.0	-12.8
6775	TI	610	F	09/04/88	0.8299	0.137	-95.0	-12.8
6776	TI	610	G	09/04/88	0.8438	0.145	-93.5	-12.3
6777	TI	610	H	09/04/88	0.8542	0.170	-93.5	-12.3
6778	TI	610	I	09/04/88	0.8646	0.292	-101.0	-14.05
6779	TI	610	J	09/04/88	0.9063	0.256	-103.5	-14.5
6994	TI	610	A	09/16/88	0.7083	0.197	-9.0	-3.5
6995	TI	610	B	09/16/88	0.7431	0.186	-13.5	-4.2
6996	TI	610	C	09/16/88	0.7708	0.180	-11.5	-3.95
6997	TI	610	D	09/16/88	0.9097	0.158	-11.5	-4.2
6998	TI	610	E	09/17/88	0.1042	0.197	-9.5	-4.05
6999	TI	610	F	09/17/88	0.1458	0.131	-9.5	-3.9
7000	TI	610	G	09/17/88	0.1771	0.165	-7.5	-3.75
7001	TI	610	H	09/17/88	0.1924	0.166	-7.5	-3.8
7002	TI	610	I	09/17/88	0.1979	0.476	-11.5	-4.2
7003	TI	610	J	09/17/88	0.2604	0.314	-12.5	-4.05
7004	TI	610	K	09/17/88	0.3750	0.093	-9.5	-3.45
7134	TI	610	A	10/01/88	0.9479	0.169	-5.0	-2.95
7135	TI	610	B	10/01/88	0.9528	0.183	-7.5	-3.25
7136	TI	610	C	10/01/88	0.9569	0.143	-8.0	-3.55
7137	TI	610	D	10/01/88	0.9611	0.185	-18.0	-4.5
7138	TI	610	E	10/01/88	0.9639	0.162	-18.0	-4.35
7139	TI	610	F	10/01/88	0.9653	0.168	-21.0	-4.55
7140	TI	610	G	10/01/88	0.9667	0.166	-20.0	-4.4
7141	TI	610	H	10/01/88	0.9688	0.179	-18.0	-3.95
7142	TI	610	I	10/01/88	0.9931	0.348	-7.0	-3
7143	TI	610	J	10/02/88	0.0208	0.320	-16.5	-4.15

7144	TI	610	K	10/02/88	0.3958	0.631	-23.0	-4.9
7145	TI	610	L	10/02/88	0.4167	0.650	-35.0	-6.4
7613	TI	610	A	01/03/89	0.3299	0.161	10.5	-0.25
7614	TI	610	B	01/03/89	0.3382	0.172	6.5	-1.3
7615	TI	610	C	01/03/89	0.3479	0.173	-7.5	-2.9
7616	TI	610	D	01/03/89	0.3639	0.140	-13.0	-3.4
7617	TI	610	E	01/03/89	0.3854	0.194	-10.5	-3.05
7618	TI	610	F	01/03/89	0.5847	0.133	-9.5	-2.85
7619	TI	610	G	01/03/89	0.5868	0.159	-12.0	-3.05
7620	TI	610	H	01/03/89	0.5972	0.132	-16.5	-3.45
7903	TI	610	A	02/28/89	0.1528	0.178	-5.0	-3.4
7904	TI	610	B	02/28/89	0.1590	0.163	-13.5	-5.05
7905	TI	610	C	02/28/89	0.1632	0.166	-16.5	-5.55
7906	TI	610	D	02/28/89	0.1875	0.152	-24.5	-6.55
7907	TI	610	E	02/28/89	0.2153	0.175	-29.5	-6.5
7908	TI	610	F	02/28/89	0.2326	0.163	-40.0	-7.6
7909	TI	610	G	02/28/89	0.2569	0.149	-53.5	-8.6
7910	TI	610	H	02/28/89	0.2813	0.069	-62.0	-9.05
8072	TI	610	A	03/30/89	0.1111	0.180	-1.5	-1.65
8073	TI	610	B	03/30/89	0.1146	0.194	-12.5	-3.35
8074	TI	610	C	03/30/89	0.1389	0.181	-14.0	-3.15
8075	TI	610	D	03/30/89	0.1701	0.180	-23.5	-3.9
8076	TI	610	E	03/30/89	0.2188	0.051	-31.0	-4.65
519	PE	900		05/20/86	0.3750	4.051	-24.5	-4.5
597	PE	900		07/01/86	0.6806	0.358	-21.5	-4.05
636	PE	900		07/17/86	0.8021	0.551	-13.5	-2.95
721	PE	900		07/27/86	0.0000	0.287	7	0.05
1050	PE	900		10/25/86	0.6667	5.979	-5.5	-3.45
1170	PE	900		11/05/86	0.2917	0.147	-15	-3.25
1171	PE	900		11/07/86	0.4375	0.117	-5.5	-1.75
1172	PE	900		11/09/86	0.6667	0.107	3.5	-1.25

1183	PE	900		11/11/86	0.3438	0.333	-11.5	-3.25
1176	PE	900		11/11/86	0.3958	0.295	9	-1.25
1175	PE	900		11/11/86	0.7083	0.267	-7.5	-2.8
1206	PE	900		11/20/86	0.4167	4.191	-58.5	-8.95
1536	PE	900		12/10/86	0.5833	0.424	-39	-7
1569	PE	900		12/13/86	0.0000	2.296	-52.5	-8.3
1605	PE	990		12/23/86	0.5764	1.016	-64	-9.55
1625	PE	900		12/24/86	0.6253	1.981	-22.5	-5.5
1694	PE	900		01/02/87	0.3125	0.470	-111	-15.3
1695	PE	900		01/05/87	0.0000	0.071	-61.5	-8.4
1724	PE	900		01/11/87	0.5938	0.340	-15	-4.3
1737	PE	900		01/15/87	0.4063	0.325	-35.5	-4.3
1775	PE	900		01/16/87	0.5104	0.719	-57.5	-8.85
1776	PE	900		01/19/87	0.2500	6.134	-19.5	-4.2
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2000	PE	900		02/22/87	0.8750	0.818	-57	-9.05
2040	PE	900		02/27/87	0.5826	3.846	-43	-7.55
2082	PE	900		02/28/87	0.8333	4.587	-23	-4.9
2201	PE	900		03/19/87	0.0417	1.600	-16	-4.6
2219	PE	900		03/25/87	0.0000	0.389	-1.5	-2.85
2220	PE	900		03/25/87	0.3333	0.165	-3	-3.25
2223	PE	900		03/27/87	0.7500	0.648	-28.5	-4.6
2224	PE	900		03/30/87	0.1250	2.913	-47.5	-7.25
2279	PE	900		04/03/87	0.4653	1.242	-39.5	-8
2307	PE	900		04/11/87	0.2813	0.236	2.5	-0.9
2331	PE	900		04/15/87	0.1708	0.295	-3.5	-1.85
2382	PE	900		05/01/87	0.9361	0.254	16	2.25
2373	PE	900		05/04/87	0.7500	0.457	4.5	-0.7
2410	PE	900		05/11/87	0.5729	0.676	-5	-2.35
2433	PE	900		05/13/87	0.0417	1.171	-20.5	-4.2
2443	PE	900		05/14/87	0.1250	0.124	-6	-2.6

2446	PE	900		05/14/87	0.7708	0.109	-1.5	-1.85
2452	PE	900		05/18/87	0.6528	0.071	10.5	1.1
2469	PE	900		05/19/87	0.6972	1.186	-11.5	-3.1
2529	PE	900		06/03/87	0.8958	0.919	-2.5	0.1
2560	PE	900		06/13/87	0.3611	2.088	-52.5	-7.5
2596	PE	900		06/13/87	0.7500	1.722	-69	-9.6
2631	PE	900		06/14/87	0.2083	0.693	-91	-12.25
2632	PE	900		06/16/87	0.3333	1.646	-51	-7.45
2633	PE	900		06/16/87	0.6194	1.443	-37	-6.05
2803	PE	900		06/17/87	0.4375	0.612	-25	-5.4
2841	PE	900		06/18/87	0.7500	0.241	-9	-2.05
2862	PE	900		06/23/87	0.6667	0.406	-18.5	-3.55
2881	PE	900		06/25/87	0.1667	0.198	-9	-2.4
2884	PE	900		06/25/87	0.8750	0.328	-18.5	-3.6
2890	PE	900		06/26/87	0.7500	0.043	0	-0.55
2905	PE	900		07/01/87	0.0521	0.170	-1	-1.8
2908	PE	900		07/01/87	0.9167	0.302	-43.5	-6.85
2912	PE	900		07/04/87	0.3646	1.778	-23	-4.35
2913	PE	900		07/04/87	0.4792	0.193	-27	-4.35
2914	PE	900		07/04/87	0.8750	0.447	-18	-3.2
2915	PE	900		07/05/87	0.7917	0.734	-5	-1.5
2916	PE	900		07/07/87	0.0833	0.279	3	-0.1
2972	PE	900		07/08/87	0.7083	0.175	-1	-0.75
3005	PE	900		07/25/87	0.8750	1.293	-0.5	-0.95
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3043	PE	900		07/31/87	0.7500	0.241	9	-0.35
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3136	PE	900		08/04/87	0.7917	2.040	-1.5	-2
3171	PE	900		08/06/87	0.7083	0.135	6	0.1
3222	PE	900		09/05/87	0.4583	0.556	-30	-5.55
3223	PE	900		09/06/87	0.8750	0.528	-16	-3.65

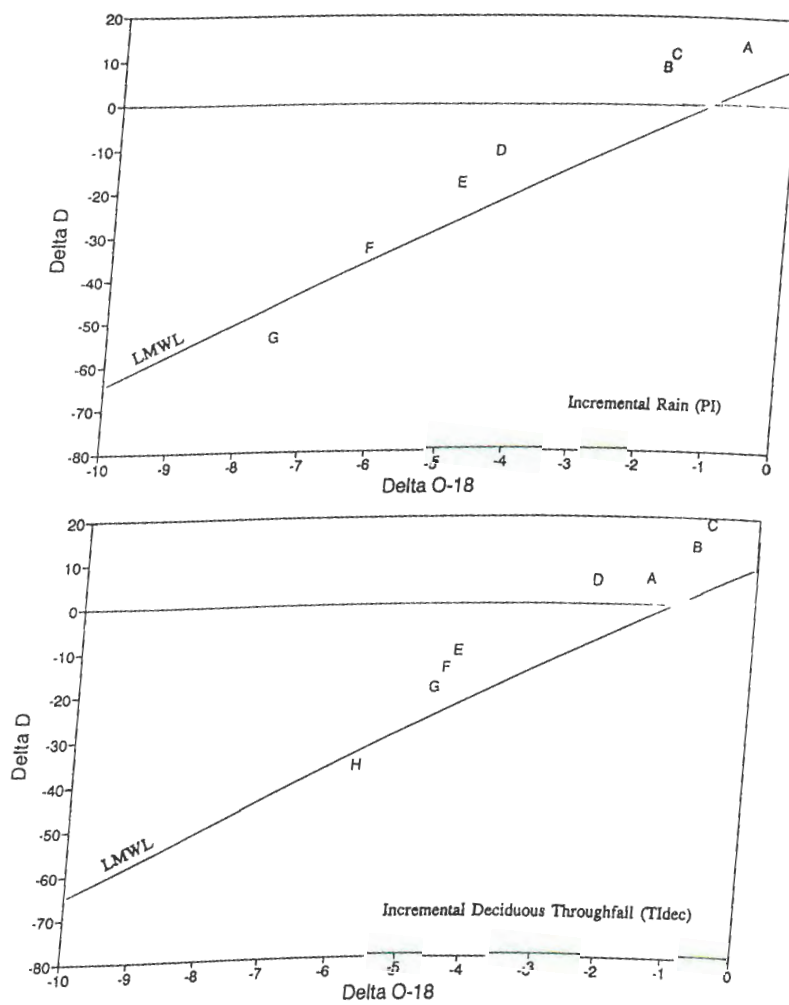
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3383	PE	900		10/27/87	0.1319	1.125	-27	-5.5
3467	PE	900		11/10/87	0.1875	2.002	-33.5	-5.75
3592	PE	900		11/17/87	0.4271	2.860	-52.5	-7.85
3679	PE	900		11/19/87	0.7708	0.066	0.5	-0.45
3691	PE	900		11/28/87	0.0958	0.759	-5	-3.3
3728	PE	900		12/10/87	0.3125	0.599	-1.5	-2.4
3729	PE	900		12/15/87	0.3646	2.413	-3	-2.6
3844	PE	900		12/20/87	0.5521	0.241	16.5	-1.05
3845	PE	900		12/22/87	0.0208	1.989	-66.5	-9.6
3891	PE	900		12/24/87	0.5729	0.351	-15.5	-4.5
3901	PE	900		12/28/87	0.5000	1.923	-5	-2.35
3961	PE	900		01/02/88	0.1875	1.643	-11.5	-3.8
3962	PE	900		01/03/88	0.9722	2.055	-90	-13.1
4127	PE	900		01/07/88	0.0000	2.395	-53.5	-9.35
4148	PE	900		01/13/88	0.3229	0.351	-7.5	-4.1
4183	PE	900		01/18/88	0.3958	2.388	-27	-6.3
4260	PE	900		01/19/88	0.3438	0.561	-27.5	-5.5
4375	PE	900		01/25/88	0.2701	0.589	-58	-10.15
4492	PE	900		02/03/88	0.1021	1.935	-29	-5.25
4562	PE	900		02/04/88	0.3042	3.881	-39	-6.4
4744	PE	900		02/12/88	0.1076	0.064	-8	-2.9
4745	PE	900		02/15/88	0.6111	0.541	-40	-6.8
5062	PE	900		04/01/88	0.0000	0.480	10	-0.9
5063	PE	900		04/04/88	0.0000	0.391	14	-0.4
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5275	PE	900		04/19/88	0.0000	1.093	-38.5	-6.35

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5946	PE	900		06/24/88	0.9271	0.158	30.5	3.3
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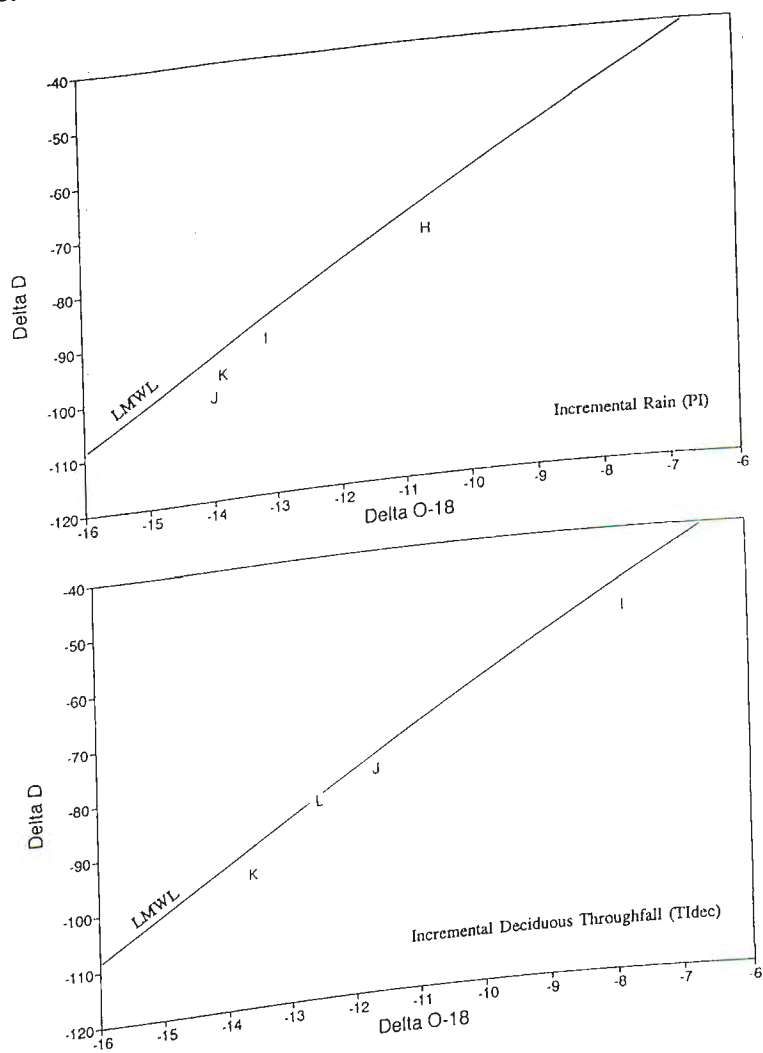
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6862	PE	900		09/11/88	0.0000	0.564	-15.5	-3.45
6863	PE	900		09/12/88	0.0000	0.231	-7	-2.45
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7180	PE	900		10/21/88	0.0000	1.252	-20	-4.85
7181	PE	900		10/22/88	0.0000	0.077	-8.5	-2.8
7215	PE	900		11/01/88	0.0000	1.203	-12.5	-4.25
7290	PE	900		11/05/88	0.0000	2.269	-37	-6.7
7299	PE	900		11/08/88	0.0000	0.225	5	-1.6
7300	PE	900		11/10/88	0.0000	0.322	-0.5	-2.75
7306	PE	900		11/17/88	0.0000	0.508	0	-1.3
7687	PE	900		11/20/88	0.0000	0.529	-11	-2.75
7306	PE	900		11/28/88	0.0000	4.102	-15	-3.7
7312	PE	900		12/18/88	0.0000	0.142	-32	-4.7
7523	PE	900		12/29/88	0.6667	0.279	0.5	-1.45
7527	PE	900		01/03/89	0.0000	2.146	-26	-4.6
7532	PE	900		01/03/89	0.0000	1.114	-8	-2.5
7533	PE	900		01/10/89	0.0000	0.071	6	-1.2
7677	PE	900		01/13/89	0.0000	1.985	-12	-3.05
7681	PE	900		01/17/89	0.0000	0.354	5	-1.65
7682	PE	900		01/31/89	0.0000	0.676	-18.5	-4.05
7690	PE	900		02/02/89	0.5208	2.081	-13	-3.5
7752	PE	900		02/21/89	0.6250	3.581	-39	-6.65
7785	PE	900		02/28/89	0.5000	1.754	-39	-7.35
7794	PE	900		03/07/89	0.0000	2.174	-27.5	-5.05
7802	PE	900						

7923	PE	900		03/21/89	0.0000	2.240	-25	-4.5
7914	PE	900		03/24/89	0.6042	4.403	-38.5	-6.75
8010	PE	900		03/30/89	0.0000	1.143	-18	-3.45
8123	PE	900		04/11/89	0.4701	1.407	-26	-3.9
8203	PE	900		04/18/89	0.3785	1.115	-6	-2.75
8293	PE	900		05/02/89	0.0000	3.892	-49	-7.65
8615	PE	900		06/05/89	0.0000	0.330	0	-1
8621	PE	900		06/06/89	0.0000	0.827	-13.5	-2.95
8687	PE	900		06/13/89	0.4167	1.252	6	1.85
8763	PE	900		06/16/89	0.0000	8.738	-48.5	-7.2
8891	PE	900		07/02/89	0.0000	2.510	-13.5	-3.65
8986	PE	900		07/19/89	0.0000	2.134	-11.5	-3.15
8987	PE	900		07/20/89	0.0000	0.737	-17.5	-3.4

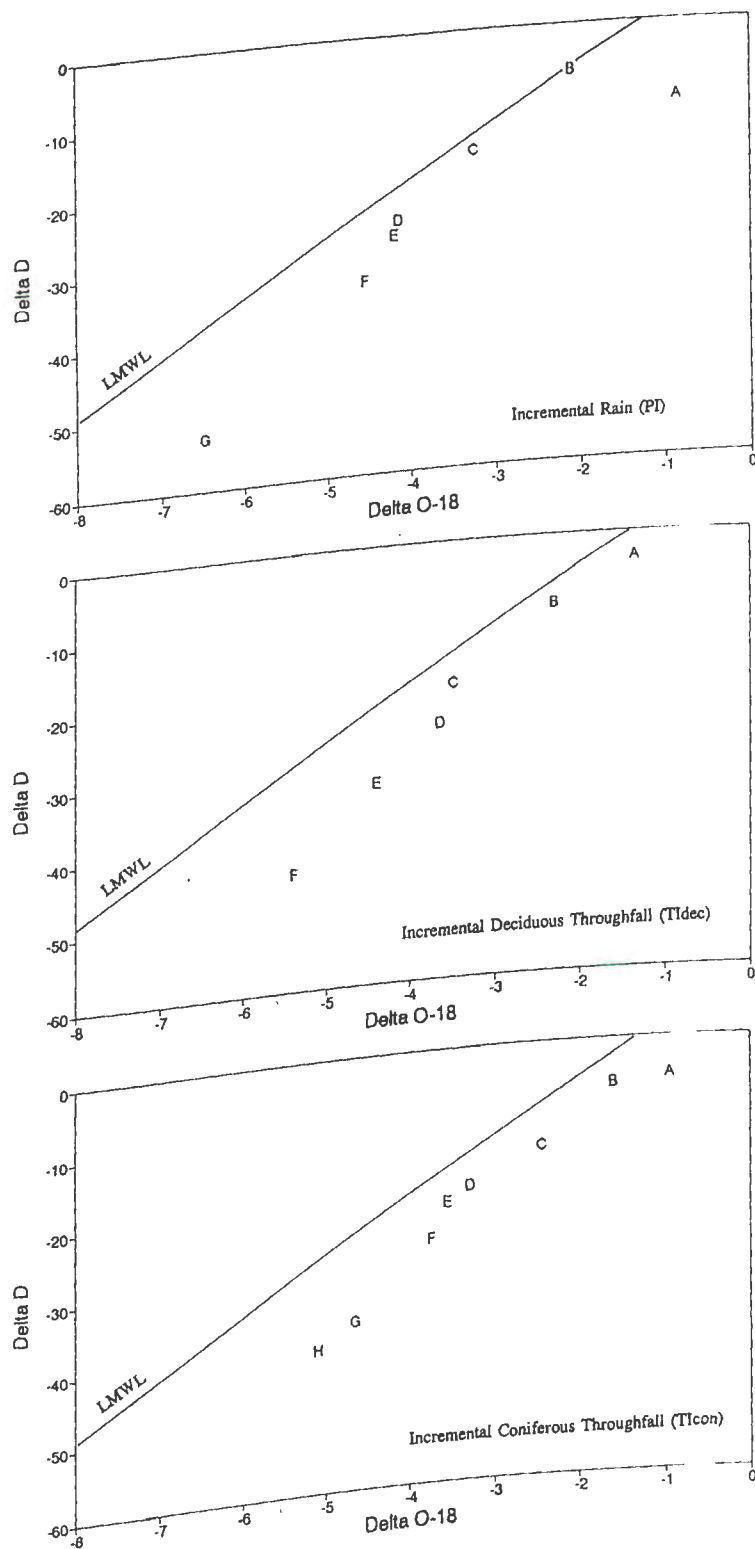
Appendix 3.1. Intrastorm variation in $\delta^{18}\text{O}$ and δD for January 1, 1988.



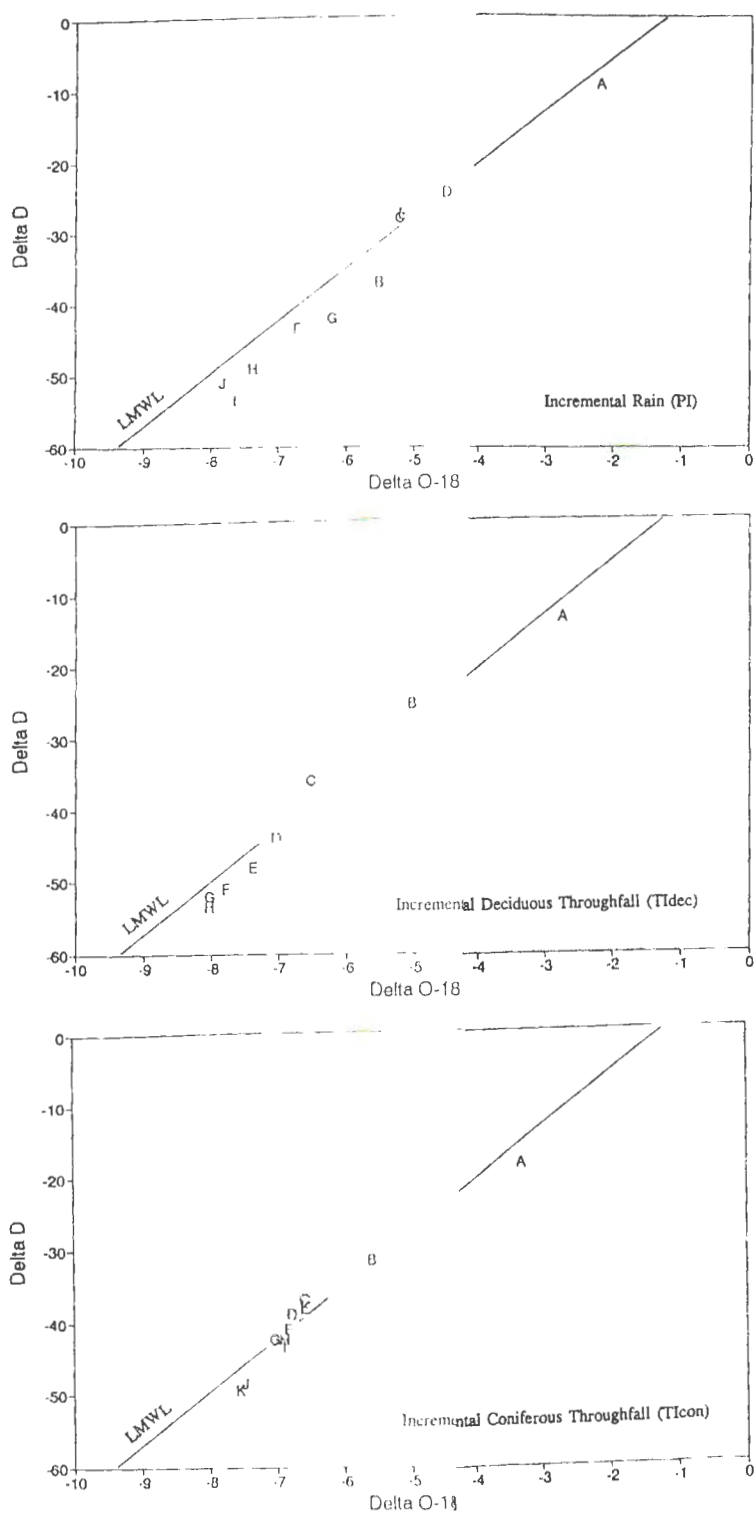
Appendix 3.2. Intrastorm variation in $\delta^{18}\text{O}$ and δD for January 3, 1988.



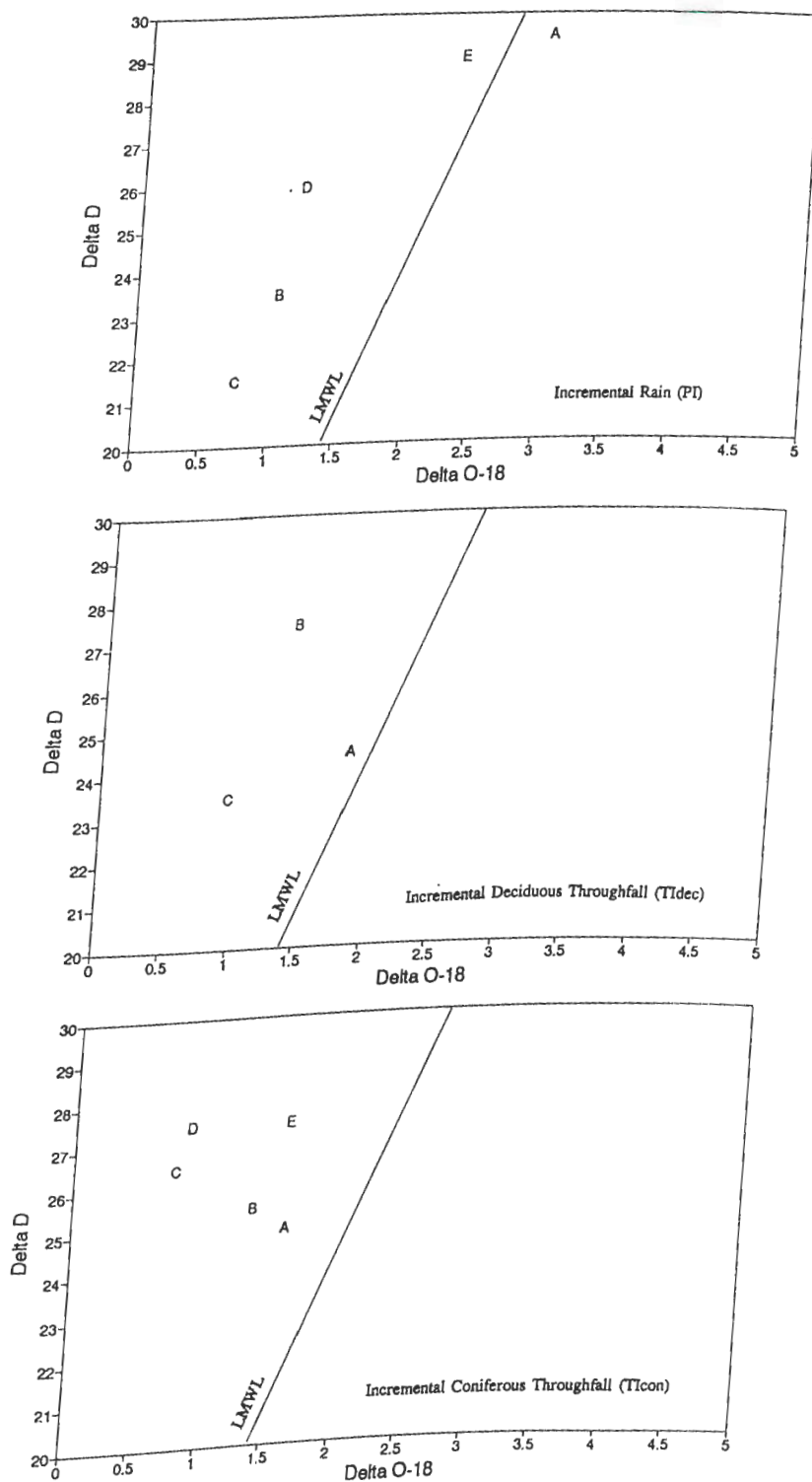
Appendix 3.3. Intrastorm variation in $\delta^{18}\text{O}$ and δD for May 10, 1988.



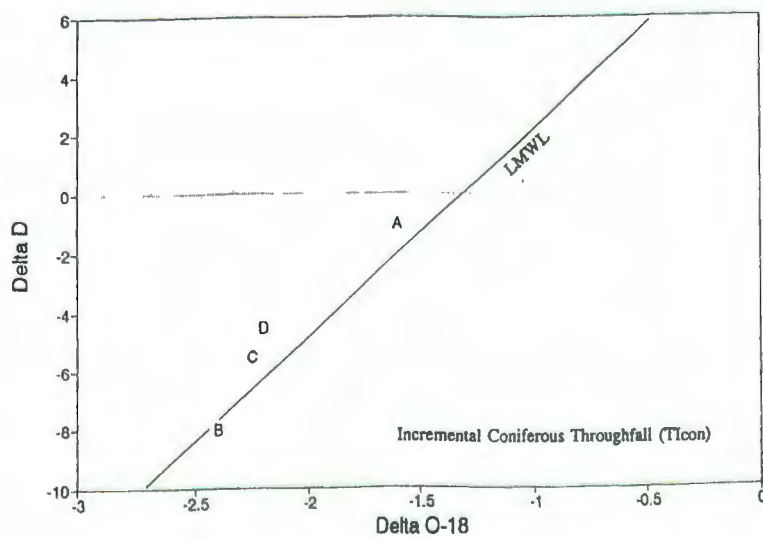
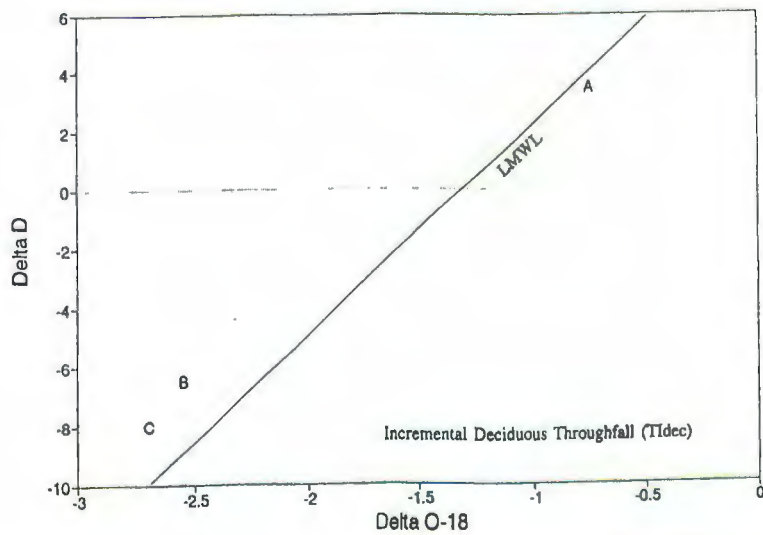
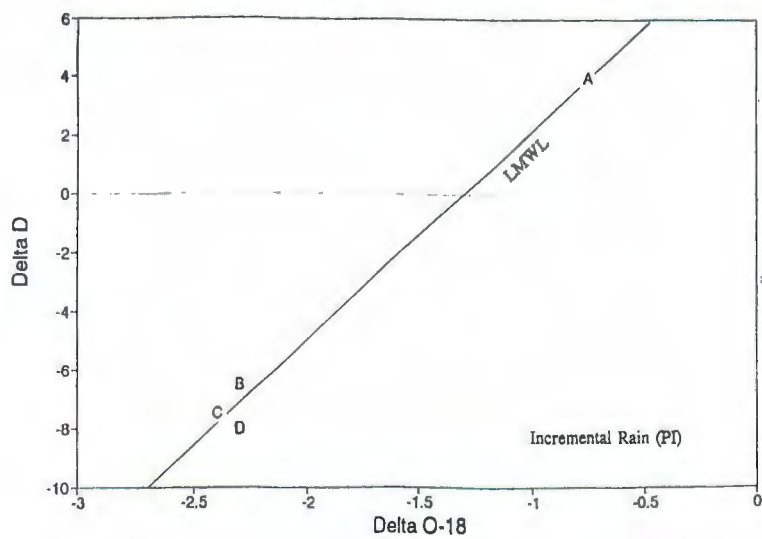
Appendix 3.4. Intrastorm variation in $\delta^{18}\text{O}$ and δD for May 15, 1988.



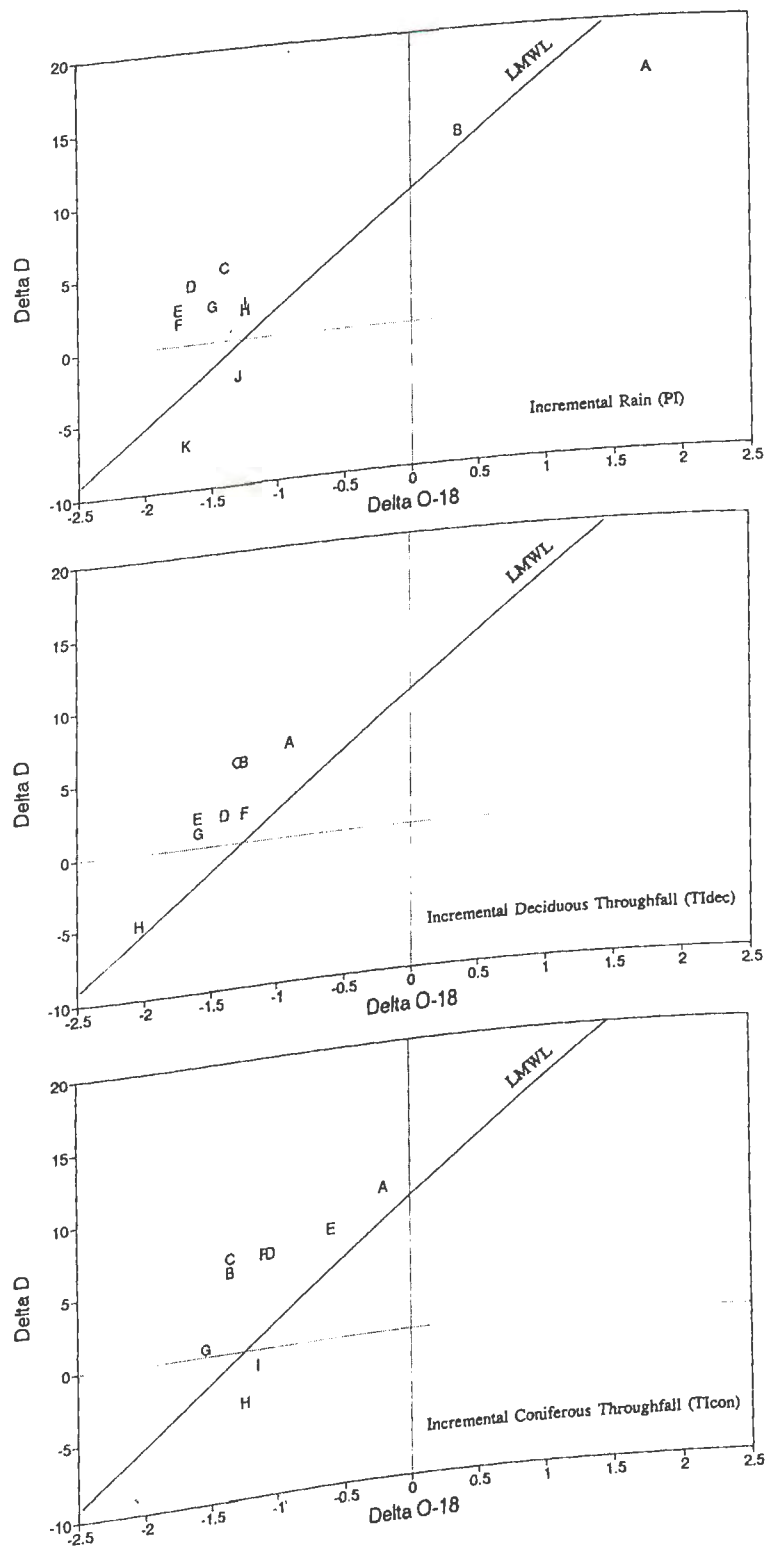
Appendix 3.5. Intrastorm variation in $\delta^{18}\text{O}$ and δD for June 2, 1988.



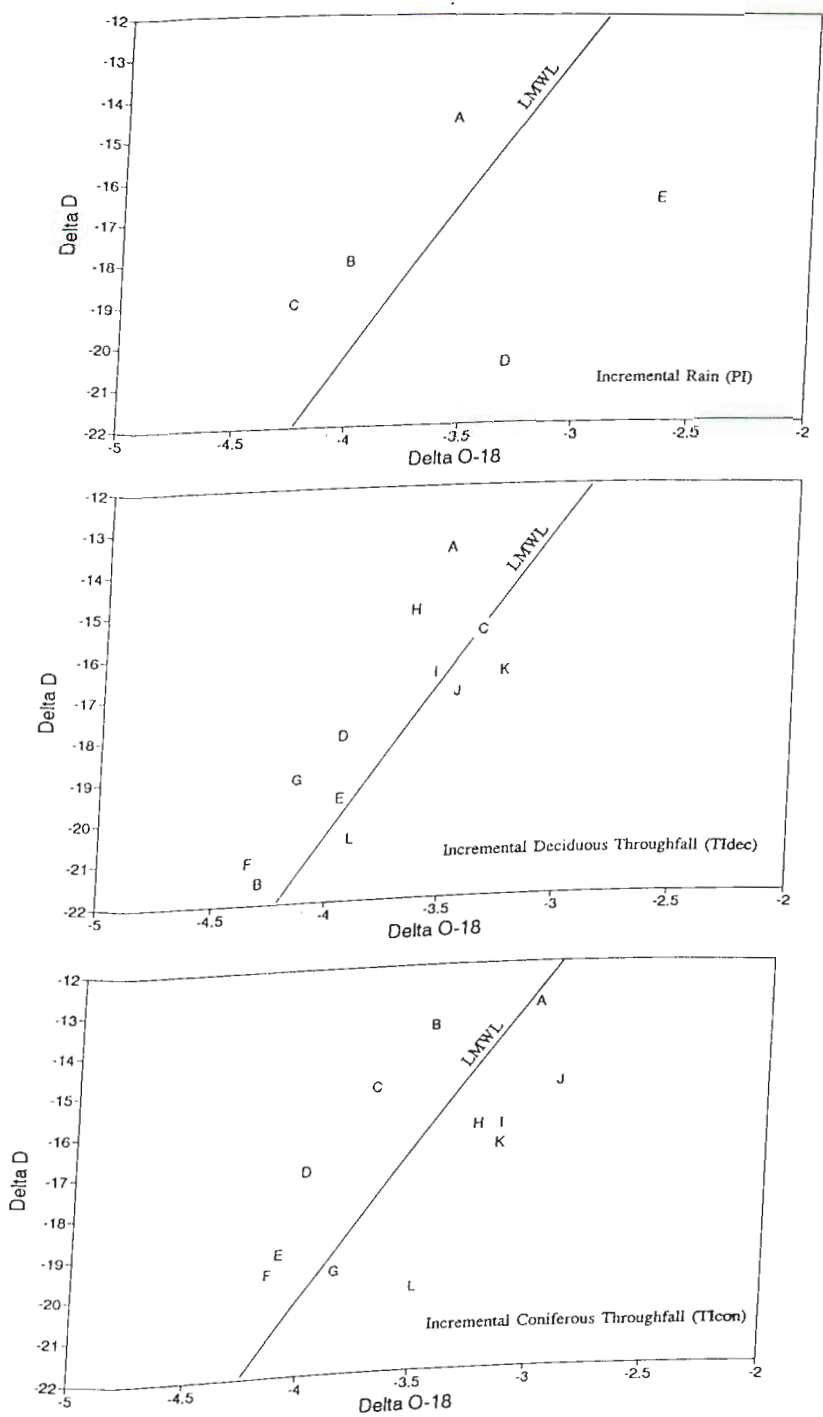
Appendix 3.6. Intrastorm variation in $\delta^{18}\text{O}$ and δD for June 9, 1988.



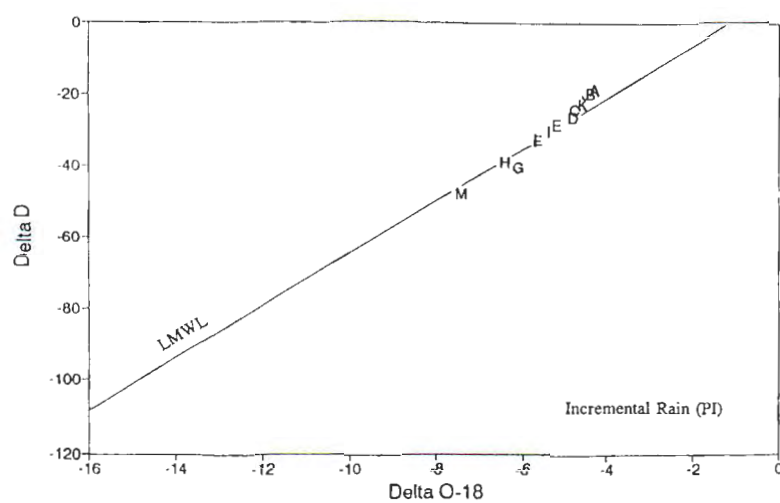
Appendix 3.7. Intrastorm variation in $\delta^{18}\text{O}$ and δD for June 18, 1988.



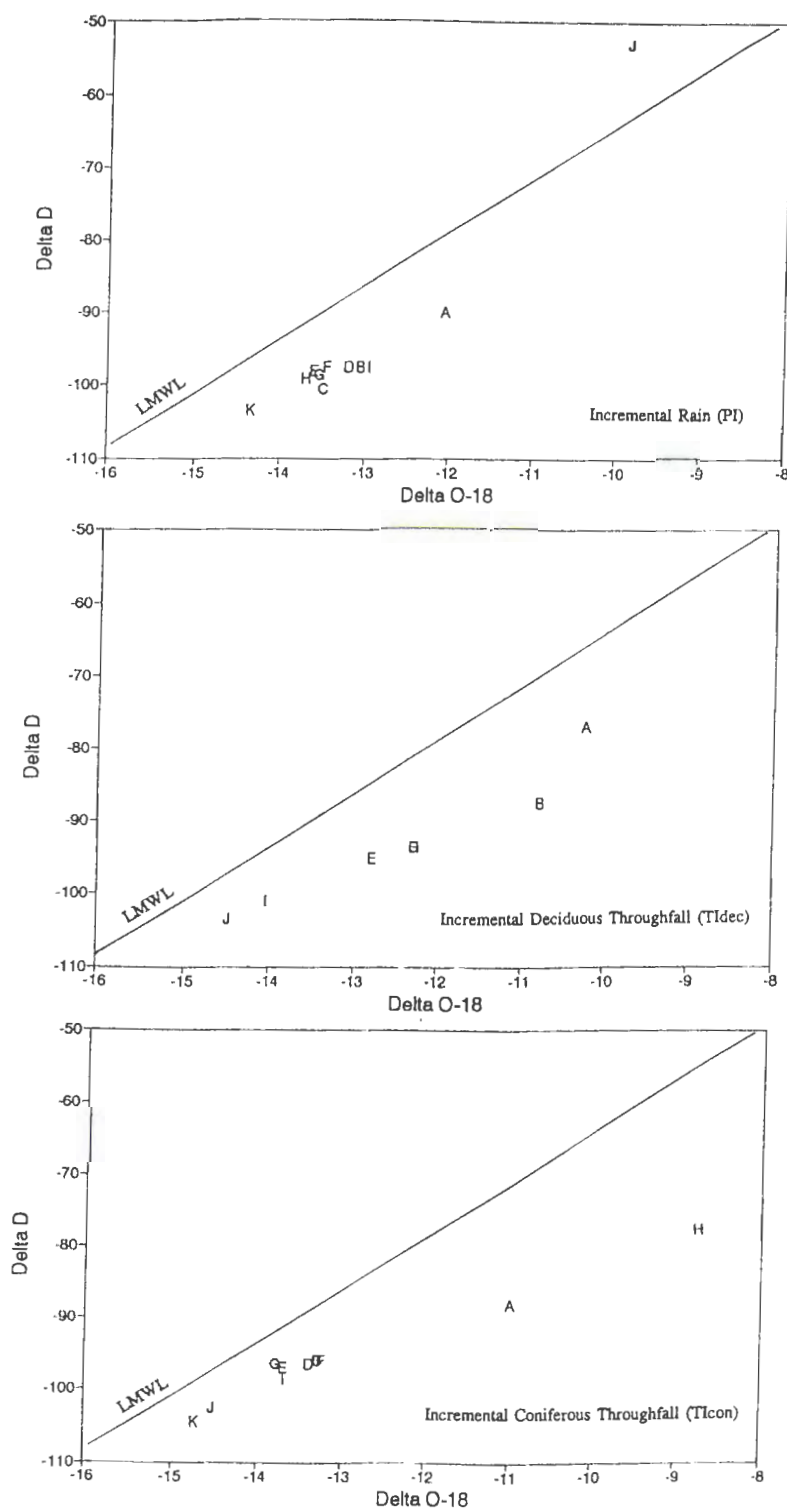
Appendix 3.8. Intrastorm variation in $\delta^{18}\text{O}$ and δD for July 27, 1988.



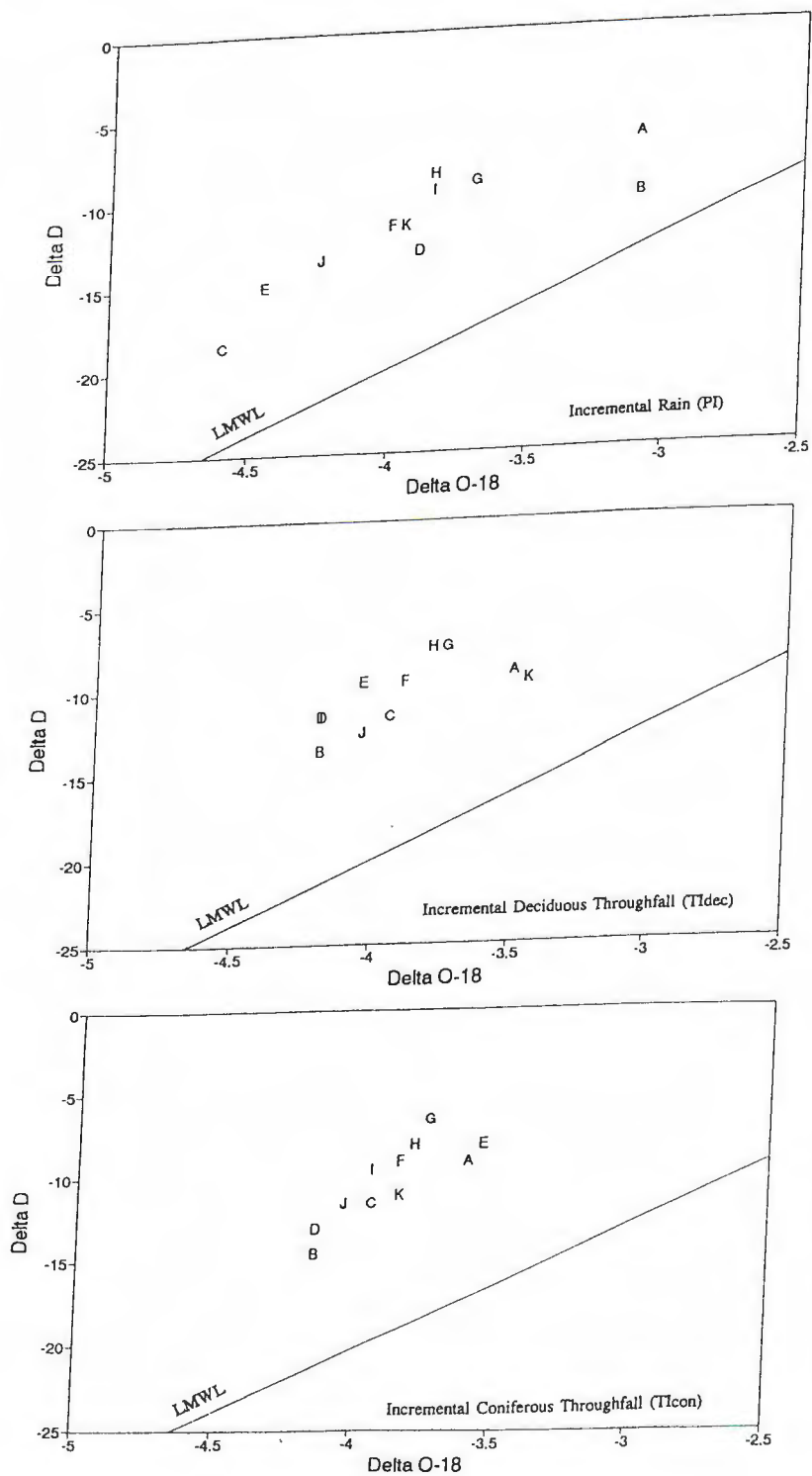
Appendix 3.9. Intrastorm variation in $\delta^{18}\text{O}$ and δD for September 3, 1988.



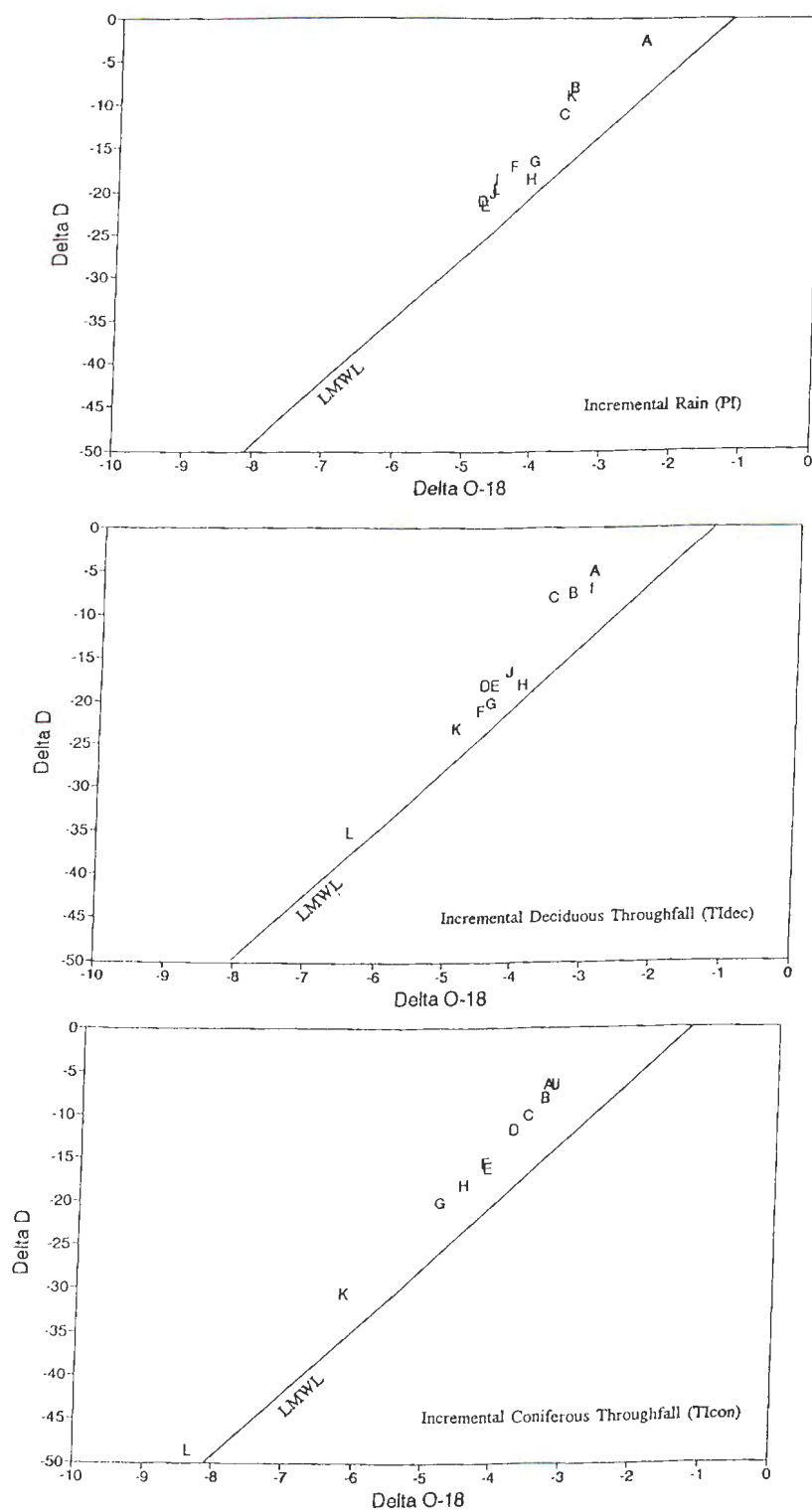
Appendix 3.10. Intrastorm variation in $\delta^{18}\text{O}$ and δD for September 4, 1988.



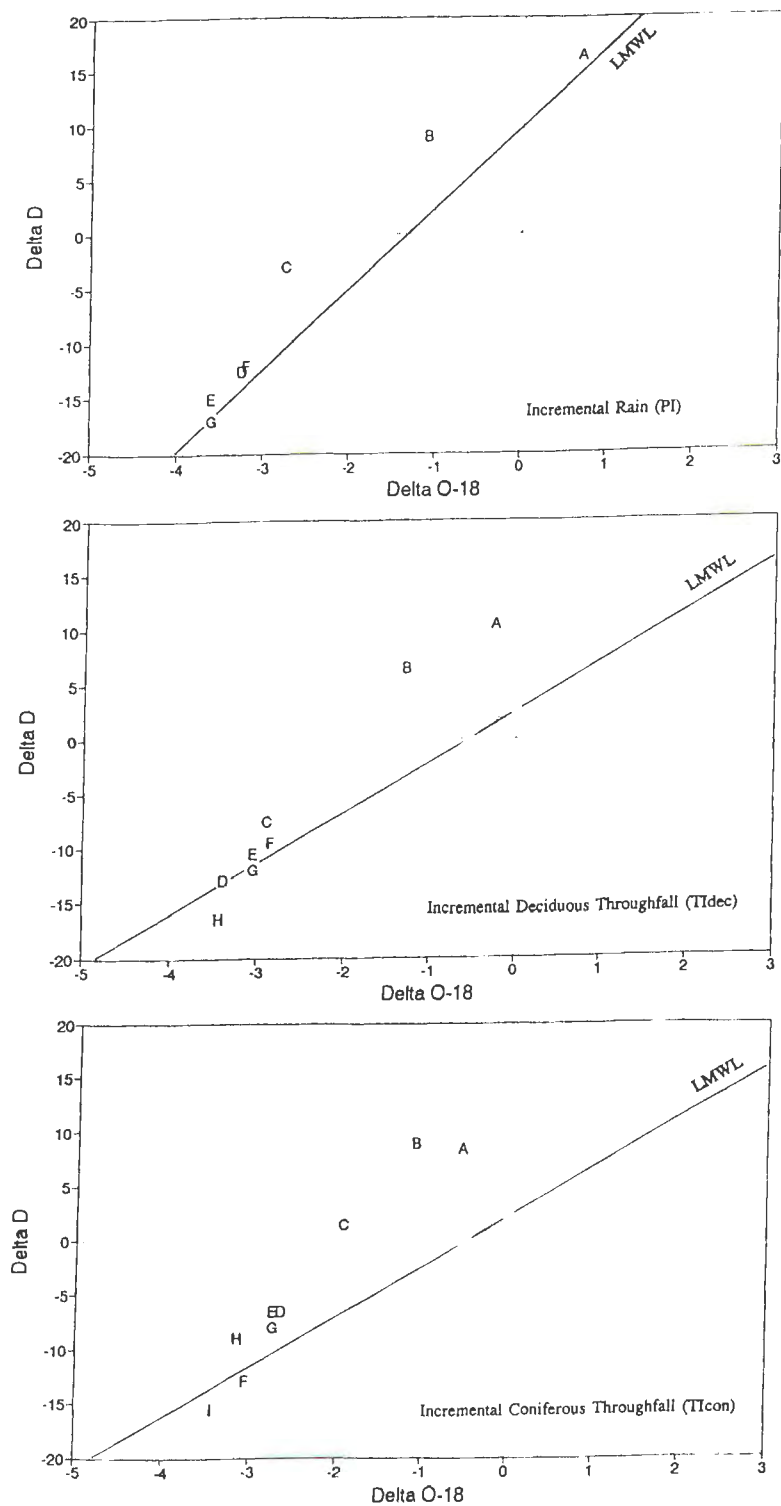
Appendix 3.11. Intrastorm variation in $\delta^{18}\text{O}$ and δD for September 16, 1988.



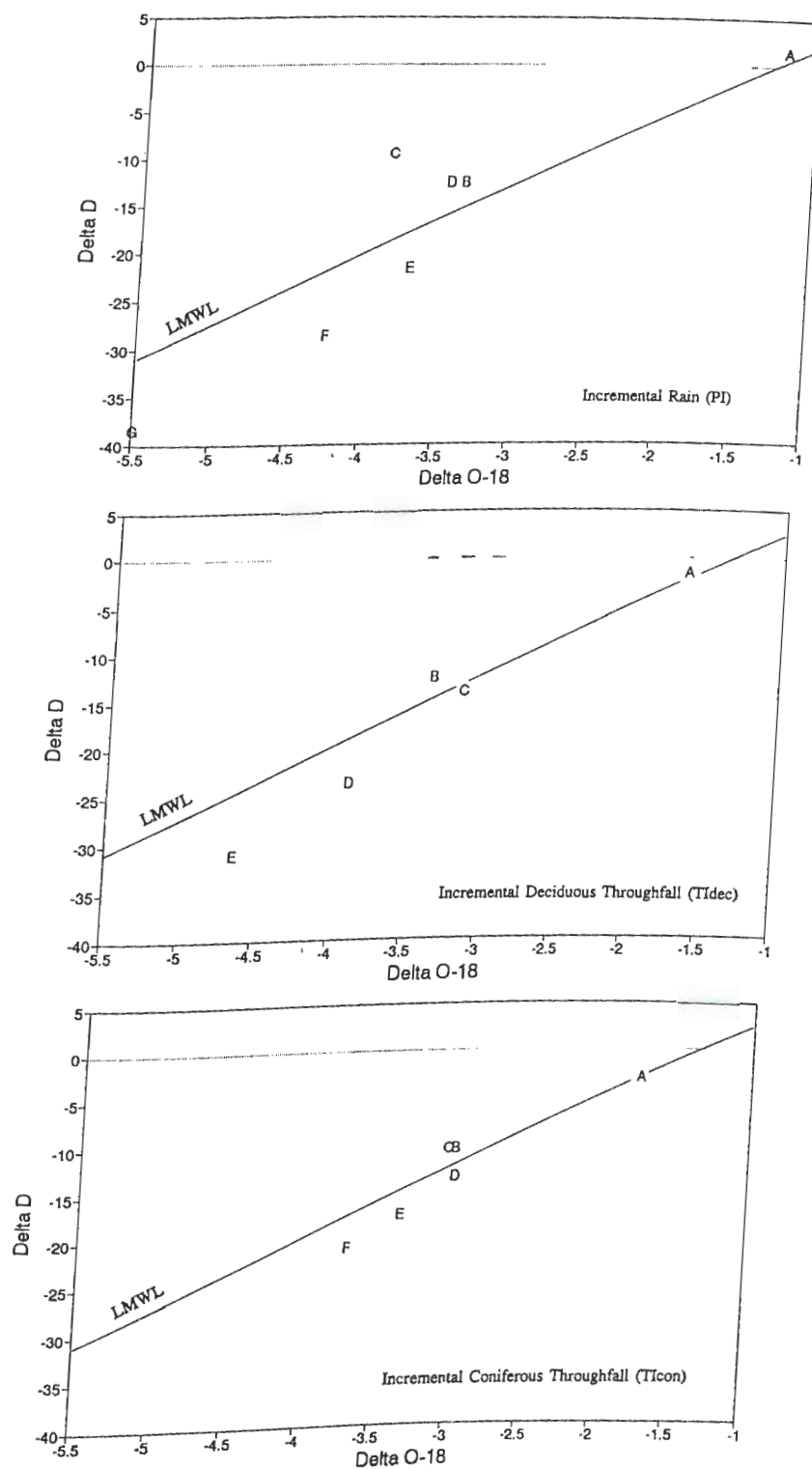
Appendix 3.12. Intrastorm variation in $\delta^{18}\text{O}$ and δD for October 1, 1988.



Appendix 3.13. Intrastorm variation in $\delta^{18}\text{O}$ and δD for January 3, 1989.



Appendix 3.14. Intrastorm variation in $\delta^{18}\text{O}$ and δD for March 30, 1989.



Appendix 4. Second-order polynomial equations fitted to incremental data.

Date	PI			TIdec			TIcon		
	Const.	x	x ²	Const.	x	x ²	Const.	x	x ²
01/01/88	16.8	2.4	-0.9	16.1	1.2	-1.3			
01/03/88	16.8	2.4	-0.9	-41.3	-1.6	-0.4			
05/10/88	-7.5	-0.8	-1.2	4.4	4.4	-0.9	-1.9	1.5	-1.2
05/15/88	3.5	5.0	-0.3	-9.3	-0.6	-0.8	-23.3	-5.1	-1.1
06/02/88	14.1	11.9	-2.3	-7.9	49.5	-17.2	32.2	-9.4	3.6
06/09/88	14.4	16.1	2.9	3.3	-2.0	-2.3	-40.0	-46.5	-13.8
06/19/88	9.7	8.6	1.9	5.7	-5.3	-5.1	14.7	13.9	3.6
07/27/88	-19.9	-2.3	-0.5	-47.7	-21.5	-3.6	-7.5	1.6	-0.3
09/03/88	49.2	19.3	0.8						
09/04/88	392.8	68.8	2.4	64.0	20.1	0.6	-59.2	1.0	-0.1
09/16/88	-60.8	-32.7	-5.1	-189.7	-99.0	-13.5	-286.2	-153.3	-21.1
10/01/88	15.8	6.3	-0.3	28.4	12.6	0.4	22.3	9.3	0.1
01/03/89	15.0	3.0	-1.6	11.4	2.2	-1.6	10.9	1.3	-1.9
02/20/89	-4.0	-3.1	-1.0	-8.2	-5.1	-1.2	-21.1	-8.9	-1.5
03/30/89	4.8	1.0	-1.3	3.3	0.3	-1.5	-10.1	-10.5	-3.7

Appendix 5. Linear regression equations for incremental rain and throughfall.

DATE	PI				TIdec				TIcon			
	slope	y-int.	r ²	n	slope	y-int.	r ²	n	slope	y-int.	r ²	n
1/01/88	9.96	27.10	.97	7	9.33	24.24	.95	8				
1/03/88	7.46	5.26	.98	4	7.01	1.68	.99	4				
5/10/88	8.13	5.03	.88	7	10.17	12.60	.98	6	8.82	7.86	.96	8
5/15/88	8.02	10.47	.97	10	7.72	10.43	.97	8	7.02	7.88	.95	11
6/02/88	3.36	20.28	.87	5	1.11	23.61	.06	3	-1.03	27.67	.14	5
6/09/88	7.14	9.34	.99	4					7.90	11.94	.92	4
6/18/88	5.01	8.85	.72	11	9.87	16.44	.84	8	6.51	11.22	.37	9
7/27/88	0.91	-14.47	.06	5	5.66	3.61	.69	12	3.56	-4.15	.43	12
9/03/88	9.68	22.47	.98	13								
9/04/88	11.28	53.09	.92	11	5.44	-25.64	.93	10	4.16	-41.05	.98	11
9/16/88	5.99	11.77	.71	11	4.97	9.20	.45	11	9.85	28.06	.68	11
10/01/88	8.63	20.07	.94	12	8.78	20.13	.96	12	8.14	19.30	.99	12
1/03/89	7.82	13.91	.95	7	8.34	14.62	.96	8	8.71	16.33	.94	9
2/28/89	9.53	33.09	.95	9	10.34	37.05	.95	8	10.39	38.11	.95	8
3/30/89	9.35	16.45	.83	7	9.89	16.55	.95	5	8.97	14.02	.89	6

Appendix 6. Standard error values for the linear regression equations of incremental samples.

Date	PI		TIdc		TIcon	
	y-int.	Slope	y-int.	Slope	y-int.	Slope
01/01/88	3.578	0.790	3.189	0.888		
01/03/88	8.572	0.660	6.396	0.551		
05/01/88	5.283	1.312	2.706	0.736	2.505	0.728
05/15/88	3.19	0.524	3.618	0.531	3.692	0.559
06/02/88	1.39	0.740	6.500	4.491	1.928	1.503
06/09/88	1.192	0.580	0.644	0.294	3.540	1.659
06/19/88	1.523	1.032	2.551	1.754	3.674	3.229
09/04/88	14.793	1.131	6.823	0.546	2.811	0.214
09/16/88	5.018	1.283	7.125	1.817	8.844	2.278
10/01/88	2.751	0.664	2.332	0.547	0.669	0.144
01/03/89	2.327	0.823	1.802	0.656	2.075	0.813
02/28/89	5.556	0.809	6.542	0.966	6.925	1.010
03/30/89	7.285	1.914	4.501	1.292	4.762	1.569

Appendix 7. Linear regressions for incremental data using Yorkfit models.*

Date	PI			Tldec			Tlcon		
	Slope	2 σ	y-int.	2 σ	Slope	y-int.	2 σ	Slope	2 σ
01/01/88	10.1	2.0	27.7	9.2	9.6	2.2	25.0	7.9	
01/03/88	7.5	2.8	6.0	8.6	7.1	2.4	2.2	27.6	
05/10/88	8.6	3.4	6.9	5.4	10.3	2.0	13.0	7.5	6.2
05/15/88	8.2	1.2	11.3	7.4	7.8	1.3	11.1	8.9	7.8
06/02/88	3.1	2.2	20.6	4.1	-1.1	10.2	26.6	-1.6	8.3
06/09/88	7.0	1.7	9.1	3.5	5.7	1.9	7.8	4.1	3.9
06/19/88	8.2	5.0	13.2	7.2	10.8	4.4	17.7	6.4	-49.1
07/27/88	-0.4	4.9	-19.2	17.6	2.9	3.5	-6.7	13.2	1.2
09/03/88	9.8	1.0	23.1	5.5					3.6
09/04/88	11.8	2.6	59.6	33.8	5.7	1.3	-23.0	15.9	4.1
09/16/88	3.0	2.8	0.3	6.3	-0.4	7.2	-11.9	28.5	0.7
10/01/88	8.9	1.5	21.1	6.2	8.9	1.2	20.8	5.2	4.1
01/03/89	8.0	2.1	14.4	6.0	8.5	1.6	15.0	4.4	8.1
02/20/89	9.8	1.9	34.7	13.2	10.6	2.4	38.8	16.1	9.0
03/30/89	10.3	5.0	19.8	19.2	10.1	4.1	17.4	14.4	10.7
									2.5
									4.4
									15.6
									13.4

* Calculated using Isoplot program, Ludwig (1991). Model-2 Yorkfits are tabulated when available; otherwise the data are for Model-1 Yorkfits.

Appendix 8. Interpolated rain amounts and trough discharges at Hydrohill.

Hours (after 7/5/89 00:00)	Rain (mm)	Discharge (m ³ /s)				
		Surface Runoff	0-30 cm	30-60 cm	60-100 cm	Total
4.4	5.1354	0.0001	0.0000	0.0000	0.0000	0.0001
4.5	5.7627	0.0002	0.0000	0.0000	0.0000	0.0003
4.6	6.3145	0.0008	0.0000	0.0000	0.0000	0.0008
4.7	7.6387	0.0016	0.0000	0.0000	0.0000	0.0016
4.8	8.2247	0.0022	0.0001	0.0000	0.0000	0.0022
4.9	8.6376	0.0027	0.0004	0.0000	0.0000	0.0027
5	9.3283	0.0026	0.0023	0.0001	0.0000	0.0027
5.1	10.958	0.0026	0.0063	0.0002	0.0000	0.0028
5.2	11.999	0.0030	0.0111	0.0004	0.0000	0.0034
5.3	12.593	0.0034	0.0188	0.0006	0.0000	0.0040
5.4	13.974	0.0034	0.0095	0.0008	0.0000	0.0042
5.5	14.636	0.0031	0.0099	0.0013	0.0000	0.0044
5.6	15.382	0.0028	0.0122	0.0030	0.0001	0.0059
5.7	16.032	0.0028	0.0459	0.0120	0.0001	0.0148
5.8	16.872	0.0029	0.1335	0.0131	0.0001	0.0161
5.9	18.369	0.0030	0.0985	0.0136	0.0004	0.0169
6	19.138	0.0031	0.1171	0.0147	0.0006	0.0185
6.1	19.973	0.0032	0.1388	0.0219	0.0007	0.0257
6.2	20.732	0.0032	0.5096	0.0300	0.0019	0.0352
6.3	21.760	0.0032	0.7019	0.0266	0.0038	0.0336
6.4	24.465	0.0479	0.5024	0.0280	0.0080	0.0838
6.5	27.662	0.8786	0.4886	0.0364	0.0349	0.9499
6.6	28.799	1.4086	0.7298	0.0391	0.0648	1.5125
6.7	30.855	0.2932	0.8744	0.0466	0.0571	0.3969
6.8	33.712	0.4981	1.0596	0.0446	0.0426	0.5853

6.9	36.686	1.3470	0.9699	0.0402	0.0514	1.4386
7	40.801	1.2910	0.7114	0.0371	0.0981	1.4261
7.1	44.443	1.8757	0.6651	0.0321	0.1282	2.0360
7.2	46.324	1.7976	0.5657	0.0296	0.1450	1.9722
7.3	48.661	1.1810	0.4885	0.0296	0.1442	1.3548
7.4	49.616	1.0178	0.4739	0.0300	0.1120	1.1598
7.5	49.758	0.3911	0.4865	0.0342	0.0997	0.5249
7.6	49.899	0.4049	0.6019	0.0321	0.0835	0.5205
7.7	50.041	0.3764	0.5972	0.0317	0.0713	0.4795
7.8	50.182	0.5970	0.3920	0.0356	0.0677	0.7004
7.9	50.323	0.5570	0.4931	0.0355	0.0705	0.6630
8	50.465	0.5282	0.5829	0.0361	0.0727	0.6370
8.1	50.606	0.0334	0.4342	0.0137	0.0830	0.1300
8.2	50.748	0.0095	0.2335	0.0072	0.0891	0.1058
8.3	50.995	0.0058	0.0609	0.0048	0.0767	0.0872
8.4	51.110	0.0046	0.0399	0.0036	0.0901	0.0982
8.5	51.292	0.0042	0.0355	0.0027	0.1021	0.1090
8.6	51.593	0.0042	0.0297	0.0022	0.0878	0.0942
8.7	51.787	0.0047	0.0261	0.0018	0.0680	0.0745
8.8	51.989	0.0102	0.0302	0.0016	0.0562	0.0681
8.9	52.389	0.1417	0.1546	0.0029	0.0474	0.1920
9	52.908	0.0695	0.2883	0.0039	0.0441	0.1174
9.1	53.730	0.0107	0.2895	0.0134	0.0413	0.0655
9.2	54.728	0.0073	0.1892	0.0136	0.0403	0.0612
9.3	55.082	0.0064	0.0975	0.0123	0.0434	0.0620
9.4	55.268	0.0060	0.1730	0.0139	0.0492	0.0691
9.5	55.904	0.0053	0.1113	0.0120	0.0574	0.0747
9.6	56.361	0.0046	0.0535	0.0094	0.0569	0.0710
9.7	56.436	0.0044	0.0289	0.0075	0.0550	0.0669
9.8	56.516	0.0051	0.0206	0.0060	0.0537	0.0648

9.9	56.641	0.0258	0.0196	0.0052	0.0537	0.0848
10	56.996	0.0341	0.1379	0.0098	0.0513	0.0951
10.1	57.916	0.0232	0.3695	0.0134	0.0478	0.0844
10.2	58.222	0.0154	0.2350	0.0151	0.0442	0.0747
10.3	58.618	0.1822	0.2063	0.0164	0.0418	0.2404
10.4	59.278	0.0431	0.3420	0.0196	0.0696	0.1323
10.5	59.820	0.0146	0.2554	0.0151	0.0676	0.0974
10.6	60.713	0.0081	0.1517	0.0118	0.0629	0.0828
10.7	60.950	0.0056	0.0646	0.0088	0.0561	0.0705
10.8	61.169	0.0048	0.0305	0.0064	0.0504	0.0616
10.9	61.222	0.0043	0.0194	0.0052	0.0462	0.0558
11	61.274	0.0041	0.0144	0.0042	0.0429	0.0512
11.1	61.274	0.0040	0.0129	0.0035	0.0399	0.0475
11.2	61.503	0.0040	0.0113	0.0028	0.0374	0.0443
11.3	61.548	0.0042	0.0094	0.0022	0.0352	0.0416
11.4	61.576	0.0044	0.0086	0.0022	0.0335	0.0401
11.5	61.623	0.0054	0.0079	0.0026	0.0330	0.0411
11.6	61.790	0.0086	0.0079	0.0072	0.0331	0.0489
11.7	62.085	0.6233	0.1041	0.0120	0.0411	0.6764
11.8	63.117	0.2277	0.4367	0.0192	0.0740	0.3209
11.9	64.717	0.0279	0.5405	0.0179	0.0644	0.1102
12	65.673	0.0100	0.1782	0.0131	0.0581	0.0813
12.1	65.893	0.0112	0.1239	0.0173	0.0542	0.0827
12.2	66.201	0.6832	0.2659	0.0234	0.0933	0.7999
12.3	67.571	0.1344	0.5855	0.0243	0.0891	0.2478
12.4	69.256	0.0297	0.3527	0.0187	0.0745	0.1229
12.5	69.574	0.0116	0.1717	0.0136	0.0660	0.0912
12.6	69.527	0.0058	0.0642	0.0106	0.0591	0.0755
12.7	69.660	0.0049	0.0309	0.0078	0.0539	0.0666
12.8	69.660	0.0040	0.0184	0.0052	0.0504	0.0596

12.9	69.666	0.0033	0.0137	0.0040	0.0473	0.0545
13	69.667	0.0033	0.0112	0.0033	0.0448	0.0515
13.1	69.825	0.0034	0.0098	0.0029	0.0430	0.0493
13.2	69.968	0.0034	0.0084	0.0025	0.0407	0.0465
13.3	70.013	0.0033	0.0073	0.0020	0.0388	0.0442
13.4	70.037	0.0033	0.0065	0.0020	0.0377	0.0429
13.5	70.053	0.0034	0.0060	0.0019	0.0361	0.0414
13.6	70.074	0.0035	0.0059	0.0015	0.0347	0.0396
13.7	70.134	0.0038	0.0058	0.0013	0.0335	0.0387
13.8	70.528	0.0042	0.0058	0.0013	0.0333	0.0388
13.9	70.690	0.0046	0.0059	0.0013	0.0333	0.0392
14	70.905	0.0044	0.0088	0.0018	0.0333	0.0395
14.1	71.472	0.0043	0.0168	0.0033	0.0333	0.0410
14.2	71.787	0.0042	0.0451	0.0048	0.0352	0.0443
14.3	72.201	0.0043	0.0701	0.0063	0.0372	0.0478
14.4	72.647	0.0043	0.0960	0.0087	0.0393	0.0524
14.5	73.017	0.0044	0.1132	0.0111	0.0435	0.0589
14.6	73.338	0.0041	0.0822	0.0106	0.0479	0.0626
14.7	73.574	0.0038	0.0616	0.0095	0.0465	0.0599
14.8	73.814	0.0037	0.0461	0.0078	0.0454	0.0569
14.9	73.982	0.0036	0.0345	0.0065	0.0452	0.0553
15	74.148	0.0035	0.0265	0.0056	0.0447	0.0537
15.1	74.455	0.0034	0.0317	0.0053	0.0440	0.0527
15.2	74.714	0.0034	0.0302	0.0051	0.0432	0.0518
15.3	74.854	0.0034	0.0219	0.0045	0.0425	0.0504
15.4	74.947	0.0034	0.0165	0.0040	0.0418	0.0492
15.5	75.014	0.0034	0.0127	0.0035	0.0412	0.0481
15.6	75.043	0.0034	0.0104	0.0030	0.0405	0.0468
15.7	75.208	0.0033	0.0094	0.0027	0.0398	0.0459
15.8	75.320	0.0033	0.0090	0.0026	0.0391	0.0451

15.9	75.390	0.0033	0.0085	0.0026	0.0385	0.0443
16	75.461	0.0034	0.0080	0.0025	0.0378	0.0437
16.1	75.531	0.0036	0.0071	0.0022	0.0372	0.0430
16.2	75.590	0.0038	0.0065	0.0018	0.0369	0.0426
16.3	75.686	0.0040	0.0061	0.0014	0.0367	0.0421
16.4	75.906	0.0040	0.0059	0.0013	0.0365	0.0418
16.5	76.049	0.0040	0.0056	0.0013	0.0362	0.0415
16.6	76.184	0.0040	0.0058	0.0012	0.0360	0.0412
16.7	76.338	0.0040	0.0060	0.0011	0.0357	0.0409
16.8	76.507	0.0040	0.0059	0.0011	0.0355	0.0407
16.9	76.667	0.0042	0.0080	0.0011	0.0353	0.0406
17	76.978	0.0047	0.0121	0.0011	0.0361	0.0419
17.1	77.722	0.0052	0.0960	0.0061	0.0372	0.0485
17.2	78.129	0.0048	0.1018	0.0084	0.0418	0.0550
17.3	78.489	0.0044	0.0839	0.0084	0.0455	0.0583
17.4	78.758	0.0042	0.0664	0.0086	0.0472	0.0601
17.5	78.969	0.0043	0.0506	0.0090	0.0478	0.0612
17.6	79.155	0.0044	0.0361	0.0074	0.0474	0.0592
17.7	79.260	0.0042	0.0233	0.0059	0.0470	0.0571
17.8	79.345	0.0041	0.0159	0.0050	0.0465	0.0555
17.9	79.430	0.0039	0.0133	0.0040	0.0463	0.0541
18	79.509	0.0036	0.0118	0.0029	0.0460	0.0525
18.1	79.586	0.0035	0.0117	0.0027	0.0458	0.0520
18.2	79.664	0.0035	0.0113	0.0024	0.0446	0.0505
18.3	79.740	0.0035	0.0091	0.0021	0.0435	0.0491
18.4	79.815	0.0035	0.0082	0.0020	0.0424	0.0478
18.5	79.890	0.0034	0.0076	0.0019	0.0419	0.0473
18.6	79.965	0.0034	0.0068	0.0017	0.0417	0.0468
18.7	80.057	0.0034	0.0061	0.0015	0.0415	0.0464
18.8	80.166	0.0034	0.0056	0.0015	0.0409	0.0459

18.9	80.285	0.0034	0.0053	0.0015	0.0401	0.0450
19	80.424	0.0034	0.0050	0.0013	0.0393	0.0441
19.1	80.529	0.0034	0.0050	0.0012	0.0385	0.0432
19.2	80.600	0.0034	0.0050	0.0012	0.0382	0.0427
19.3	80.664	0.0034	0.0049	0.0013	0.0378	0.0425
19.4	80.719	0.0034	0.0047	0.0012	0.0374	0.0420
19.5	80.774	0.0034	0.0046	0.0010	0.0370	0.0414
19.6	80.786	0.0034	0.0045	0.0010	0.0365	0.0408
19.7	80.794	0.0033	0.0042	0.0009	0.0361	0.0404
19.8	80.802	0.0033	0.0038	0.0009	0.0357	0.0399
19.9	80.864	0.0033	0.0035	0.0009	0.0352	0.0394
20	80.926	0.0032	0.0032	0.0009	0.0346	0.0386
20.1	80.978	0.0029	0.0035	0.0008	0.0339	0.0376
20.2	81.025	0.0027	0.0036	0.0007	0.0338	0.0373
20.3	81.071	0.0025	0.0036	0.0007	0.0338	0.0369
20.4	81.113	0.0023	0.0037	0.0006	0.0335	0.0365
20.5	81.154	0.0021	0.0038	0.0006	0.0332	0.0359
20.6	81.049	0.0024	0.0037	0.0006	0.0329	0.0359
20.7	81.188	0.0026	0.0036	0.0005	0.0327	0.0358
20.8	81.327	0.0044	0.0060	0.0005	0.0340	0.0389
20.9	82.286	0.0207	0.1318	0.0081	0.0387	0.0675
21	83.540	0.3134	0.3244	0.0150	0.0473	0.3756
21.1	84.677	0.8284	0.5838	0.0175	0.0926	0.9384
21.2	86.834	0.6641	0.5648	0.0213	0.1008	0.7862
21.3	88.363	1.0377	0.6666	0.0272	0.1110	1.1758
21.4	90.630	0.4673	0.5405	0.0303	0.1192	0.6169
21.5	91.704	0.1892	0.3588	0.0297	0.1079	0.3268
21.6	92.262	0.0745	0.2935	0.0279	0.0898	0.1922
21.7	92.580	0.0391	0.2013	0.0224	0.0917	0.1533
21.8	92.949	0.0134	0.1020	0.0165	0.0850	0.1149

21.9	93.071	0.0057	0.0526	0.0120	0.0792	0.0969
22	93.132	0.0043	0.0277	0.0090	0.0740	0.0873
22.1	93.152	0.0032	0.0149	0.0071	0.0688	0.0791
22.2	93.161	0.0027	0.0112	0.0054	0.0663	0.0744
22.3	93.205	0.0022	0.0101	0.0045	0.0642	0.0709
22.4	93.368	0.0026	0.0104	0.0054	0.0625	0.0705
22.5	93.805	0.0064	0.1292	0.0133	0.0613	0.0809
22.6	94.707	0.0173	0.1785	0.0135	0.0630	0.0938
22.7	94.915	0.0084	0.1051	0.0114	0.0690	0.0888
22.8	94.944	0.0064	0.0605	0.0092	0.0702	0.0858
22.9	94.991	0.0049	0.0283	0.0075	0.0665	0.0789
23	95.045	0.0040	0.0184	0.0060	0.0653	0.0753
23.1	95.105	0.0036	0.0143	0.0051	0.0643	0.0730
23.2	95.167	0.0031	0.0104	0.0044	0.0618	0.0693
23.3	95.230	0.0027	0.0090	0.0038	0.0604	0.0670
23.4	95.291	0.0023	0.0076	0.0035	0.0598	0.0657
23.5	95.312	0.0023	0.0075	0.0033	0.0587	0.0643
23.6	95.437	0.0025	0.0070	0.0031	0.0574	0.0630
23.7	95.569	0.0030	0.0067	0.0029	0.0569	0.0627
23.8	95.664	0.0030	0.0067	0.0027	0.0566	0.0622
23.9	95.922	0.0030	0.0073	0.0026	0.0563	0.0618
24	96.008	0.0033	0.0180	0.0026	0.0582	0.0641
24.1	96.582	0.0039	0.0854	0.0026	0.0604	0.0669
24.2	96.733	0.0037	0.1016	0.0026	0.0625	0.0688
24.3	96.797	0.0033	0.0379	0.0026	0.0626	0.0684
24.4	96.864	0.0030	0.0256	0.0025	0.0613	0.0668
24.5	97.047	0.0031	0.0211	0.0025	0.0601	0.0657
24.6	97.055	0.0032	0.0162	0.0019	0.0597	0.0649
24.7	97.078	0.0029	0.0106	0.0016	0.0593	0.0638
24.8	97.110	0.0025	0.0092	0.0016	0.0589	0.0630

24.9	97.182	0.0025	0.0099	0.0017	0.0585	0.0627
25	97.573	0.0030	0.0135	0.0052	0.0779	0.0861
25.1	98.139	0.2687	0.3560	0.0319	0.1376	0.4381
25.2	101.01	1.6594	0.8823	0.0344	0.1540	1.8478
25.3	103.66	0.5759	0.4830	0.0256	0.1295	0.7310
25.4	104.04	0.0820	0.2877	0.0198	0.1071	0.2089
25.5	104.59	0.0327	0.2342	0.0149	0.0869	0.1345
25.6	104.84	0.1284	0.2267	0.0234	0.0827	0.2345
25.7	106.57	1.3612	0.6785	0.0483	0.1614	1.5709
25.8	109.68	1.9079	0.8306	0.0416	0.1617	2.1112
25.9	113.00	1.1618	0.6775	0.0334	0.1448	1.3400
26	115.24	0.8022	0.6218	0.0303	0.1262	0.9587
26.1	116.52	0.4024	0.4618	0.0215	0.1306	0.5545
26.2	116.98	0.1222	0.2827	0.0120	0.1138	0.2479
26.3	117.13	0.0182	0.1175	0.0090	0.0946	0.1218
26.4	117.22	0.0070	0.0604	0.0065	0.0816	0.0951
26.5	117.28	0.0044	0.0431	0.0115	0.0728	0.0886
26.6	117.78	0.0052	0.1675	0.0160	0.0784	0.0997
26.7	118.83	0.1326	0.2560	0.0140	0.0877	0.2343
26.8	119.09	0.0345	0.2174	0.0107	0.0893	0.1345
26.9	119.17	0.0160	0.0987	0.0082	0.0832	0.1074
27	119.34	0.0053	0.0648	0.0063	0.0771	0.0887
27.1	119.50	0.0040	0.0450	0.0040	0.0710	0.0791
27.2	119.57	0.0033	0.0298	0.0035	0.0696	0.0764
27.3	119.62	0.0029	0.0223	0.0031	0.0682	0.0741
27.4	119.63	0.0027	0.0168	0.0026	0.0668	0.0721
27.5	119.64	0.0025	0.0112	0.0022	0.0655	0.0701
27.6	119.65	0.0023	0.0099	0.0019	0.0641	0.0683
27.7	119.65	0.0022	0.0086	0.0016	0.0627	0.0664
27.8	119.65	0.0021	0.0074	0.0011	0.0613	0.0645

27.9	119.65	0.0019	0.0061	0.0011	0.0603	0.0633
28	119.66	0.0018	0.0055	0.0011	0.0606	0.0635
28.1	119.66	0.0017	0.0052	0.0008	0.0609	0.0634
28.2	119.67	0.0017	0.0048	0.0007	0.0613	0.0636
28.3	119.68	0.0017	0.0045	0.0006	0.0604	0.0627
28.4	119.69	0.0017	0.0041	0.0005	0.0589	0.0610
28.5	119.69	0.0017	0.0038	0.0005	0.0573	0.0594
28.6	119.70	0.0017	0.0035	0.0004	0.0557	0.0577
28.7	119.70	0.0017	0.0031	0.0003	0.0550	0.0569
28.8	119.70	0.0017	0.0029	0.0002	0.0545	0.0564
28.9	119.69	0.0016	0.0027	0.0002	0.0539	0.0558
29	119.69	0.0015	0.0025	0.0003	0.0534	0.0552
29.1	119.69	0.0014	0.0023	0.0002	0.0529	0.0546
29.2	119.70	0.0013	0.0021	0.0002	0.0524	0.0539
29.3	119.70	0.0012	0.0021	0.0002	0.0519	0.0533
29.4	119.70	0.0011	0.0020	0.0002	0.0514	0.0527
29.5	119.71	0.0010	0.0019	0.0002	0.0508	0.0520
29.6	119.72	0.0009	0.0018	0.0002	0.0503	0.0514
29.7	119.73	0.0009	0.0018	0.0002	0.0496	0.0507
29.8	119.74	0.0009	0.0017	0.0001	0.0488	0.0499
29.9	119.74	0.0009	0.0017	0.0001	0.0481	0.0492
30	119.74	0.0009	0.0017	0.0001	0.0474	0.0484
30.1	119.74	0.0009	0.0016	0.0001	0.0467	0.0477
30.2	119.74	0.0009	0.0016	0.0001	0.0463	0.0473
30.3	119.74	0.0009	0.0015	0.0001	0.0459	0.0469
30.4	119.74	0.0009	0.0015	0.0000	0.0456	0.0465
30.5	119.74	0.0009	0.0015	0.0000	0.0452	0.0462
30.6	119.74	0.0000	0.0014	0.0000	0.0448	0.0448
30.7	119.74	0.0000	0.0014	0.0000	0.0443	0.0443
30.8	119.74	0.0000	0.0013	0.0000	0.0438	0.0438

30.9	119.74	0.0000	0.0013	0.0000	0.0433	0.0433
31	119.74	0.0000	0.0013	0.0000	0.0428	0.0428
31.1	119.74	0.0000	0.0012	0.0000	0.0423	0.0423
31.2	119.74	0.0000	0.0012	0.0000	0.0417	0.0417
31.3	119.74	0.0000	0.0011	0.0000	0.0413	0.0413
31.4	119.74	0.0000	0.0011	0.0000	0.0412	0.0412
31.5	119.74	0.0000	0.0011	0.0000	0.0411	0.0411
31.6	119.74	0.0000	0.0010	0.0000	0.0410	0.0410
31.7	119.74	0.0000	0.0010	0.0000	0.0408	0.0408
31.8	119.74	0.0000	0.0009	0.0000	0.0407	0.0407
31.9	119.74	0.0000	0.0009	0.0000	0.0406	0.0406
32	119.74	0.0000	0.0009	0.0000	0.0404	0.0404
32.1	119.74	0.0000	0.0008	0.0000	0.0402	0.0402
32.2	119.74	0.0000	0.0007	0.0000	0.0400	0.0400
32.3	119.74	0.0000	0.0006	0.0000	0.0398	0.0398
32.4	119.74	0.0000	0.0005	0.0000	0.0396	0.0396
32.5	119.74	0.0000	0.0004	0.0000	0.0394	0.0394
32.6	119.74	0.0000	0.0003	0.0000	0.0392	0.0392
32.7	119.74	0.0000	0.0003	0.0000	0.0391	0.0391
32.8	119.74	0.0000	0.0002	0.0000	0.0391	0.0391
32.9	119.74	0.0000	0.0002	0.0000	0.0390	0.0390
33	119.74	0.0000	0.0002	0.0000	0.0389	0.0389
33.1	119.74	0.0000	0.0002	0.0000	0.0388	0.0388
33.2	119.74	0.0000	0.0001	0.0000	0.0387	0.0387
33.3	119.74	0.0000	0.0001	0.0000	0.0387	0.0387
33.4	119.74	0.0000	0.0001	0.0000	0.0386	0.0386
33.5	119.74	0.0000	0.0001	0.0000	0.0384	0.0384
33.6	119.74	0.0000	0.0001	0.0000	0.0381	0.0381
33.7	119.74	0.0000	0.0001	0.0000	0.0378	0.0378
33.8	119.74	0.0000	0.0001	0.0000	0.0376	0.0376

33.9	119.74	0.0000	0.0000	0.0000	0.0373	0.0373
34	119.74	0.0000	0.0000	0.0000	0.0370	0.0370
34.1	119.74	0.0000	0.0000	0.0000	0.0368	0.0368
34.2	119.74	0.0000	0.0000	0.0000	0.0365	0.0365
34.3	119.74	0.0000	0.0000	0.0000	0.0362	0.0362
34.4	119.74	0.0000	0.0000	0.0000	0.0360	0.0360
34.5	119.74	0.0000	0.0000	0.0000	0.0358	0.0358

Appendix 9. Water table levels at Hydrohill.

Well No.	Month	Day	Hour	Minute	Hours after July 5 00:00	Water level (m)	Well bottom level (m)	Well top level (m)
A1	7	5	14	0	0.5833		37.89	39.15
	7	5	21	20	0.8889	37.95		
	7	5	23	20	0.9722	37.96		
	7	6	5	55	24.2465	38.15		
	7	6	8	30	24.3542	37.98		
	7	7	9	30	48.3958			
	7	7	16	10	48.6736			
	7	8	8	40	72.3611	37.91		
	7	8	14	40	72.6111	37.96		
	7	9	7	35	96.3160			
	8	4	16	19	720.6799			
	8	4	21	0	720.8750	38		
	8	5	8	9	744.3396	38.1		
	8	6	20	25	768.8507	37.92		
	8	7	10	11	792.4243			
	9	1	8	3	1392.335	37.91		
	9	2	8	1	1416.334			
A2	7	5	14	1	0.5840		37.85	39.05
	7	5	21	21	0.8896	37.91		
	7	5	23	21	0.9729	37.9		
	7	6	5	56	24.2472	37.93		
	7	6	8	31	24.3549	37.92		
	7	7	9	31	48.3965	37.87		
	7	7	16	12	48.6750	37.92		
	7	8	8	41	72.3618	37.87		
	7	8	14	41	72.6118	37.91		
	7	9	7	36	96.3167	37.9		

	7	9	14	57	96.6229	37.89		
	7	10	8	10	120.3403			
	8	4	21	1	720.8757			
	8	5	8	10	744.3403	38		
	8	6	20	16	768.8444	37.97		
	8	7	10	12	792.4250	37.92		
	8	8	10	22	816.4319	37.91		
	8	9	8	15	840.3438	37.89		
	8	10	8	21	864.3479			
A3	7	5	6	32	0.2722		38.06	39.25
	7	5	9	2	0.3764	38.2		
	7	5	14	2	0.5847	38.19		
	7	5	21	22	0.8903	38.17		
	7	5	23	22	0.9736	38.23		
	7	6	5	57	24.2479	38.25		
	7	6	8	33	24.3563	38.19		
	7	7	9	33	48.3979	38.11		
	7	7	16	13	48.6757	38.13		
	7	8	8	42	72.3625	38.16		
	7	8	14	42	72.6125	38.18		
	7	9	8	38	96.3597	38.09		
	7	9	14	58	96.6236	38.07		
	7	10	8	11	120.3410			
	8	4	16	21	720.6813	38.1		
	8	4	21	2	720.8764	38.35		
	8	5	8	11	744.3410	38.43		
	8	6	20	37	768.8590	38.17		
	8	7	10	13	792.4257	38.08		
	8	8	10	23	816.4326			
	8	9	8	16	840.3444			
	8	10	8	22	864.3486	38.08		

	8	11	8	32	888.3556			
A4	7	5	6	33	0.2729		38.21	39.5
	7	5	9	3	0.3771			
	7	5	14	3	0.5854	38.24		
	7	5	21	23	0.8910	38.28		
	7	5	23	23	0.9743	38.32		
	7	6	5	58	24.2486	38.61		
	7	6	8	34	24.3569	38.42		
	7	7	9	34	48.3986	38.3		
	7	7	16	14	48.6764	38.3		
	7	8	8	43	72.3632	38.36		
	7	8	14	43	72.6132	38.38		
	7	9	8	39	96.3604	38.29		
	7	9	14	59	96.6243	38.27		
	7	10	8	12	120.3417			
	8	4	16	22	720.6819	38.27		
	8	4	21	3	720.8771	38.33		
	8	5	8	12	744.3417	38.64		
	8	6	20	28	768.8528	38.42		
	8	7	10	14	792.4264	38.32		
	8	8	10	24	816.4333	38.24		
	8	9	8	17	840.3451			
B1	7	5	6	34	0.2736		38.42	39.7
	7	5	23	24	0.9750			
	7	6	5	59	24.2493	38.62		
	7	6	8	35	24.3576	38.63		
	7	7	9	35	48.3993	38.64		
	7	7	16	15	48.6771	38.61		
	7	8	8	44	72.3639	38.6		
	7	8	14	44	72.6139	38.62		
	7	9	8	39	96.3604	38.62		

	7	9	15	0	96.6250	38.6		
	7	10	8	13	120.3424	38.57		
	7	10	18	45	120.7813	38.56		
	7	12	8	22	168.3486	38.53		
	7	12	14	21	168.5979	38.52		
	7	12	16	40	168.6944	38.5		
	7	13	8	12	192.3417	38.5		
	7	14	8	30	216.3542	38.5		
	7	15	8	0	240.3333	38.48		
	7	15	17	35	240.7326	38.5		
	7	16	8	10	264.3403	38.49		
	7	17	16	0	288.6667	38.46		
	7	17	17	40	288.7361	38.46		
	7	18	8	20	312.3472			
	8	4	16	23	720.6826			
	8	4	21	4	720.8778	38.63		
	8	5	8	13	744.3424	39.04		
	8	6	20	29	768.8535	38.71		
	8	7	10	15	792.4271	38.61		
	8	8	10	25	816.4340	38.56		
	8	9	8	18	840.3458	38.55		
	8	10	8	24	864.3500	38.51		
	8	11	8	34	888.3569	38.5		
	8	12	8	22	912.3486	38.47		
	8	13	8	29	936.3535			
B2	7	5	21	25	0.8924		38.34	39.6
	7	5	23	25	0.9757	38.37		
	7	6	6	0	24.2500	38.4		
	7	6	8	36	24.3583	38.47		
	7	7	9	36	48.4000	38.45		
	7	7	16	16	48.6778	38.43		

	7	8	8	45	72.3646	38.42		
	7	8	14	45	72.6146	38.46		
	7	9	8	39	96.3604	38.44		
	7	9	15	1	96.6257	38.44		
	7	10	8	14	120.3431	38.37		
	7	10	18	34	120.7736	38.39		
	7	12	8	30	168.3542			
	8	4	16	24	720.6833	38.35		
	8	4	21	5	720.8785			
B3	7	5	6	36	0.2750		38.54	39.8
	7	5	21	26	0.8931			
	7	5	23	26	0.9764	38.56		
	7	6	6	1	24.2507	39.11		
	7	6	8	37	24.3590	39.05		
	7	7	9	37	48.4007	38.79		
	7	7	16	17	48.6785	38.81		
	7	8	8	46	72.3653	38.78		
	7	8	14	46	72.6153	38.95		
	7	9	8	39	96.3604	38.76		
	7	9	15	1	96.6257	38.71		
	7	10	8	15	120.3438	38.62		
	7	10	18	45	120.7813	38.6		
	7	12	8	25	168.3507			
	7	12	14	20	168.5972	38.59		
	7	12	16	24	168.6833	38.61		
	7	13	8	14	192.3431	38.62		
	7	14	8	24	216.3500	38.56		
	7	15	8	2	240.3347			
	8	4	16	25	720.6840			
	8	4	21	6	720.8792	38.67		
	8	5	8	15	744.3438	39.2		

	8	6	20	31	768.8549	39.03		
	8	7	10	17	792.4285	38.75		
	8	8	10	27	816.4354	38.61		
	8	9	8	20	840.3472	38.61		
	8	10	8	26	864.3514			
	8	12	8	34	912.3569			
	8	13	8	31	936.3549	38.59		
	8	14	8	17	960.3451			
B4	7	5	9	7	0.3799		38.77	40
	7	5	14	7	0.5882	38.83		
	7	5	21	27	0.8938	39.18		
	7	5	23	27	0.9771	39.2		
	7	6	6	2	24.2514	39.24		
	7	6	8	38	24.3597	39.22		
	7	7	9	38	48.4014	39.08		
	7	7	16	18	48.6792	39.08		
	7	8	8	47	72.3660	39.13		
	7	8	14	47	72.6160	39.18		
	7	9	8	40	96.3611	39.04		
	7	9	15	2	96.6264	39.01		
	7	10	8	16	120.3444	38.97		
	7	10	18	45	120.7813	38.94		
	7	12	8	25	168.3507	38.86		
	7	12	14	25	168.6007	38.92		
	7	12	16	25	168.6840	38.91		
	7	13	8	10	192.3403	38.91		
	7	14	8	20	216.3472	38.85		
	7	15	8	2	240.3347	38.82		
	7	15	17	34	240.7319			
	8	4	16	26	720.6847			
	8	4	21	7	720.8799	38.96		

	8	5	8	16	744.3444	39.42		
	8	6	20	32	768.8556	39.2		
	8	7	10	18	792.4292	39.04		
	8	8	10	28	816.4361	38.95		
	8	9	8	21	840.3479	38.91		
	8	10	8	27	864.3521	38.83		
	8	11	8	37	888.3590			
C1	7	5	6	38	0.2764		39.41	40.6
	7	5	9	7	0.3799	39.42		
	7	5	14	8	0.5889	39.53		
	7	5	21	28	0.8944	39.48		
	7	5	23	28	0.9778	39.53		
	7	6	6	3	24.2521	39.87		
	7	6	8	39	24.3604	39.72		
	7	7	9	39	48.4021	39.54		
	7	7	16	19	48.6799	39.56		
	7	8	8	48	72.3667	39.77		
	7	8	14	48	72.6167	39.66		
	7	9	8	41	96.3618	39.52		
	7	9	15	3	96.6271	39.49		
	7	10	8	19	120.3465	39.43		
	7	12	8	20	168.3472			
	7	12	14	30	168.6042	39.47		
	7	12	16	40	168.6944	39.5		
	7	13	8	11	192.3410	39.47		
	7	14	8	20	216.3472			
	8	4	16	27	720.6854			
	8	4	21	8	720.8806			
	8	5	8	17	744.3451	40		
	8	6	20	33	768.8563	39.68		
	8	7	10	19	792.4299	39.51		

	8	8	10	29	816.4368	39.45		
	8	9	8	22	840.3486	39.48		
	8	10	8	28	864.3528			
C2	7	5	9	8	0.3806		39.37	40.5
	7	5	14	9	0.5896	39.61		
	7	5	21	29	0.8951	39.36		
	7	5	23	28	0.9778	39.85		
	7	6	6	4	24.2528	40.02		
	7	6	8	40	24.3611	39.88		
	7	7	9	40	48.4028	39.54		
	7	7	16	20	48.6806	39.51		
	7	8	8	49	72.3674	39.51		
	7	8	14	49	72.6174	39.61		
	7	9	8	42	96.3625	39.51		
	7	9	15	4	96.6278	39.48		
	7	10	8	20	120.3472	39.4		
	7	10	18	35	120.7743	39.41		
	7	12	8	10	168.3403	39.35		
	7	12	14	10	168.5903	39.36		
	7	12	16	38	168.6931	39.36		
	7	13	8	18	192.3458	39.37		
	7	14	8	20	216.3472	39.36		
	7	15	8	9	240.3396	39.36		
	7	15	17	29	240.7285	39.34		
	7	17	8	0	288.3333			
	8	4	16	28	720.6861	39.35		
	8	4	21	9	720.8813			
	8	5	8	18	744.3458	40.13		
	8	6	20	34	768.8569	39.71		
	8	7	10	20	792.4306	39.53		
	8	8	10	30	816.4375	39.42		

	8	9	8	23	840.3493	39.4		
	8	10	8	29	864.3535	39.35		
	8	11	8	39	888.3604	39.36		
	8	12	8	27	912.3521			
C3	7	5	6	40	0.2778		39.46	40.75
	7	5	9	9	0.3813			
	7	5	14	10	0.5903	39.5		
	7	5	21	30	0.8958	39.53		
	7	5	23	29	0.9785	39.57		
	7	6	6	5	24.2535	39.94		
	7	6	8	41	24.3618	40.04		
	7	7	9	41	48.4035	39.88		
	7	7	16	21	48.6813	39.94		
	7	8	8	50	72.3681	40.05		
	7	8	14	50	72.6181	40.05		
	7	9	8	43	96.3632	39.83		
	7	9	15	5	96.6285	39.76		
	7	10	8	21	120.3479	39.67		
	7	10	18	45	120.7813	39.67		
	7	12	8	22	168.3486	39.61		
	7	12	14	22	168.5986	39.66		
	7	12	16	22	168.6819	39.67		
	7	13	8	22	192.3486	39.69		
	7	14	8	22	216.3486	39.64		
	7	15	8	50	240.3681	39.59		
	7	15	17	29	240.7285	39.59		
	7	16	8	13	264.3424	39.57		
	7	17	16	4	288.6694	39.54		
	7	17	17	40	288.7361	39.55		
	7	18	8	15	312.3438	39.53		
	7	20	8	21	360.3479			

	8	4	16	29	720.6868			
	8	4	21	10	720.8819	39.55		
	8	5	8	19	744.3465	40.21		
	8	6	20	35	768.8576	40.04		
	8	7	10	21	792.4313	39.82		
	8	8	10	31	816.4382	39.7		
	8	9	8	24	840.3500	39.65		
	8	10	8	30	864.3542	39.59		
	8	11	8	40	888.3611	39.57		
	8	12	8	28	912.3528	39.55		
	8	13	8	35	936.3576			
	8	19	8	33	1080.356			
	8	20	8	41	1104.361	39.52		
	8	21	8	20	1128.347			
C4	7	5	6	41	0.2785		39.78	41
	7	5	14	11	0.5910			
	7	5	21	31	0.8965	39.86		
	7	5	23	30	0.9792	40.21		
	7	6	6	6	24.2542	40.41		
	7	6	8	42	24.3625	40.39		
	7	7	9	42	48.4042	40.23		
	7	7	16	21	48.6813	40.3		
	7	8	8	51	72.3688	40.4		
	7	8	14	51	72.6188	40.42		
	7	9	8	44	96.3639	40.15		
	7	9	15	6	96.6292	40.14		
	7	10	8	22	120.3486	39.81		
	7	10	18	45	120.7813	39.83		
	7	12	8	25	168.3507	39.9		
	7	12	14	22	168.5986	39.96		
	7	12	16	40	168.6944	39.99		

	7	13	8	10	192.3403	39.97		
	7	14	8	35	216.3576	39.9		
	7	15	8	6	240.3375	39.87		
	7	15	17	30	240.7292	39.89		
	7	16	8	15	264.3438	39.84		
	7	17	16	2	288.6681			
	8	4	16	30	720.6875			
	8	4	21	11	720.8826	39.86		
	8	5	8	20	744.3472	40.55		
	8	6	20	36	768.8583	40.35		
	8	7	10	22	792.4319	40.18		
	8	8	10	22	816.4319	40.02		
	8	9	8	25	840.3507	39.92		
	8	10	8	31	864.3549	39.84		
	8	11	8	41	888.3618	39.87		
	8	12	8	29	912.3535			
D1	7	5	6	42	0.2792		41.59	42.8
	7	5	9	11	0.3826	41.71		
	7	5	14	12	0.5917	42.05		
	7	5	21	32	0.8972	42.01		
	7	5	23	31	0.9799	42.23		
	7	6	6	7	24.2549	42.23		
	7	6	8	42	24.3625	42.12		
	7	7	9	43	48.4049	41.76		
	7	7	16	22	48.6819	41.78		
	7	8	8	52	72.3694	41.9		
	7	8	14	52	72.6194	41.95		
	7	9	8	45	96.3646	41.7		
	7	9	15	7	96.6299	41.64		
	7	10	8	23	120.3493	41.58		
	7	12	16	27	168.6854			

	7	13	8	11	192.3410	41.61		
	7	14	8	27	216.3521			
	8	4	16	31	720.6882	41.86		
	8	4	21	11	720.8826	42.37		
	8	5	8	21	744.3479	42.39		
	8	6	20	37	768.8590	42.16		
	8	7	10	23	792.4326	41.67		
	8	8	10	33	816.4396			
D2	7	5	9	12	0.3833		41.48	42.7
	7	5	14	13	0.5924	41.78		
	7	5	21	33	0.8979	42.08		
	7	5	23	32	0.9806	42.14		
	7	6	6	8	24.2556	42.12		
	7	6	8	43	24.3632	42.04		
	7	7	9	44	48.4056	41.66		
	7	7	16	23	48.6826	41.68		
	7	8	8	52	72.3694	41.79		
	7	8	14	52	72.6194	41.88		
	7	9	8	46	96.3653	41.62		
	7	9	15	8	96.6306	41.58		
	7	10	8	24	120.3500			
	8	4	16	32	720.6889			
	8	4	21	12	720.8833	42.18		
	8	5	8	22	744.3486	42.27		
	8	6	20	38	768.8597	41.88		
	8	7	10	24	792.4333	41.6		
	8	8	10	34	816.4403			
D3	7	5	6	44	0.2806	42.1	41.71	42.9
	7	5	9	13	0.3840	42.18		
	7	5	14	14	0.5931	42.25		
	7	5	21	34	0.8986	41.88		

	7	5	23	33	0.9813	42.3		
	7	6	6	9	24.2563	42.38		
	7	6	8	44	24.3639	42.22		
	7	7	9	45	48.4063	41.98		
	7	7	16	24	48.6833	42.09		
	7	8	8	53	72.3701	42.33		
	7	8	14	52	72.6194	42.19		
	7	9	8	47	96.3660	41.96		
	7	9	15	9	96.6313	41.9		
	7	10	8	15	120.3438	41.77		
	7	10	18	50	120.7847	41.76		
	7	12	8	20	168.3472	41.73		
	7	12	14	34	168.6069	41.76		
	7	12	16	40	168.6944	41.81		
	7	13	8	12	192.3417	41.72		
	7	14	8	27	216.3521			
	8	4	16	33	720.6896	42.27		
	8	4	21	13	720.8840	42.25		
	8	5	8	23	744.3493	42.56		
	8	6	20	39	768.8604	42.16		
	8	7	10	25	792.4340	41.96		
	8	8	10	35	816.4410	41.74		
	8	9	8	28	840.3528			
D4	7	5	14	15	0.5938		41.95	43.2
	7	5	21	35	0.8993	42.19		
	7	5	23	34	0.9819	42.06		
	7	6	6	10	24.2569	42.47		
	7	6	8	45	24.3646	42.33		
	7	7	9	46	48.4069	42.1		
	7	7	16	25	48.6840	42.1		
	7	8	8	54	72.3708	42.17		

	7	8	14	53	72.6201	42.24		
	7	9	8	48	96.3667	42.05		
	7	9	15	10	96.6319	42.01		
	7	10	8	26	120.3514			
	8	4	21	14	720.8847			
	8	5	8	24	744.3500	42.61		
	8	6	20	40	768.8611	42.23		
	8	7	20	26	792.8514	42.01		
	8	8	10	36	816.4417			
D5	7	5	14	15	0.5938		42.21	43.5
	7	5	21	36	0.9000	42.3		
	7	5	23	34	0.9819	42.35		
	7	6	6	11	24.2576	42.32		
	7	6	8	46	24.3653	42.24		
	7	7	9	47	48.4076			
	8	4	21	15	720.8854			
	8	5	8	25	744.3507	42.52		
	8	6	20	41	768.8618	42.3		
	8	7	10	27	792.4354			
E1	7	5	14	16	0.5944		43.86	44.95
	7	5	21	37	0.9007	44.1		
	7	5	23	35	0.9826	44.4		
	7	6	6	12	24.2583	44.51		
	7	6	8	47	24.3660	44.43		
	7	7	9	48	48.4083	44.53		
	7	7	16	27	48.6854	44.53		
	7	8	8	55	72.3715	44.61		
	7	8	14	54	72.6208	44.56		
	7	9	8	49	96.3674	44.33		
	7	9	15	11	96.6326	44.36		
	7	10	8	17	120.3451	44.22		

	7	12	8	16	168.3444	44.21		
	7	12	14	38	168.6097	44.43		
	7	12	16	40	168.6944	44.42		
	7	13	8	18	192.3458	44.25		
	7	14	8	31	216.3549	44.18		
	7	15	8	6	240.3375	44.14		
	7	15	17	30	240.7292	44.11		
	7	16	8	16	264.3444	44.08		
	7	17	16	0	288.6667	44.01		
	7	17	17	38	288.7347	44.02		
	7	18	8	20	312.3472	43.98		
	7	20	8	19	360.3465			
	8	4	21	16	720.8861			
	8	5	8	21	744.3479	44.58		
	8	6	20	42	768.8625	44.47		
	8	7	10	28	792.4361	44.33		
	8	8	10	38	816.4431	44.18		
	8	9	8	31	840.3549	44.11		
	8	10	8	37	864.3590	44.03		
	8	11	8	47	888.3660	44.02		
	8	12	8	35	912.3576	43.97		
	8	13	8	42	936.3625	43.9		
	8	14	8	28	960.3528	43.91		
	8	15	8	31	984.3549			
E2	7	5	9	17	0.3868		43.72	44.75
	7	5	14	16	0.5944	43.87		
	7	5	21	37	0.9007	44.14		
	7	5	23	36	0.9833	44.31		
	7	6	6	12	24.2583	44.43		
	7	6	8	48	24.3667	44.44		
	7	7	9	49	48.4090	44.43		

	7	7	16	27	48.6854	44.53		
	7	8	8	55	72.3715	44.54		
	7	8	14	55	72.6215	44.53		
	7	9	8	50	96.3681	44.62		
	7	9	15	12	96.6333	44.26		
	7	10	8	28	120.3528	44.17		
	7	10	18	51	120.7854	44.15		
	7	12	8	18	168.3458	44.33		
	7	12	15	41	168.6535	44.49		
	7	16	18	20	264.7639	43.95		
	7	17	16	3	288.6688	43.95		
	8	4	21	17	720.8868			
	8	5	8	27	744.3521	44.51		
	8	6	20	43	768.8632	44.49		
	8	7	10	29	792.4368	44.32		
	8	8	10	39	816.4438	44.13		
	8	9	8	32	840.3556	44.06		
	8	10	8	38	864.3597	43.98		
	8	11	8	48	888.3667	43.94		
	8	12	8	36	912.3583	43.9		
	8	13	8	43	936.3632	43.85		
	8	14	8	29	960.3535	43.91		
	8	15	8	32	984.3556	43.91		
	8	16	8	27	1008.352	43.87		
	8	17	8	22	1032.348	43.8		
	8	19	8	41	1080.361	43.76		
	8	20	8	48	1104.366	43.78		
	8	21	8	28	1128.352	43.87		
	8	22	8	37	1152.359	42.89		
	8	23	8	46	1176.365			
E3	7	5	6	49	0.2840		43.81	44.8

	7	5	9	18	0.3875	43.94		
	7	5	14	17	0.5951	43.92		
	7	5	21	37	0.9007	44.28		
	7	5	23	37	0.9840	44.56		
	7	6	6	13	24.2590	44.49		
	7	6	8	49	24.3674	44.58		
	7	7	9	50	48.4097	44.52		
	7	7	16	18	48.6792	44.61		
	7	8	8	56	72.3722	44.65		
	7	8	14	56	72.6222	44.63		
	7	9	8	51	96.3688	44.42		
	7	9	15	13	96.6340	44.36		
	7	10	8	29	120.3535	44.26		
	7	12	8	17	168.3451	44.39		
	7	12	14	39	168.6104	44.55		
	7	12	16	41	168.6951	44.54		
	7	13	8	19	192.3465	44.35		
	7	14	8	32	216.3556	44.24		
	7	15	8	7	240.3382	44.25		
	7	15	17	30	240.7292	44.19		
	7	16	8	17	264.3451	44.14		
	7	17	16	2	288.6681	44.06		
	7	17	17	46	288.7403	44.06		
	7	18	8	21	312.3479	44.03		
	7	20	8	21	360.3479	43.92		
	8	4	16	38	720.6931			
	8	4	21	18	720.8875	44.05		
	8	5	8	28	744.3528	44.59		
	8	6	20	44	768.8639	44.58		
	8	7	10	30	792.4375	44.42		
	8	8	10	40	816.4444	44.24		

	8	9	8	33	840.3563	44.16		
	8	10	8	39	864.3604	44.07		
	8	11	8	49	888.3674	44.04		
	8	12	8	37	912.3590	43.99		
	8	13	8	44	936.3639	43.96		
	8	14	8	30	960.3542	43.93		
	8	15	8	33	984.3563	43.96		
	8	16	8	28	1008.352	43.95		
	8	17	8	23	1032.349	43.91		
	8	19	8	42	1080.362	43.87		
	8	20	8	49	1104.367	43.96		
	8	21	8	29	1128.353	44.06		
	8	22	8	38	1152.359	44.07		
	8	23	8	47	1176.366			
							44.02	45.05
E4	7	5	14	18	0.5958			
	7	5	21	38	0.9014	44.25		
	7	5	23	38	0.9847	44.53		
	7	6	6	14	24.2597	44.69		
	7	6	8	50	24.3681	44.59		
	7	7	9	51	48.4104	44.51		
	7	7	16	29	48.6868	44.43		
	7	8	8	57	72.3729	44.72		
	7	8	14	57	72.6229	44.72		
	7	9	8	52	96.3694	44.45		
	7	9	15	14	96.6347	44.4		
	7	10	8	31	120.3549	44.3		
	7	10	18	49	120.7840	44.27		
	7	12	8	14	168.3431	44.31		
	7	12	14	39	168.6104	44.54		
	7	12	16	41	168.6951	44.51		
	7	13	8	21	192.3479	44.37		

	7	14	8	31	216.3549	44.29		
	7	15	8	6	240.3375	44.24		
	7	15	17	34	240.7319	44.22		
	7	16	8	19	264.3465	44.18		
	7	17	16	1	288.6674	44.1		
	7	17	17	40	288.7361	44.1		
	7	18	8	20	312.3472			
	8	4	21	19	720.8882			
	8	5	8	29	744.3535	44.78		
	8	6	20	45	768.8646	44.63		
	8	7	10	31	792.4382	44.48		
	8	8	10	41	816.4451	44.29		
	8	9	8	34	840.3569	44.21		
	8	10	8	40	864.3611	44.12		
	8	11	8	50	888.3681	44.11		
	8	12	8	38	912.3597			
F1	7	5	6	51	0.2854		45.01	46
	7	5	9	19	0.3882	45.14		
	7	5	14	19	0.5965	45.14		
	7	5	21	39	0.9021	45.16		
	7	5	23	39	0.9854	45.32		
	7	6	6	15	24.2604	45.8		
	7	6	8	51	24.3688	45.64		
	7	7	9	52	48.4111	45.54		
	7	7	16	30	48.6875	45.61		
	7	8	8	58	72.3736	45.68		
	7	8	14	58	72.6236	45.67		
	7	9	8	53	96.3701	45.48		
	7	9	15	15	96.6354	45.43		
	7	10	8	30	120.3542	45.3		
	7	10	18	50	120.7847	45.26		

	7	12	8	15	168.3438	45.24		
	7	12	14	45	168.6146	45.46		
	7	12	16	42	168.6958	45.46		
	7	13	8	20	192.3472	45.31		
	7	14	8	30	216.3542	45.33		
	7	15	8	5	240.3368	45.19		
	7	16	8	20	264.3472	45.13		
	7	17	16	0	288.6667	45.09		
	7	17	17	40	288.7361	45.1		
	7	18	8	20	312.3472	45.08		
	7	20	8	20	360.3472			
	8	4	16	40	720.6944	45.26		
	8	4	21	20	720.8889	45.46		
	8	5	8	30	744.3542	45.7		
	8	6	20	46	768.8653	45.59		
	8	7	10	32	792.4389	45.45		
	8	8	10	42	816.4458	45.28		
	8	9	8	35	840.3576	45.21		
	8	10	8	41	864.3618	45.13		
	8	11	8	51	888.3688	45.13		
	8	12	8	39	912.3604	45.08		
	8	13	8	46	936.3653			
	8	19	8	44	1080.363			
	8	20	8	51	1104.368	45.15		
	8	21	8	28	1128.352	45.06		
	8	22	8	40	1152.361			

Appendix 10. Isotopic and chemical compositions of samples at Hydrohill.

Sample type	Other data	$\delta^{18}\text{O}$	Hours after July 5 00:00	Chloride ueq/L	SiO_2 umol/L
Rain		-8.3	4.583	36.96	28.25
gage		-11.75	5.500	56.98	-99
		-11.25	6.500	15.80	9.15
		-12.05	7.333	15.52	7.05
		-12.05	8.583	8.75	-99
		-12.7	9.700	10.44	2.87
		-13.65	13.500	5.08	2.87
		-13.25	15.083	16.08	4.95
		-12.9	17.283	31.03	2.87
		-11.6	18.500	16.36	2.87
		-10.95	22.000	39.49	2.87
		-9.9	23.000	4.80	2.87
		-10.15	24.500	15.80	-99
		-9.65	26.000	18.34	4.95
		-6.5	618.550	11.28	2.87
Rain		-8.5	4.500	24.82	19.72
trough		-11.6	5.500	16.93	19.72
		-11.4	6.500	4.51	4.95
		-12	7.367	3.39	4.95
		-12.05	9.700	7.05	7.05
		-13.45	13.500	3.67	2.87
		-12.75	15.083	7.62	4.95
		-11.9	17.283	4.80	7.05
		-10.7	18.500	9.59	11.25
		-10.35	22.000	6.21	7.05
		-10	23.000	5.64	9.15
		-9.75	24.500	9.59	9.15

		-8.75	26.000	3.67	7.05
		-9.05	27.500	4.51	9.15
		-6.15	618.550	8.46	4.95
GW wells	A3	-7.4	10.500	89.71	442.92
	C1	-10.35	10.583	66.01	695.67
	D1	-7.65	10.667	43.16	620.2
	D3	-12.1	10.750	45.14	413.08
	F	-9.7	10.833	80.96	446.9
	B3	-6.85	17.500	46.26	620.2
	C2	-10.65	17.500	45.42	429.92
	D1	-7.5	17.667	32.16	498.73
	D2	-7.2	17.667	33.57	469.77
	D3	-11.55	17.750	40.62	273.52
	E2	-9.4	17.750	42.88	668.53
	E3	-6.3	17.833	66.01	495.82
	F	-9.65	17.833	55.86	507.52
	A3	-6.85	17.833	99.02	938.43
	A4	-6.9	34.500	147.82	915.13
	B2	-6.65	34.500	72.22	874.77
	B3	-6.1	34.583	50.21	761.77
	B4	-6.55	34.583	42.32	467.3
	C4	-6.6	34.667	44.01	346.7
	C2	-10	34.667	40.90	247.87
	C1	-9.3	34.750	35.26	280.23
	D1	-7.5	34.750	26.80	277.72
	D2	-6.45	34.833	25.11	285.27
	D3	-9.65	34.833	31.31	272.72
	D4	-6.25	34.917	86.04	426.32
	E4	-6.25	34.917	29.90	260.25
	E3	-6.6	35.000	57.83	257.77

	E2	-8.7	35.000	34.42	242.95
	E1	-6.2	35.083	33.01	242.95
	F	-8.05	35.083	46.83	220.95
Lysimeter 1		-9.75	7.167	69.96	336.33
		-9.45	8.167	44.01	218.52
		-7.2	13.550	36.96	292.83
		-8.55	18.550	16.36	375.53
		-6.5	21.500	33.01	277.72
		-6.65	26.400	31.03	277.72
		-6.75	84.000	33.57	290.3
		-6.3	618.250	79.27	328.58
Lysimeter		-7.95	6.500	33.29	481.13
		-8.1	8.333	90.55	442.62
		-8.35	13.417	29.06	486.7
		-8.25	17.500	29.90	489.48
		-8.35	21.500	29.34	481.13
		-8.45	26.167	28.49	475.58
		-8.4	35.833	29.06	475.58
		-8.25	52.067	31.88	486.7
		-8.75	63.450	25.95	467.3
		-7.4	600.000	61.50	431.73
River water		-8.7	35.917	83.78	138.08
		-8.05	58.167	88.58	156.65
		-6.65	576.000	87.73	122.02
		-6.65	624.000	99.58	145.02
Surface runoff		-8.4	-3.417	110.58	81.5
		-8.3	-3.417	123.84	81.5

		-11.6	4.917	14.11	18.57
		-12.15	6.283	25.67	149.67
		-12.25	6.550	4.23	3.82
		-12.1	6.917	13.82	131.18
		-12.55	7.667	12.69	74.85
		-12.45	8.667	6.77	22.82
		-13.2	10.483	18.05	170.72
		-13	11.333	17.77	173.08
		-12.45	11.500	8.18	31.35
		-12.9	13.200	6.21	10.12
		-10.55	21.000	5.08	10.12
		-10.55	21.250	18.05	173.08
		-9.95	22.083	10.44	24.95
		-10.3	24.250	12.41	18.57
		-9.4	25.250	14.67	158.98
		-9	25.883	9.31	124.3
		-9.35	26.733	14.11	145.02
		-9.15	27.000	12.98	92.63
		-9.2	34.500	16.64	-99
		-6.25	600.000	53.88	29.22
Subsurface runoff					
		-11.1	4.917	128.92	52.93
0-30 cm		-10.95	5.500	69.40	184.92
		-11.25	6.083	60.37	208.85
		-11.5	7.000	19.46	158.98
		-12.05	8.667	25.95	206.45
		-12.65	10.167	21.44	189.68
		-12.5	10.833	23.41	208.85
		-13.15	11.333	14.95	175.43
		-12.9	11.417	19.18	213.68
		-13.2	12.417	14.11	175.43

		-12.45	14.083	31.31	208.85
		-12.95	14.583	27.36	223.38
		-11.7	16.167	31.88	223.38
		-11.1	21.000	34.42	180.17
		-10.45	23.500	36.11	223.38
		-9.55	25.250	15.80	163.67
		-9.35	26.750	16.08	156.65
		-9.5	32.000	107.20	216.1
		-6.25	600.000	44.57	177.8
		-6.4	600.000	39.78	128.88
		-6.45	600.000	49.09	216.1
		-6.25	600.000	68.83	262.73
Subsurface runoff		-11.45	8.000	18.34	170.72
30-60 cm		-11.2	12.517	-99.00	-99
		-9	20.917	37.80	211.27
		-10.3	21.750	22.57	168.37
		-9.3	25.500	20.31	168.37
		-9.35	27.167	22.00	175.43
		-6.3	600.000	41.75	135.78
Subsurface runoff		-5.85	-234.72	42.60	242.35
60-100 cm		-5.45	-77.04		
		-9	5.833	48.52	223.38
		-11.1	6.500	34.70	175.43
		-10.25	7.500	23.98	175.43
		-10.3	11.917	25.67	204.03
		-7.45	19.917	39.78	247.87
		-8.85	21.250	35.83	208.85
		-8.4	24.833	36.11	218.52
		-7.8	26.750	35.54	238.03

		-6.85	31.500	35.26	277.72
		-6.5	600.000	42.03	233.13
		-6.75	600.000	41.19	220.95
		-6.1			
		-6.16			
		-5.65			
		-7	600.000	35.26	245.4
		-5.38			

Appendix 11. Percentages of new water in groundwater samples, calculated using isotopic and chemical compositions.

Well #	Time (h)	$\delta^{18}\text{O}$		Chloride		Silica	
		seq. rain	cum. rain	40 $\mu\text{eq/L}$	100 $\mu\text{eq/L}$	275 $\mu\text{M/L}$	400 $\mu\text{M/L}$
A3	10.500	20	26	-151	11	-63	-11
C1	10.583	63	80	-79	37	-158	-75
D1	10.667	24	30	-10	61	-129	-56
D3	10.750	88	112	-16	59	-52	-3
F	10.833	54	68	-124	20	-64	-12
A3	17.833	13	14	-179	1	-248	-137
B3	17.500	13	14	-19	58	-129	-56
C2	17.500	70	79	-16	59	-58	-8
D1	17.667	22	25	24	73	-84	-25
D2	17.667	18	20	19	71	-73	-18
D3	17.750	83	94	-2	64	1	32
E2	17.750	51	58	-9	61	-147	-69
E3	17.833	4	5	-79	37	-83	-24
F	17.833	55	62	-48	47	-87	-27
A4	34.500	25	17	-327	-51	-240	-131
B2	34.500	18	12	-98	30	-225	-121
B3	34.583	3	2	-31	54	-182	-92
B4	34.583	15	10	-7	62	-72	-17
C1	34.750	90	62	14	70	-2	31
C2	34.667	110	75	-3	64	10	39
C4	34.667	16	11	-12	60	-27	14
D1	34.750	41	28	40	79	-1	31
D2	34.833	12	8	45	81	-4	29
D3	34.833	100	68	26	74	1	32
D4	34.917	7	5	-140	15	-57	-7
E1	35.083	5	4	21	72	12	40

E2	35.000	74	51	17	71	12	40
E3	35.000	16	11	-54	45	6	36
E4	34.917	7	5	31	75	6	36
F	35.083	56	38	-21	57	20	46

Appendix 12. Discharge at Hunting Creek, Hauver Branch,
and Owens Creek.

Year	Month	Day	Discharge (in m ³ /s)		
			Hunting Creek	Hauver Branch	Owens Creek
1985	1	1	0.1218	0.0481	
1985	1	2	0.2690	0.1274	
1985	1	3	0.1869	0.0878	
1985	1	4	0.1671	0.0793	
1985	1	5	0.1558	0.0736	
1985	1	6	0.1529	0.0680	
1985	1	7	0.1416	0.0623	
1985	1	8	0.1246	0.0623	
1985	1	9	0.1104	0.0566	
1985	1	10	0.1133	0.0538	
1985	1	11	0.1161	0.0538	
1985	1	12	0.1218	0.0538	
1985	1	13	0.1218	0.0510	
1985	1	14	0.1218	0.0510	
1985	1	15	0.1189	0.0453	
1985	1	16	0.1246	0.0425	
1985	1	17	0.1104	0.0425	
1985	1	18	0.1133	0.0453	
1985	1	19	0.1104	0.0425	
1985	1	20	0.1133	0.0425	
1985	1	21	0.1076	0.0425	
1985	1	22	0.1076	0.0396	
1985	1	23	0.1020	0.0396	
1985	1	24	0.1020	0.0368	
1985	1	25	0.0963	0.0368	
1985	1	26	0.0963	0.0340	

1985	1	27	0.0878	0.0340	
1985	1	28	0.0878	0.0312	
1985	1	29	0.0850	0.0312	
1985	1	30	0.0793	0.0283	
1985	1	31	0.0793	0.0283	
1985	2	1	0.1133	0.0425	
1985	2	2	0.1189	0.0481	
1985	2	3	0.0991	0.0368	
1985	2	4	0.0906	0.0368	
1985	2	5	0.0850	0.0340	
1985	2	6	0.0878	0.0340	
1985	2	7	0.0878	0.0340	
1985	2	8	0.0850	0.0312	
1985	2	9	0.0821	0.0312	
1985	2	10	0.0821	0.0283	
1985	2	11	0.0821	0.0283	
1985	2	12	1.7275	0.7363	
1985	2	13	0.6514	0.4248	
1985	2	14	0.3115	0.2294	
1985	2	15	0.2492	0.1643	
1985	2	16	0.2407	0.1331	
1985	2	17	0.2011	0.1161	
1985	2	18	0.1897	0.1020	
1985	2	19	0.2039	0.1048	
1985	2	20	0.2067	0.1076	
1985	2	21	0.2152	0.1133	
1985	2	22	0.3965	0.2152	
1985	2	23	0.6230	0.4248	
1985	2	24	0.5098	0.3398	
1985	2	25	0.3682	0.2436	
1985	2	26	0.3398	0.2096	

1985	2	27	0.2832	0.1756	
1985	2	28	0.2464	0.1416	
1985	3	1	0.2322	0.1274	
1985	3	2	0.2181	0.1161	
1985	3	3	0.1982	0.0991	
1985	3	4	0.1897	0.0906	
1985	3	5	0.1926	0.0878	
1985	3	6	0.1699	0.0765	
1985	3	7	0.1586	0.0708	
1985	3	8	0.1699	0.0708	
1985	3	9	0.1558	0.0623	
1985	3	10	0.1473	0.0595	
1985	3	11	0.1586	0.0623	
1985	3	12	0.2096	0.0906	
1985	3	13	0.1558	0.0680	
1985	3	14	0.1473	0.0623	
1985	3	15	0.1388	0.0566	
1985	3	16	0.1303	0.0538	
1985	3	17	0.1303	0.0538	
1985	3	18	0.1218	0.0481	
1985	3	19	0.1161	0.0453	
1985	3	20	0.1189	0.0425	
1985	3	21	0.1133	0.0396	
1985	3	22	0.1104	0.0368	
1985	3	23	0.5098	0.1982	
1985	3	24	0.5098	0.2605	
1985	3	25	0.3682	0.2039	
1985	3	26	0.2747	0.1529	
1985	3	27	0.2464	0.1331	
1985	3	28	0.2322	0.1189	
1985	3	29	0.3965	0.1501	

1985	3	30	0.6230	0.2266	
1985	3	31	0.4531	0.2039	
1985	4	1	0.5098	0.2662	
1985	4	2	0.3398	0.1841	
1985	4	3	0.3115	0.1558	
1985	4	4	0.2719	0.1331	
1985	4	5	0.2492	0.1218	
1985	4	6	0.2322	0.1133	
1985	4	7	0.2096	0.0963	
1985	4	8	0.2011	0.0878	
1985	4	9	0.1954	0.0850	
1985	4	10	0.1841	0.0765	
1985	4	11	0.1812	0.0708	
1985	4	12	0.1671	0.0680	
1985	4	13	0.1558	0.0623	
1985	4	14	0.1501	0.0566	
1985	4	15	0.1473	0.0566	
1985	4	16	0.1444	0.0538	
1985	4	17	0.1416	0.0510	
1985	4	18	0.1274	0.0453	
1985	4	19	0.1218	0.0425	
1985	4	20	0.1189	0.0425	
1985	4	21	0.1104	0.0396	
1985	4	22	0.1048	0.0368	
1985	4	23	0.0991	0.0340	
1985	4	24	0.0963	0.0312	
1985	4	25	0.1020	0.0340	
1985	4	26	0.0963	0.0312	
1985	4	27	0.0850	0.0275	
1985	4	28	0.0821	0.0258	
1985	4	29	0.0793	0.0249	

1985	4	30	0.0736	0.0235	
1985	5	1	0.0708	0.0221	
1985	5	2	0.1699	0.0623	
1985	5	3	0.6230	0.3115	
1985	5	4	0.1812	0.0963	
1985	5	5	0.1388	0.0736	
1985	5	6	0.1189	0.0651	
1985	5	7	0.1104	0.0566	
1985	5	8	0.1048	0.0481	
1985	5	9	0.0963	0.0425	
1985	5	10	0.0906	0.0396	
1985	5	11	0.0850	0.0340	
1985	5	12	0.1331	0.0595	
1985	5	13	0.1359	0.0566	
1985	5	14	0.0850	0.0340	
1985	5	15	0.0793	0.0312	
1985	5	16	0.1161	0.0510	
1985	5	17	0.2152	0.0963	
1985	5	18	0.3398	0.1926	
1985	5	19	0.1388	0.0821	
1985	5	20	0.1048	0.0623	
1985	5	21	0.1020	0.0595	
1985	5	22	0.1161	0.0651	
1985	5	23	0.2436	0.1529	
1985	5	24	0.1643	0.1048	
1985	5	25	0.1161	0.0736	
1985	5	26	0.0963	0.0566	
1985	5	27	0.0850	0.0453	
1985	5	28	0.0935	0.0453	
1985	5	29	0.0963	0.0425	
1985	5	30	0.0850	0.0368	

1985	5	31	0.1189	0.0623	
1985	6	1	0.0906	0.0425	
1985	6	2	0.0708	0.0312	
1985	6	3	0.0651	0.0261	
1985	6	4	0.0623	0.0238	
1985	6	5	0.3115	0.1048	
1985	6	6	0.1444	0.0623	
1985	6	7	0.0878	0.0368	
1985	6	8	0.0850	0.0312	
1985	6	9	0.0736	0.0258	
1985	6	10	0.0651	0.0207	
1985	6	11	0.0595	0.0181	
1985	6	12	0.0595	0.0176	
1985	6	13	0.0566	0.0159	
1985	6	14	0.0538	0.0142	
1985	6	15	0.0538	0.0147	
1985	6	16	0.0765	0.0181	
1985	6	17	0.0651	0.0150	
1985	6	18	0.0566	0.0127	
1985	6	19	0.0510	0.0110	
1985	6	20	0.0481	0.0102	
1985	6	21	0.0453	0.0096	
1985	6	22	0.0396	0.0088	
1985	6	23	0.0510	0.0108	
1985	6	24	0.0425	0.0091	
1985	6	25	0.0368	0.0082	
1985	6	26	0.0340	0.0071	
1985	6	27	0.0340	0.0065	
1985	6	28	0.0340	0.0065	
1985	6	29	0.0368	0.0065	
1985	6	30	0.0340	0.0059	

1985	7	1	0.0368	0.0065	
1985	7	2	0.0396	0.0071	
1985	7	3	0.0396	0.0065	
1985	7	4	0.0312	0.0057	
1985	7	5	0.0283	0.0051	
1985	7	6	0.0396	0.0147	
1985	7	7	0.0453	0.0105	
1985	7	8	0.0312	0.0062	
1985	7	9	0.0283	0.0059	
1985	7	10	0.0283	0.0065	
1985	7	11	0.0280	0.0057	
1985	7	12	0.0368	0.0068	
1985	7	13	0.0312	0.0062	
1985	7	14	0.0246	0.0051	
1985	7	15	0.0269	0.0082	
1985	7	16	0.0425	0.0079	
1985	7	17	0.0224	0.0045	
1985	7	18	0.0195	0.0037	
1985	7	19	0.0184	0.0031	
1985	7	20	0.0187	0.0028	
1985	7	21	0.0198	0.0028	
1985	7	22	0.0176	0.0028	
1985	7	23	0.0176	0.0025	
1985	7	24	0.0150	0.0023	
1985	7	25	0.0396	0.0074	
1985	7	26	0.5098	0.2436	
1985	7	27	0.1303	0.0821	
1985	7	28	0.0453	0.0142	
1985	7	29	0.0340	0.0096	
1985	7	30	0.0275	0.0082	
1985	7	31	0.0275	0.0076	

1985	8	1	0.0340	0.0082	
1985	8	2	0.0252	0.0065	
1985	8	3	0.0215	0.0059	
1985	8	4	0.0215	0.0057	
1985	8	5	0.0204	0.0051	
1985	8	6	0.0201	0.0048	
1985	8	7	0.0224	0.0057	
1985	8	8	0.2067	0.0246	
1985	8	9	0.0396	0.0079	
1985	8	10	0.0312	0.0065	
1985	8	11	0.0258	0.0059	
1985	8	12	0.0244	0.0054	
1985	8	13	0.0210	0.0048	
1985	8	14	0.0204	0.0042	
1985	8	15	0.0278	0.0054	
1985	8	16	0.0204	0.0042	
1985	8	17	0.0204	0.0042	
1985	8	18	0.0221	0.0048	
1985	8	19	0.0258	0.0051	
1985	8	20	0.0215	0.0048	
1985	8	21	0.0765	0.0116	
1985	8	22	0.0283	0.0059	
1985	8	23	0.0215	0.0045	
1985	8	24	0.0312	0.0057	
1985	8	25	0.0793	0.0110	
1985	8	26	0.1048	0.0396	
1985	8	27	0.0821	0.0263	
1985	8	28	0.0368	0.0088	
1985	8	29	0.0272	0.0071	
1985	8	30	0.0246	0.0062	
1985	8	31	0.0246	0.0059	

1985	9	1	0.0246	0.0057	
1985	9	2	0.0227	0.0054	
1985	9	3	0.0204	0.0045	
1985	9	4	0.0195	0.0042	
1985	9	5	0.0176	0.0037	
1985	9	6	0.0176	0.0034	
1985	9	7	0.0159	0.0034	
1985	9	8	0.0176	0.0037	
1985	9	9	0.0623	0.0093	
1985	9	10	0.0368	0.0068	
1985	9	11	0.0212	0.0045	
1985	9	12	0.0178	0.0042	
1985	9	13	0.0159	0.0034	
1985	9	14	0.0156	0.0031	
1985	9	15	0.0156	0.0031	
1985	9	16	0.0150	0.0028	
1985	9	17	0.0150	0.0028	
1985	9	18	0.0150	0.0028	
1985	9	19	0.0150	0.0028	
1985	9	20	0.0150	0.0028	
1985	9	21	0.0150	0.0025	
1985	9	22	0.0150	0.0025	
1985	9	23	0.0241	0.0045	
1985	9	24	0.0204	0.0040	
1985	9	25	0.0153	0.0037	
1985	9	26	0.0153	0.0034	
1985	9	27	0.1246	0.0187	
1985	9	28	0.0340	0.0054	
1985	9	29	0.0212	0.0028	
1985	9	30	0.0178	0.0020	
1985	10	1	0.0176	0.0017	

1985	10	2	0.0396	0.0054	
1985	10	3	0.0396	0.0057	
1985	10	4	0.0396	0.0057	
1985	10	5	0.0453	0.0076	
1985	10	6	0.0278	0.0059	
1985	10	7	0.0227	0.0040	
1985	10	8	0.0201	0.0031	
1985	10	9	0.0195	0.0028	
1985	10	10	0.0195	0.0028	
1985	10	11	0.0195	0.0028	
1985	10	12	0.0195	0.0025	
1985	10	13	0.0198	0.0025	
1985	10	14	0.0218	0.0034	
1985	10	15	0.0280	0.0051	
1985	10	16	0.0312	0.0051	
1985	10	17	0.0269	0.0048	
1985	10	18	0.0266	0.0042	
1985	10	19	0.0266	0.0048	
1985	10	20	0.0283	0.0062	
1985	10	21	0.1529	0.0425	
1985	10	22	0.3398	0.1501	
1985	10	23	0.2011	0.0708	
1985	10	24	0.1586	0.0481	
1985	10	25	0.1218	0.0396	
1985	10	26	0.0793	0.0232	
1985	10	27	0.0708	0.0187	
1985	10	28	0.0651	0.0156	
1985	10	29	0.0595	0.0139	
1985	10	30	0.0595	0.0130	
1985	10	31	0.0595	0.0122	
1985	11	1	0.0595	0.0130	

1985	11	2	0.0595	0.0136	
1985	11	3	0.6230	0.3965	
1985	11	4	2.3506	1.3594	
1985	11	5	1.8974	1.1894	
1985	11	6	0.7080	0.5664	
1985	11	7	0.4248	0.2832	
1985	11	8	0.3115	0.1897	
1985	11	9	0.2662	0.1444	
1985	11	10	0.2407	0.1218	
1985	11	11	0.2266	0.1048	
1985	11	12	0.2152	0.0963	
1985	11	13	0.2067	0.0906	
1985	11	14	0.2322	0.0991	
1985	11	15	0.2096	0.0935	
1985	11	16	0.3965	0.1784	
1985	11	17	0.4248	0.2436	
1985	11	18	0.2577	0.1444	
1985	11	19	0.2379	0.1246	
1985	11	20	0.2209	0.1104	
1985	11	21	0.2011	0.0991	
1985	11	22	0.7646	0.5098	
1985	11	23	0.5098	0.3965	
1985	11	24	0.3398	0.2322	
1985	11	25	0.2832	0.1784	
1985	11	26	0.3115	0.1671	
1985	11	27	0.3682	0.1897	
1985	11	28	0.8496	0.6514	
1985	11	29	0.6230	0.5381	
1985	11	30	0.5947	0.4814	
1985	12	1	0.6514	0.5098	
1985	12	2	0.7080	0.5381	

1985	12	3	0.4248	0.3115	
1985	12	4	0.3682	0.2379	
1985	12	5	0.3682	0.2039	
1985	12	6	0.3398	0.1897	
1985	12	7	0.3115	0.1643	
1985	12	8	0.2832	0.1501	
1985	12	9	0.2832	0.1359	
1985	12	10	0.2634	0.1246	
1985	12	11	0.2492	0.1189	
1985	12	12	0.2379	0.1076	
1985	12	13	0.5381	0.3115	
1985	12	14	0.3682	0.2237	
1985	12	15	0.2719	0.1614	
1985	12	16	0.2634	0.1473	
1985	12	17	0.2492	0.1274	
1985	12	18	0.2124	0.1133	
1985	12	19	0.1982	0.0963	
1985	12	20	0.1926	0.0906	
1985	12	21	0.1812	0.0878	
1985	12	22	0.1756	0.0793	
1985	12	23	0.1926	0.0821	
1985	12	24	0.1926	0.0765	
1985	12	25	0.1926	0.0736	
1985	12	26	0.1841	0.0623	
1985	12	27	0.1841	0.0623	
1985	12	28	0.1614	0.0623	
1985	12	29	0.1501	0.0623	
1985	12	30	0.1416	0.0566	
1985	12	31	0.1388	0.0510	
1986	1	1	0.1359	0.0510	
1986	1	2	0.1303	0.0481	

1986	1	3	0.1501	0.0538
1986	1	4	0.1444	0.0510
1986	1	5	0.1388	0.0481
1986	1	6	0.1133	0.0453
1986	1	7	0.1076	0.0368
1986	1	8	0.1076	0.0368
1986	1	9	0.1076	0.0340
1986	1	10	0.1048	0.0368
1986	1	11	0.1048	0.0368
1986	1	12	0.1048	0.0368
1986	1	13	0.1020	0.0368
1986	1	14	0.0991	0.0340
1986	1	15	0.0963	0.0312
1986	1	16	0.0906	0.0283
1986	1	17	0.1020	0.0312
1986	1	18	0.1161	0.0340
1986	1	19	0.1954	0.0538
1986	1	20	0.2351	0.0850
1986	1	21	0.1388	0.0510
1986	1	22	0.1416	0.0538
1986	1	23	0.1303	0.0538
1986	1	24	0.1133	0.0453
1986	1	25	0.1189	0.0453
1986	1	26	0.1558	0.0651
1986	1	27	0.1416	0.0680
1986	1	28	0.1416	0.0651
1986	1	29	0.1416	0.0566
1986	1	30	0.1388	0.0481
1986	1	31	0.1331	0.0453
1986	2	1	0.1303	0.0453
1986	2	2	0.1529	0.0708

1986	2	3	0.1982	0.0878
1986	2	4	0.3398	0.2039
1986	2	5	0.5947	0.3965
1986	2	6	0.3682	0.2747
1986	2	7	0.2775	0.1926
1986	2	8	0.2407	0.1501
1986	2	9	0.2266	0.1274
1986	2	10	0.2096	0.1133
1986	2	11	0.2039	0.1076
1986	2	12	0.1926	0.0906
1986	2	13	0.1841	0.0906
1986	2	14	0.1756	0.0850
1986	2	15	0.1699	0.0793
1986	2	16	0.1699	0.0736
1986	2	17	0.3398	0.1699
1986	2	18	0.7930	0.4814
1986	2	19	0.9346	0.7363
1986	2	20	0.9062	0.7080
1986	2	21	0.8496	0.6797
1986	2	22	0.5664	0.4814
1986	2	23	0.4814	0.3398
1986	2	24	0.3965	0.2492
1986	2	25	0.3398	0.2096
1986	2	26	0.3115	0.1756
1986	2	27	0.2832	0.1586
1986	2	28	0.2634	0.1331
1986	3	1	0.2520	0.1189
1986	3	2	0.2379	0.1076
1986	3	3	0.2209	0.1020
1986	3	4	0.2237	0.0991
1986	3	5	0.2209	0.0963

1986	3	6	0.2124	0.0906	
1986	3	7	0.1982	0.0821	
1986	3	8	0.1982	0.0765	
1986	3	9	0.2237	0.0765	
1986	3	10	0.3115	0.1274	
1986	3	11	0.4814	0.3398	
1986	3	12	0.2719	0.1671	
1986	3	13	0.5098	0.3398	
1986	3	14	0.9912	0.6514	
1986	3	15	1.4726	0.9912	
1986	3	16	0.7363	0.5664	
1986	3	17	0.5381	0.3682	
1986	3	18	0.4531	0.2804	
1986	3	19	0.4248	0.2436	
1986	3	20	0.3682	0.1982	
1986	3	21	0.3115	0.1558	
1986	3	22	0.2804	0.1359	
1986	3	23	0.2747	0.1246	
1986	3	24	0.2549	0.1104	
1986	3	25	0.2379	0.0991	
1986	3	26	0.2294	0.0963	
1986	3	27	0.2209	0.0906	
1986	3	28	0.2039	0.0878	
1986	3	29	0.1982	0.0793	
1986	3	30	0.1897	0.0765	
1986	3	31	0.1784	0.0736	
1986	4	1	0.1671	0.0680	
1986	4	2	0.1614	0.0651	
1986	4	3	0.1501	0.0595	
1986	4	4	0.1473	0.0595	
1986	4	5	0.1586	0.0538	

1986	4	6	0.2096	0.0736	
1986	4	7	0.1728	0.0651	
1986	4	8	0.1473	0.0566	
1986	4	9	0.1359	0.0481	
1986	4	10	0.1303	0.0481	
1986	4	11	0.1359	0.0481	
1986	4	12	0.1303	0.0481	
1986	4	13	0.1218	0.0453	
1986	4	14	0.1161	0.0425	
1986	4	15	0.2577	0.1246	
1986	4	16	0.9062	0.6514	
1986	4	17	0.7080	0.5947	
1986	4	18	0.4531	0.3965	
1986	4	19	0.3398	0.2634	
1986	4	20	0.2832	0.2181	
1986	4	21	0.2719	0.1869	
1986	4	22	0.3115	0.1756	
1986	4	23	0.2747	0.1614	
1986	4	24	0.2294	0.1331	
1986	4	25	0.2124	0.1218	
1986	4	26	0.2039	0.1104	
1986	4	27	0.1897	0.1020	
1986	4	28	0.1784	0.0935	
1986	4	29	0.1954	0.0878	
1986	4	30	0.1643	0.0765	
1986	5	1	0.1558	0.0736	
1986	5	2	0.1444	0.0651	
1986	5	3	0.1359	0.0595	
1986	5	4	0.1274	0.0538	
1986	5	5	0.1218	0.0510	
1986	5	6	0.1161	0.0453	

1986	5	7	0.1161	0.0425	
1986	5	8	0.1048	0.0396	
1986	5	9	0.1048	0.0368	
1986	5	10	0.0991	0.0340	
1986	5	11	0.0935	0.0312	
1986	5	12	0.0850	0.0278	
1986	5	13	0.0850	0.0263	
1986	5	14	0.0991	0.0283	
1986	5	15	0.1020	0.0312	
1986	5	16	0.0991	0.0283	
1986	5	17	0.1784	0.0368	
1986	5	18	0.0935	0.0249	
1986	5	19	0.0793	0.0210	
1986	5	20	0.7646	0.3965	
1986	5	21	0.3682	0.1529	
1986	5	22	0.3115	0.1586	
1986	5	23	0.1926	0.0935	
1986	5	24	0.1614	0.0736	
1986	5	25	0.1359	0.0595	
1986	5	26	0.1189	0.0481	
1986	5	27	0.1189	0.0453	
1986	5	28	0.1133	0.0425	
1986	5	29	0.0963	0.0340	
1986	5	30	0.0850	0.0283	
1986	5	31	0.0793	0.0241	
1986	6	1	0.0736	0.0212	0.0161
1986	6	2	0.0708	0.0212	0.0164
1986	6	3	0.0651	0.0184	0.0156
1986	6	4	0.0623	0.0164	0.0156
1986	6	5	0.0623	0.0156	0.0150
1986	6	6	0.7930	0.3115	0.2492

1986	6	7	0.5947	0.5098	0.0935
1986	6	8	0.2096	0.1586	0.0368
1986	6	9	0.1444	0.0991	0.0283
1986	6	10	0.1218	0.0708	0.0269
1986	6	11	0.1104	0.0595	0.0261
1986	6	12	0.1020	0.0510	0.0252
1986	6	13	0.0963	0.0453	0.0244
1986	6	14	0.0850	0.0368	0.0227
1986	6	15	0.0765	0.0312	0.0212
1986	6	16	0.0708	0.0275	0.0204
1986	6	17	0.0821	0.0269	0.0261
1986	6	18	0.0651	0.0227	0.0195
1986	6	19	0.0623	0.0207	0.0181
1986	6	20	0.0708	0.0227	0.0207
1986	6	21	0.0566	0.0187	0.0176
1986	6	22	0.0538	0.0159	0.0164
1986	6	23	0.0510	0.0144	0.0153
1986	6	24	0.1020	0.0340	0.0396
1986	6	25	0.0566	0.0176	0.0190
1986	6	26	0.0481	0.0142	0.0167
1986	6	27	0.0453	0.0122	0.0156
1986	6	28	0.0453	0.0116	0.0161
1986	6	29	0.0453	0.0110	0.0139
1986	6	30	0.0368	0.0088	0.0125
1986	7	1	0.0396	0.0085	0.0136
1986	7	2	0.0850	0.0215	0.0275
1986	7	3	0.0453	0.0116	0.0144
1986	7	4	0.0368	0.0088	0.0125
1986	7	5	0.0340	0.0071	0.0125
1986	7	6	0.0312	0.0065	0.0119
1986	7	7	0.0283	0.0059	0.0113

1986	7	8	0.0269	0.0054	0.0113
1986	7	9	0.0510	0.0091	0.0193
1986	7	10	0.0368	0.0074	0.0119
1986	7	11	0.0280	0.0057	0.0113
1986	7	12	0.0283	0.0059	0.0108
1986	7	13	0.0272	0.0057	0.0091
1986	7	14	0.0249	0.0059	0.0079
1986	7	15	0.0215	0.0042	0.0071
1986	7	16	0.0215	0.0037	0.0079
1986	7	17	0.0249	0.0042	0.0082
1986	7	18	0.0232	0.0042	0.0071
1986	7	19	0.0198	0.0045	0.0071
1986	7	20	0.0425	0.0062	0.0127
1986	7	21	0.0396	0.0057	0.0085
1986	7	22	0.0227	0.0040	0.0062
1986	7	23	0.0207	0.0034	0.0059
1986	7	24	0.0212	0.0037	0.0059
1986	7	25	0.0207	0.0034	0.0057
1986	7	26	0.0187	0.0031	0.0054
1986	7	27	0.0170	0.0031	0.0042
1986	7	28	0.0147	0.0028	0.0040
1986	7	29	0.0139	0.0025	0.0037
1986	7	30	0.0122	0.0020	0.0034
1986	7	31	0.0130	0.0020	0.0031
1986	8	1	0.0113	0.0020	0.0028
1986	8	2	0.0153	0.0020	0.0054
1986	8	3	0.0181	0.0020	0.0040
1986	8	4	0.0144	0.0020	0.0034
1986	8	5	0.0105	0.0020	0.0031
1986	8	6	0.0241	0.0057	0.0091
1986	8	7	0.0283	0.0040	0.0034

1986	8	8	0.0212	0.0034	0.0031
1986	8	9	0.0147	0.0025	0.0020
1986	8	10	0.0099	0.0020	0.0017
1986	8	11	0.0091	0.0020	0.0014
1986	8	12	0.0079	0.0017	0.0014
1986	8	13	0.0079	0.0017	0.0014
1986	8	14	0.0068	0.0017	0.0011
1986	8	15	0.0065	0.0017	0.0014
1986	8	16	0.0068	0.0017	0.0014
1986	8	17	0.0071	0.0020	0.0025
1986	8	18	0.0127	0.0028	0.0023
1986	8	19	0.0065	0.0020	0.0014
1986	8	20	0.0068	0.0023	0.0020
1986	8	21	0.0510	0.0096	0.0119
1986	8	22	0.0187	0.0040	0.0025
1986	8	23	0.0125	0.0028	0.0017
1986	8	24	0.0088	0.0023	0.0011
1986	8	25	0.0057	0.0020	0.0011
1986	8	26	0.0057	0.0017	0.0011
1986	8	27	0.0108	0.0023	0.0028
1986	8	28	0.0241	0.0031	0.0037
1986	8	29	0.0105	0.0020	0.0011
1986	8	30	0.0059	0.0017	0.0008
1986	8	31	0.0057	0.0017	0.0008
1986	9	1	0.0057	0.0017	0.0011
1986	9	2	0.0170	0.0031	0.0031
1986	9	3	0.0312	0.0045	0.0045
1986	9	4	0.0252	0.0048	0.0040
1986	9	5	0.0156	0.0031	0.0023
1986	9	6	0.0130	0.0025	0.0017
1986	9	7	0.0071	0.0017	0.0014

1986	9	8	0.0062	0.0017	0.0011
1986	9	9	0.0057	0.0017	0.0008
1986	9	10	0.0057	0.0014	0.0008
1986	9	11	0.0057	0.0014	0.0008
1986	9	12	0.0057	0.0014	0.0008
1986	9	13	0.0054	0.0014	0.0000
1986	9	14	0.0051	0.0014	0.0000
1986	9	15	0.0051	0.0011	0.0006
1986	9	16	0.0051	0.0011	0.0000
1986	9	17	0.0051	0.0011	0.0000
1986	9	18	0.0051	0.0011	0.0000
1986	9	19	0.0051	0.0011	0.0008
1986	9	20	0.0051	0.0014	0.0008
1986	9	21	0.0051	0.0014	0.0008
1986	9	22	0.0051	0.0011	0.0008
1986	9	23	0.0051	0.0011	0.0008
1986	9	24	0.0065	0.0014	0.0017
1986	9	25	0.0108	0.0017	0.0017
1986	9	26	0.0085	0.0017	0.0011
1986	9	27	0.0059	0.0014	0.0000
1986	9	28	0.0065	0.0014	0.0008
1986	9	29	0.0110	0.0014	0.0020
1986	9	30	0.0119	0.0014	0.0000
1986	10	1	0.0278	0.0051	0.0136
1986	10	2	0.0566	0.0062	0.0057
1986	10	3	0.0147	0.0025	0.0020
1986	10	4	0.0181	0.0034	0.0051
1986	10	5	0.0266	0.0051	0.0048
1986	10	6	0.0119	0.0028	0.0014
1986	10	7	0.0065	0.0017	0.0008
1986	10	8	0.0054	0.0017	0.0008

1986	10	9	0.0059	0.0017	0.0008
1986	10	10	0.0057	0.0014	0.0008
1986	10	11	0.0054	0.0011	0.0008
1986	10	12	0.0068	0.0011	0.0014
1986	10	13	0.0164	0.0023	0.0042
1986	10	14	0.0396	0.0057	0.0079
1986	10	15	0.0195	0.0031	0.0023
1986	10	16	0.0125	0.0023	0.0017
1986	10	17	0.0116	0.0017	0.0017
1986	10	18	0.0113	0.0017	0.0017
1986	10	19	0.0105	0.0017	0.0017
1986	10	20	0.0096	0.0017	0.0017
1986	10	21	0.0093	0.0014	0.0014
1986	10	22	0.0091	0.0014	0.0011
1986	10	23	0.0105	0.0014	0.0011
1986	10	24	0.0119	0.0014	0.0014
1986	10	25	0.0125	0.0014	0.0017
1986	10	26	0.0368	0.0054	0.0082
1986	10	27	0.0278	0.0040	0.0042
1986	10	28	0.0207	0.0031	0.0034
1986	10	29	0.0190	0.0025	0.0025
1986	10	30	0.0193	0.0025	0.0025
1986	10	31	0.0198	0.0025	0.0025
1986	11	1	0.0195	0.0025	0.0028
1986	11	2	0.0453	0.0130	0.0079
1986	11	3	0.0312	0.0093	0.0042
1986	11	4	0.0224	0.0057	0.0031
1986	11	5	0.0906	0.0283	0.0340
1986	11	6	0.0935	0.0278	0.0159
1986	11	7	0.0481	0.0113	0.0079
1986	11	8	0.0821	0.0283	0.0170

1986	11	9	0.0595	0.0161	0.0116
1986	11	10	0.0538	0.0122	0.0085
1986	11	11	0.1274	0.0566	0.0396
1986	11	12	0.0821	0.0368	0.0136
1986	11	13	0.0510	0.0156	0.0076
1986	11	14	0.0425	0.0125	0.0065
1986	11	15	0.0396	0.0110	0.0062
1986	11	16	0.0396	0.0102	0.0065
1986	11	17	0.0396	0.0091	0.0062
1986	11	18	0.0850	0.0261	0.0312
1986	11	19	0.1558	0.0765	0.0229
1986	11	20	0.1812	0.1331	0.0425
1986	11	21	0.2322	0.1897	0.0340
1986	11	22	0.0850	0.0368	0.0136
1986	11	23	0.0651	0.0246	0.0099
1986	11	24	0.0765	0.0238	0.0144
1986	11	25	0.0651	0.0201	0.0096
1986	11	26	0.1274	0.0651	0.0238
1986	11	27	0.1133	0.0708	0.0167
1986	11	28	0.0708	0.0312	0.0105
1986	11	29	0.0623	0.0229	0.0093
1986	11	30	0.0595	0.0181	0.0082
1986	12	1	0.0538	0.0153	0.0076
1986	12	2	0.8779	0.5664	0.1756
1986	12	3	0.7080	0.4814	0.0906
1986	12	4	0.1897	0.1020	0.0244
1986	12	5	0.1274	0.0623	0.0173
1986	12	6	0.1020	0.0453	0.0144
1986	12	7	0.0906	0.0340	0.0133
1986	12	8	0.0850	0.0312	0.0122
1986	12	9	0.3965	0.1756	0.0566

1986	12	10	0.2407	0.1246	0.0312
1986	12	11	0.1614	0.0850	0.0215
1986	12	12	0.1388	0.0680	0.0195
1986	12	13	0.1133	0.0538	0.0176
1986	12	14	0.0963	0.0425	0.0170
1986	12	15	0.1020	0.0425	0.0164
1986	12	16	0.1020	0.0396	0.0156
1986	12	17	0.1020	0.0396	0.0150
1986	12	18	0.5098	0.2634	0.0793
1986	12	19	0.2407	0.1359	0.0312
1986	12	20	0.1728	0.0935	0.0218
1986	12	21	0.1416	0.0736	0.0181
1986	12	22	0.1218	0.0623	0.0159
1986	12	23	0.1161	0.0538	0.0150
1986	12	24	0.6797	0.3398	0.1161
1986	12	25	0.7646	0.5664	0.0878
1986	12	26	0.3115	0.2011	0.0340
1986	12	27	0.2181	0.1416	0.0266
1986	12	28	0.1869	0.1189	0.0235
1986	12	29	0.1614	0.0991	0.0218
1986	12	30	0.1473	0.0850	0.0201
1986	12	31	0.1359	0.0736	0.0193
1987	1	1	0.1274	0.0651	0.0187
1987	1	2	0.1359	0.0651	0.0204
1987	1	3	0.1246	0.0595	0.0190
1987	1	4	0.1189	0.0538	0.0178
1987	1	5	0.1104	0.0481	0.0167
1987	1	6	0.1104	0.0481	0.0176
1987	1	7	0.1246	0.0566	0.0195
1987	1	8	0.1246	0.0566	0.0184
1987	1	9	0.1133	0.0510	0.0170

1987	1	10	0.1133	0.0481	0.0176
1987	1	11	0.1133	0.0481	0.0170
1987	1	12	0.1048	0.0453	0.0159
1987	1	13	0.1020	0.0396	0.0153
1987	1	14	0.1133	0.0453	0.0181
1987	1	15	0.2832	0.1473	0.0425
1987	1	16	0.2209	0.1416	0.0283
1987	1	17	0.1586	0.1048	0.0232
1987	1	18	0.1501	0.0935	0.0218
1987	1	19	0.3965	0.2436	0.0538
1987	1	20	0.2662	0.1699	0.0312
1987	1	21	0.1926	0.1274	0.0255
1987	1	22	0.1529	0.1331	0.0229
1987	1	23	0.1897	0.1048	0.0212
1987	1	24	0.1699	0.1133	0.0198
1987	1	25	0.1586	0.0850	0.0184
1987	1	26	0.1473	0.0821	0.0181
1987	1	27	0.1359	0.0765	0.0181
1987	1	28	0.1274	0.0708	0.0212
1987	1	29	0.1218	0.0651	0.0181
1987	1	30	0.1189	0.0651	0.0176
1987	1	31	0.1189	0.0651	0.0201
1987	2	1	0.1161	0.0623	0.0190
1987	2	2	0.1558	0.0708	0.0229
1987	2	3	0.2181	0.0963	0.0278
1987	2	4	0.2039	0.0991	0.0255
1987	2	5	0.1614	0.0878	0.0224
1987	2	6	0.1501	0.0821	0.0210
1987	2	7	0.1558	0.0821	0.0215
1987	2	8	0.1586	0.0878	0.0215
1987	2	9	0.1359	0.0793	0.0201

1987	2	10	0.1274	0.0680	0.0204
1987	2	11	0.1274	0.0651	0.0201
1987	2	12	0.1274	0.0651	0.0195
1987	2	13	0.1218	0.0623	0.0190
1987	2	14	0.1133	0.0566	0.0178
1987	2	15	0.1048	0.0510	0.0178
1987	2	16	0.0935	0.0538	0.0178
1987	2	17	0.0963	0.0510	0.0178
1987	2	18	0.1020	0.0481	0.0184
1987	2	19	0.1020	0.0453	0.0187
1987	2	20	0.1020	0.0425	0.0181
1987	2	21	0.0991	0.0425	0.0181
1987	2	22	0.0991	0.0425	0.0178
1987	2	23	0.1246	0.0538	0.0232
1987	2	24	0.1076	0.0453	0.0178
1987	2	25	0.1048	0.0453	0.0178
1987	2	26	0.1076	0.0453	0.0176
1987	2	27	0.1048	0.0481	0.0170
1987	2	28	0.1841	0.0906	0.0368
1987	3	1	1.4160	0.9062	0.1614
1987	3	2	0.8213	0.6230	0.0963
1987	3	3	0.5098	0.3398	0.0651
1987	3	4	0.3965	0.2379	0.0481
1987	3	5	0.3115	0.1841	0.0368
1987	3	6	0.3115	0.1728	0.0396
1987	3	7	0.3682	0.2152	0.0595
1987	3	8	0.4248	0.2577	0.0623
1987	3	9	0.3682	0.2152	0.0510
1987	3	10	0.2804	0.1614	0.0368
1987	3	11	0.2407	0.1331	0.0312
1987	3	12	0.2351	0.1274	0.0312

1987	3	13	0.2209	0.1161	0.0283
1987	3	14	0.2039	0.1048	0.0278
1987	3	15	0.1982	0.0963	0.0278
1987	3	16	0.1897	0.0878	0.0266
1987	3	17	0.1784	0.0821	0.0252
1987	3	18	0.1699	0.0765	0.0244
1987	3	19	0.1643	0.0708	0.0238
1987	3	20	0.1586	0.0680	0.0238
1987	3	21	0.1529	0.0623	0.0232
1987	3	22	0.1501	0.0566	0.0224
1987	3	23	0.1501	0.0538	0.0212
1987	3	24	0.1444	0.0538	0.0207
1987	3	25	0.1473	0.0510	0.0215
1987	3	26	0.1529	0.0538	0.0218
1987	3	27	0.1388	0.0481	0.0201
1987	3	28	0.1473	0.0510	0.0221
1987	3	29	0.1359	0.0453	0.0201
1987	3	30	0.2096	0.0793	0.0340
1987	3	31	0.7930	0.4531	0.0878
1987	4	1	0.3398	0.2096	0.0368
1987	4	2	0.2549	0.1614	0.0312
1987	4	3	0.2832	0.1728	0.0396
1987	4	4	5.4091	2.1523	1.0478
1987	4	5	1.5576	1.1045	0.2719
1987	4	6	1.2744	0.8779	0.2096
1987	4	7	1.1328	0.7363	0.1897
1987	4	8	0.7930	0.4531	0.1473
1987	4	9	0.5947	0.3115	0.1303
1987	4	10	0.5098	0.2407	0.1161
1987	4	11	0.4531	0.1982	0.1048
1987	4	12	0.3965	0.1897	0.1020

1987	4	13	0.3682	0.1643	0.0906
1987	4	14	0.3115	0.1388	0.0821
1987	4	15	0.2832	0.1274	0.0793
1987	4	16	0.4814	0.2294	0.1161
1987	4	17	1.2744	0.9912	0.2237
1987	4	18	0.6797	0.6230	0.1246
1987	4	19	0.4814	0.4248	0.1048
1987	4	20	0.4248	0.3398	0.0906
1987	4	21	0.3682	0.2775	0.0878
1987	4	22	0.3398	0.2351	0.0821
1987	4	23	0.3115	0.2011	0.0793
1987	4	24	0.3115	0.1954	0.0793
1987	4	25	0.2775	0.1728	0.0736
1987	4	26	0.2464	0.1501	0.0708
1987	4	27	0.2351	0.1359	0.0680
1987	4	28	0.2237	0.1246	0.0680
1987	4	29	0.2124	0.1161	0.0651
1987	4	30	0.1954	0.1048	0.0651
1987	5	1	0.1869	0.0963	0.0623
1987	5	2	0.1869	0.0906	0.0651
1987	5	3	0.1897	0.0878	0.0651
1987	5	4	0.5381	0.3398	0.1161
1987	5	5	0.2747	0.1982	0.0708
1987	5	6	0.2266	0.1558	0.0623
1987	5	7	0.2011	0.1388	0.0595
1987	5	8	0.1926	0.1246	0.0566
1987	5	9	0.1812	0.1104	0.0538
1987	5	10	0.1699	0.0991	0.0538
1987	5	11	0.1586	0.0906	0.0510
1987	5	12	0.1614	0.0906	0.0595
1987	5	13	0.1558	0.0850	0.0538

1987	5	14	0.1473	0.0793	0.0510
1987	5	15	0.1473	0.0765	0.0510
1987	5	16	0.1359	0.0680	0.0481
1987	5	17	0.1274	0.0623	0.0453
1987	5	18	0.1246	0.0566	0.0481
1987	5	19	0.1699	0.0651	0.0595
1987	5	20	0.4814	0.2832	0.0963
1987	5	21	0.2209	0.1501	0.0623
1987	5	22	0.1756	0.1161	0.0538
1987	5	23	0.1841	0.1076	0.0481
1987	5	24	0.1784	0.0991	0.0453
1987	5	25	0.1473	0.0821	0.0453
1987	5	26	0.1473	0.0821	0.0453
1987	5	27	0.1388	0.0793	0.0396
1987	5	28	0.1274	0.0708	0.0312
1987	5	29	0.1161	0.0595	0.0235
1987	5	30	0.1076	0.0510	0.0198
1987	5	31	0.1020	0.0453	0.0201
1987	6	1	0.0963	0.0425	0.0198
1987	6	2	0.0991	0.0396	0.0218
1987	6	3	0.0906	0.0368	0.0204
1987	6	4	0.1218	0.0453	0.0453
1987	6	5	0.0963	0.0396	0.0241
1987	6	6	0.0736	0.0312	0.0156
1987	6	7	0.0680	0.0269	0.0156
1987	6	8	0.0595	0.0227	0.0147
1987	6	9	0.0708	0.0238	0.0181
1987	6	10	0.0595	0.0207	0.0147
1987	6	11	0.0510	0.0167	0.0144
1987	6	12	0.0595	0.0187	0.0156
1987	6	13	0.1161	0.0425	0.0623

1987	6	14	0.1048	0.0425	0.0340
1987	6	15	0.0595	0.0221	0.0153
1987	6	16	0.0481	0.0153	0.0142
1987	6	17	0.0425	0.0127	0.0130
1987	6	18	0.0368	0.0108	0.0125
1987	6	19	0.0368	0.0091	0.0119
1987	6	20	0.0396	0.0108	0.0153
1987	6	21	0.0538	0.0142	0.0144
1987	6	22	0.0425	0.0116	0.0127
1987	6	23	0.0453	0.0096	0.0119
1987	6	24	0.0368	0.0079	0.0105
1987	6	25	0.0312	0.0068	0.0093
1987	6	26	0.0680	0.0125	0.0210
1987	6	27	0.0595	0.0127	0.0133
1987	6	28	0.0340	0.0079	0.0105
1987	6	29	0.0283	0.0059	0.0091
1987	6	30	0.0255	0.0051	0.0085
1987	7	1	0.0263	0.0051	0.0093
1987	7	2	0.0396	0.0116	0.0133
1987	7	3	0.0595	0.0212	0.0136
1987	7	4	0.0283	0.0076	0.0091
1987	7	5	0.0340	0.0071	0.0074
1987	7	6	0.0340	0.0076	0.0102
1987	7	7	0.0708	0.0133	0.0283
1987	7	8	0.0906	0.0312	0.0261
1987	7	9	0.0312	0.0096	0.0110
1987	7	10	0.0266	0.0071	0.0108
1987	7	11	0.0278	0.0062	0.0113
1987	7	12	0.0312	0.0074	0.0105
1987	7	13	0.0340	0.0068	0.0119
1987	7	14	0.0765	0.0280	0.0312

1987	7	15	0.0481	0.0190	0.0133
1987	7	16	0.0258	0.0082	0.0105
1987	7	17	0.0224	0.0062	0.0091
1987	7	18	0.0198	0.0048	0.0076
1987	7	19	0.0170	0.0040	0.0068
1987	7	20	0.0153	0.0031	0.0057
1987	7	21	0.0136	0.0028	0.0048
1987	7	22	0.0122	0.0025	0.0042
1987	7	23	0.0116	0.0025	0.0042
1987	7	24	0.0116	0.0023	0.0040
1987	7	25	0.0108	0.0020	0.0037
1987	7	26	0.0105	0.0023	0.0037
1987	7	27	0.0108	0.0020	0.0034
1987	7	28	0.0088	0.0017	0.0028
1987	7	29	0.0079	0.0014	0.0023
1987	7	30	0.0079	0.0014	0.0020
1987	7	31	0.0076	0.0014	0.0020
1987	8	1	0.0082	0.0014	0.0023
1987	8	2	0.0096	0.0017	0.0025
1987	8	3	0.0076	0.0014	0.0023
1987	8	4	0.0074	0.0014	0.0017
1987	8	5	0.0167	0.0031	0.0074
1987	8	6	0.0193	0.0025	0.0045
1987	8	7	0.0105	0.0020	0.0034
1987	8	8	0.0119	0.0020	0.0028
1987	8	9	0.0091	0.0017	0.0020
1987	8	10	0.0082	0.0014	0.0017
1987	8	11	0.0074	0.0011	0.0011
1987	8	12	0.0065	0.0011	0.0014
1987	8	13	0.0065	0.0011	0.0011
1987	8	14	0.0065	0.0011	0.0011

1987	8	15	0.0065	0.0011	0.0011
1987	8	16	0.0065	0.0011	0.0011
1987	8	17	0.0065	0.0011	0.0011
1987	8	18	0.0065	0.0011	0.0008
1987	8	19	0.0076	0.0011	0.0011
1987	8	20	0.0065	0.0011	0.0008
1987	8	21	0.0059	0.0008	0.0006
1987	8	22	0.0198	0.0034	0.0037
1987	8	23	0.0113	0.0017	0.0011
1987	8	24	0.0059	0.0011	0.0008
1987	8	25	0.0059	0.0008	0.0008
1987	8	26	0.0059	0.0011	0.0008
1987	8	27	0.0085	0.0014	0.0014
1987	8	28	0.0059	0.0014	0.0008
1987	8	29	0.0062	0.0014	0.0008
1987	8	30	0.0059	0.0011	0.0006
1987	8	31	0.0059	0.0011	0.0008
1987	9	1	0.0059	0.0011	0.0011
1987	9	2	0.0059	0.0008	0.0006
1987	9	3	0.0059	0.0008	0.0006
1987	9	4	0.0059	0.0008	0.0006
1987	9	5	0.0059	0.0008	0.0006
1987	9	6	0.0252	0.0048	0.0059
1987	9	7	0.0147	0.0031	0.0023
1987	9	8	0.2152	0.0651	0.0425
1987	9	9	0.0368	0.0130	0.0054
1987	9	10	0.0125	0.0042	0.0017
1987	9	11	0.0074	0.0028	0.0011
1987	9	12	0.0159	0.0040	0.0054
1987	9	13	0.0595	0.0062	0.0085
1987	9	14	0.0178	0.0048	0.0025

1987	9	15	0.0091	0.0031	0.0014
1987	9	16	0.0074	0.0025	0.0014
1987	9	17	0.0278	0.0082	0.0167
1987	9	18	0.3115	0.0510	0.0481
1987	9	19	0.0368	0.0110	0.0068
1987	9	20	0.0538	0.0167	0.0113
1987	9	21	0.0396	0.0164	0.0071
1987	9	22	0.0244	0.0091	0.0042
1987	9	23	0.0210	0.0065	0.0040
1987	9	24	0.0150	0.0045	0.0023
1987	9	25	0.0119	0.0034	0.0020
1987	9	26	0.0096	0.0028	0.0017
1987	9	27	0.0088	0.0020	0.0014
1987	9	28	0.0076	0.0017	0.0014
1987	9	29	0.0074	0.0017	0.0017
1987	9	30	0.0266	0.0045	0.0020
1987	10	1	0.0139	0.0032	
1987	10	2	0.0093	0.0007	
1987	10	3	0.0127	0.0025	
1987	10	4	0.0159	0.0043	
1987	10	5	0.0116	0.0019	
1987	10	6	0.0108	0.0015	
1987	10	7	0.0481	0.0220	
1987	10	8	0.0161	0.0044	
1987	10	9	0.0116	0.0019	
1987	10	10	0.0108	0.0015	
1987	10	11	0.0108	0.0015	
1987	10	12	0.0125	0.0024	
1987	10	13	0.0105	0.0013	
1987	10	14	0.0096	0.0008	
1987	10	15	0.0096	0.0008	

1987	10	16	0.0096	0.0008	
1987	10	17	0.0099	0.0010	
1987	10	18	0.0105	0.0013	
1987	10	19	0.0105	0.0013	
1987	10	20	0.0113	0.0018	
1987	10	21	0.0224	0.0078	
1987	10	22	0.0195	0.0063	
1987	10	23	0.0159	0.0043	
1987	10	24	0.0156	0.0041	
1987	10	25	0.0181	0.0055	
1987	10	26	0.0193	0.0061	
1987	10	27	0.0906	0.0454	
1987	10	28	0.1161	0.0594	
1987	10	29	0.0425	0.0189	
1987	10	30	0.0312	0.0127	
1987	10	31	0.0283	0.0111	
1987	11	1	0.0272	0.0105	
1987	11	2	0.0263	0.0100	
1987	11	3	0.0263	0.0100	
1987	11	4	0.0263	0.0100	
1987	11	5	0.0263	0.0100	
1987	11	6	0.0258	0.0097	
1987	11	7	0.0266	0.0102	
1987	11	8	0.0275	0.0107	
1987	11	9	0.0280	0.0110	
1987	11	10	0.0680	0.0329	
1987	11	11	0.0680	0.0329	
1987	11	12	0.0595	0.0283	
1987	11	13	0.0765	0.0376	
1987	11	14	0.0878	0.0439	
1987	11	15	0.0680	0.0329	

1987	11	16	0.0538	0.0251	
1987	11	17	0.0623	0.0298	
1987	11	18	0.1218	0.0626	
1987	11	19	0.0623	0.0298	
1987	11	20	0.0510	0.0236	
1987	11	21	0.0425	0.0189	
1987	11	22	0.0340	0.0142	
1987	11	23	0.0340	0.0142	
1987	11	24	0.0396	0.0174	
1987	11	25	0.0368	0.0158	
1987	11	26	0.0340	0.0142	
1987	11	27	0.0368	0.0158	
1987	11	28	0.0680	0.0329	
1987	11	29	1.6992	0.9308	
1987	11	30	0.4531	0.2449	
1987	12	1	0.1954	0.1031	
1987	12	2	0.1529	0.0797	
1987	12	3	0.1331	0.0688	
1987	12	4	0.1388	0.0719	
1987	12	5	0.1246	0.0641	
1987	12	6	0.1161	0.0594	
1987	12	7	0.1104	0.0563	
1987	12	8	0.1076	0.0548	
1987	12	9	0.1076	0.0548	
1987	12	10	0.1048	0.0532	
1987	12	11	0.1020	0.0516	
1987	12	12	0.0991	0.0501	
1987	12	13	0.0906	0.0454	
1987	12	14	0.0878	0.0439	
1987	12	15	0.1954	0.1031	
1987	12	16	0.1501	0.0781	

1987	12	17	0.1189	0.0610	
1987	12	18	0.1076	0.0548	
1987	12	19	0.1076	0.0548	
1987	12	20	0.1784	0.0937	
1987	12	21	0.1416	0.0735	
1987	12	22	0.1218	0.0626	
1987	12	23	0.1189	0.0610	
1987	12	24	0.1161	0.0594	
1987	12	25	0.1501	0.0781	
1987	12	26	0.2011	0.1062	
1987	12	27	0.1529	0.0797	
1987	12	28	0.1473	0.0766	
1987	12	29	0.1444	0.0750	
1987	12	30	0.1189	0.0610	
1987	12	31	0.1246	0.0641	

Appendix 13. Carbon isotope and alkalinity data at Catoctin.

Sample ID	Julian Date 001 = 850101	$\delta^{13}\text{C}$	Alkalinity ueq/L
HC-850209/1	40	-8.50	
HC-850209/2	40	-8.55	
HC-850402/1	92		278
HC-850402/2	92	-8.45	278
HC-850402/3	92	-8.40	278
HC-850402/4	92	-8.85	278
HC-850430/1	120	-8.65	465
HC-850430/2	120	-8.65	465
HC-850430/3	120	-9.20	465
HC-850430/4	120	-9.15	465
HC-850702/1	183	-9.80	
HC-850702/2	183	-8.00	
HC-851112	316	-9.50	371
HC-860114	379	-8.70	330
HC-860416	471	-11.2	
HC-860507	492	-8.2	
HC.1-860521	506	-11.20	344
HC.2-860521	506		344
HC.1-860528	513	-9.30	
HC.2-860528	513	-9.55	
HC-18	529.09	-8.95	
HC.1-860617	533	-9.75	490
HC.2-860617	533	-9.70	490
HC-860624	540	-9.80	
HC-860701	547	-9.60	529
HC-860722	568	-11.15	
HC-860728	574	-11.25	
HC-6-860812	589.09	-10.10	

HC-860916	624	-11.15	753
HC-861014	652	-11.15	643
HC-861028	666	-10.55	
HC-861103	672	-9.75	
HC-861112	681	-8.00	477
HC-861118	687	-8.25	
HC-861125	694	-7.60	
HC-861202	701	-14.85	
HC-861208	707	-6.30	
HC-861216	715	-6.20	323
HC-861223	722	-6.85	
HC-861230	729	-6.65	
HC-870107	737	-5.95	
HC-870112	742	-5.70	312
HC-870120	750		
HC-870128	758	-6.35	
HC-870203	764	-6.70	
HC-870210	771	-6.25	
HC-870217	778	-7.50	278
HC-870225	786	-6.15	
HC-870303	792	-7.75	
HC-870310	799	-5.95	
HC-870317	806	-6.25	262
HC-870324	813	-6.15	
HC-870331	820	-10.20	
HC-870407	827	-14.05	
HC-870414	834	-7.25	303
HC-870421	841	-9.45	
HC-870428	848	-8.00	332
HC-870504	854	-10.05	337
HC-870513	863	-9.45	431

HC-870519	869	-10.35	
HC-870526	876	-10.05	
HC-870602	883	-10.40	
HC-870609	890	-11.05	
HC-870616	897	-10.85	445
HC-870623	904	-11.10	
HC-870630	911	-10.05	
HC-870708	919	-11.95	
HC-870714	925	-12.35	540
HC-870721	932	-11.65	
HC-870728	939	-11.30	
HC-870804	946	-11.45	
HC-870811	953	-11.65	691
HC870812-08	954.09	-10.95	
HC-870819	961	-12.55	
HC-870824	966	-10.95	
HC870830-8	972.09	-10.70	
HC-870901	974	-11.00	
HC-870908	981	-14.20	
HC-870915	988	-11.10	729
HC-870922	995	-17.55	
HC-870930	1003	-20.25	
HC-871005	1008	-14.95	
HC-871013	1016	-10.30	669
HC-871020	1023	-9.55	
HC-871027	1030	-9.50	
HC-871102	1036	-9.40	
HC-871110	1044	-12.85	
HC-871117	1051	-9.10	517
HC-871124	1058	-6.85	
HC-871201	1065	-7.75	

HC-871208	1072	-6.60	
HB-850209/1	40	-11.60	
HB-850209/2	40	-10.85	
HB-850402/1	92	-9.05	243
HB-850402/2	92		243
HB-850402/3	92	-7.65	243
HB-850402/4	92	-8.85	243
HB-850430/1	120	-10.50	395
HB-850430/2	120	-10.55	395
HB-850430/3	120	-12.70	395
HB-850430/4	120	-10.90	395
HB-850702/1	183	-9.40	
HB-850702/2	183	-9.10	
HB-851112	316	-13.10	304
HB-860114	379	-11.70	275
HB-860416	471	-12.45	
HB-860507	492	-10.7	
HB.1-860521	506	-10.80	
HB.2-860521	506	-12.30	
HB.1-860528	513	-11.40	
HB.2-860528	513	-10.80	
HB-09	529.11	-10.65	
HB-860617	533	-11.10	425
HB-860624	540	-11.75	
HB-860701	547	-12.55	435
HB-860722	568	-13.95	
HB-860728	574	-14.60	
HB-6-860812	589.11	-14.40	447
HB-860916	624	-15.60	418
HB-861014	652	-14.40	513
HB-861028	666	-14.90	

HB-861103	672	-13.65	
HB-861112	681	-11.20	422
HB-861118	687	-13.10	
HB-861125	694	-10.20	
HB-861202	701	-11.20	
HB-861208	707	-9.05	
HB-861216	715	-8.05	268
HB-861223	722	-7.60	
HB-861230	729	-7.75	
HB-870107	737	-6.90	
HB-870112	742	-6.50	234
HB-870120	750	-8.30	
HB-870128	758	-7.00	
HB-870203	764	-7.05	
HB-870210	771	-7.65	
HB-870217	778	-6.90	227
HB-870225	786	-6.65	
HB-870303	792	-8.60	
HB-870310	799	-7.55	
HB-870317	806	-8.55	212
HB-870324	813	-7.75	
HB-870331	820	-10.55	
HB-870407	827	-7.95	
HB-870414	834	-8.70	268
HB-870421	841	-9.80	
HB-870428	848	-8.85	276
HB-870504	854	-9.55	300
HB-870513	863	-10.15	348
HB-870519	869	-11.60	
HB-870526	876	-10.95	
HB-870602	883	-12.00	

HB-870609	890	-12.85	
HB-870616	897	-12.60	358
HB-870623	904	-12.40	
HB-870630	911	-13.05	
HB-870708	919	-12.30	
HB-870714	925	-14.10	488
HB-870721	932	-14.30	
HB-870728	939	-14.40	
HB-870804	946	-14.70	
HB-870811	953	-15.40	467
HB870812-07	954.11	-15.15	
HB-870819	961	-15.95	
HB-870824	966	-14.55	
HB870830-7	972.11	-14.80	
HB-870901	974	-14.60	
HB-870908	981		
HB-870915	988	-14.05	494
HB-870922	995	-16.20	
HB-870930	1003	-18.60	
HB-871005	1008	-23.20	
HB-871013	1016	-20.90	461
HB-871020	1023	-16.10	
HB-871027	1030	-16.35	
HB-871102	1036	-14.50	
HB-871110	1044	-15.40	
HB-871117	1051	-12.70	461
HB-871124	1058	-11.55	
HB-871201	1065	-8.40	
HB-871208	1072	-8.65	
OC-860617	533	-11.75	480
OC-860624	540	-12.60	436

OC-860701	547	-11.20	461
OC-860722	568	-11.55	562
OC-860728	574	-12.10	584
OC-860805	582	-12.10	541
OC-860812	589	-12.65	611
OC-860816	593	-12.50	614
OC-860826	603	-12.15	600
OC-860904	612	-11.40	567
OC-860909	617	-10.55	569
OC-860916	624	-13.55	642
OC-860923	631	-12.50	604
OC-860930	638	-14.20	706
OC-861007	645	-13.00	639
OC-861014	652	-13.55	648
OC-861021	659	-11.75	597
OC-861028	666	-13.40	656
OC-861103	672		641
OC-861112	681	-11.95	444
OC-861118	687	-12.60	499
OC-861125	694	-11.20	401
OC-861202	701		322
OC-861208	707	-10.25	336
OC-861216	715	-9.30	317
OC-861223	722	-9.40	306
OC-861230	729	-9.40	296
OC-870107	737	-9.15	305
OC-870112	742	-9.00	305
OC-870120	750	-9.40	268
OC-870128	758	-10.15	308
OC-870203	764	-10.35	294
OC-870210	771	-11.20	328

OC-870217	778	-10.65	310
OC-870225	786	-9.90	301
OC-870303	792	-9.55	259
OC-870310	799	-9.20	288
OC-870316	805	-9.10	313
OC-870324	813	-9.45	331
OC-870331	820	-13.95	325
OC-870407	827	-10.85	263
OC-870414	834	-10.40	305
OC-870421	841	-11.55	405
OC-870428	848	-10.45	343
OC-870504	854	-12.90	355
OC-870513	863	-12.05	420
OC-870519	869	-13.25	433
OC-870526	876	-12.05	422
OC-870602	883	-14.45	457
OC-870609	890	-13.65	460
OC-870616	897	-12.75	465
OC-870623	904	-12.30	494
OC-870630	911	-12.05	500
OC-870708	919	-12.70	500
OC-870714	925	-13.85	512
OC-870721	932	-12.55	545
OC-870728	939	-12.65	529
OC-870804	946	-13.45	525
OC-870811	953	-12.75	505
OC-870819	961	-14.75	635
OC-870824	966	-11.70	582
OC-870901	974	-12.05	712
OC-870908	981	-15.65	640
OC-870915	988	-12.50	621

OC-870922	995	-12.15	581
OCT-861021	659	-15.90	642
OCT-861028	666	-15.90	671
OCT-861103	672	-15.00	638
OCT-861112	681	-12.85	462
OCT-861118	687	-14.90	487
OCT-861125	694	-13.45	395
OCT-861202	701	-14.20	260
OCT-861208	707	-12.50	333
OCT-861216	715	-11.15	315
OCT-861223	722	-10.95	302
OCT-861230	729	-11.05	291
OCT-870107	737	-10.75	288
OCT-870112	742	-10.00	282
OCT-870120	750	-10.25	279
OCT-870128	758	-10.05	299
OCT-870203	764	-10.50	275
OCT-870210	771	-9.90	273
OCT-870217	778	-9.65	265
OCT-870225	786	-10.10	271
OCT-870303	792	-11.30	268
OCT-870310	799	-10.70	273
OCT-870316	805	-9.60	270
OCT-870324	813	-10.50	287
OCT-870331	820	-11.75	297
OCT-870407	827	-11.20	265
OCT-870414	834	-11.50	279
OCT-870421	841	-12.50	374
OCT-870428	848	-12.15	376
OCT-870504	854	-11.90	403
OCT-870513	863	-13.05	434

OCT-870519	869	-13.90	472
OCT-870526	876	-13.75	443
OCT-870602	883	-12.55	462
OCT-870609	890	-14.40	480
OCT-870616	897	-13.90	488
OCT-870623	904	-14.80	500
OCT-870630	911	-15.10	503
OCT-870708	919	-13.20	531
OCT-870714	925	-14.35	546
OCT-870721	932	-14.20	545
OCT-870728	939	-14.80	488
OCT-870804	946	-14.50	485
OCT-870811	953	-13.95	508
OCT-870819	961	-14.20	537
OCT-870824	966	-13.35	523
OCT-870901	974	-14.75	550
OCT-870908	981	-16.25	510
OCT-870915	988	-16.60	557
OCT-870922	995	-13.65	551

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