ABSTRACT

Title of Thesis: A COMPARISON OF THE STORMFLOW RESPONSE OF FOUR ZERO ORDER WATERSHEDS IN WESTERN MARYLAND

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Surface mining and reclamation activities have been shown to significantly affect watershed hydrologic processes. Using natural isotopic and chemical tracers, the present study sought to quantify the impacts of surface mining and reclamation on old water and new water contributions to stormflow hydrographs for four zero order watersheds in western Maryland. The primary goal of the study was to determine whether results from the hydroisotopic and straight line hydrograph separations could be used to assess the success of reclamation at three zero order mined watersheds of various reclamation ages. Similarly, a secondary goal was to determine whether such conventional methods could be employed as successfully at zero order watersheds in the mid-Atlantic as they are at the small watershed and river basin scale. A final goal was to determine the effectiveness of the three natural tracers used in this study: (1) ^{18}O; (2) dissolved silica; and (3) specific conductance. To achieve these goals, 13 storms occurring between September 2004 and June 2006 were analyzed and used to characterize the rainfall-runof

response of each of the four watersheds via the straightline hydrograph separation technique. Likewise, three storms occurring on September 17, 2004, April 22, 2006 and May 14, 2006 were sampled and hydrographs were separated by the hydroisotopic method to generate new water contributions to hydrographs at the four watersheds.

This study found that ^{18}O, silica and specific conductance time series data to be valuable, as dilutions in stream water values of the tracers were obvious and timing of the dilutions generally corresponded to peak discharge. Likewise, all three tracers estimated that old water provided over 50% of total runoff at the forested TNEF, which was encouraging, as these results were similar to the results from other studies in similar ecological settings. Despite these encouraging results, all tracers exhibited serious limitations for the three storms examined in this study. All three tracers were thought to violate critical assumptions of the mixing theory of the hydroisotopic hydrograph separation technique. Despite the problems encountered with each of the tracers, data from the hydroisotopic separations provided insight into how each of the watersheds generated runoff. Results from the hydroisotopic and straightline separation techniques illustrated that two of the three mined watersheds (denoted TMAT and TSSR) exhibited considerably higher peak runoff, total runoff, and new water percentages when compared to the other mined watershed (TSNR) and TNEF. Therefore, surface mining and reclamation impacted the hydrologic response of the mined TMAT and TSSR watersheds more than the mined TSNR watershed. The differences in stormflow response of the four watersheds were thought to be explained by soil compaction and the mixing of clays into the topsoil during reapplication of the overburden during reclamation activities. The limited infiltration capacities observed at TMAT and TSSR, combined with the results from the hydroisotopic and straightline separations, indicate that the likely runoff mechanism at these sites is Hortonian overland flow. The moderate infiltration capacity and the large storage capacity of soils at the TSNR site are thought to explain, in part, the dampened hydrologic response of this watershed. Runoff at the TSNR site may be dominated by saturation overland flow, specifically by precipitation onto saturated areas near the stream channel. As hypothesized, the forested watershed, TNEF, exhibited the lowest runoff volumes, runoff ratios and the lowest estimates of peak and total new water for two of the three tracers. The primary runoff mechanism at the TNEF site, like other forested watersheds, is likely shallow subsurface flow. While it may be erroneous to depend on the hydroisotopic results alone, by integrating the results from the three independent field measurements (hydroisotopic, straightline and infiltration results) one is able to quantify and assess the impacts of surface mining and reclamation.

A COMPARISON OF THE STORMFLOW RESPONSE OF FOUR ZERO ORDER WATERSHEDS IN WESTERN MARYLAND

By

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Thesis submitted to the Faculty of the Graduate School of the
University of Maryland College Park in partial fulfillment
of the requirements for the degree of
Master of Science
2007

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DEDICATION

I dedicate this thesis to my loving wife, Melanie, who has been by my side through this entire enduring process. I love you and thank you.

ACKNOWLEDGEMENTS

I would like to acknowledge my committee members Drs. Keith Eshleman, Phil Townsend and Danny Welsch for their guidance, patience and advice on this project and thesis. Field assistance was provided by Dr. Keith Eshleman, Randy Richardson, Melanie Sloan, Jeff Cole, Geoff Frech, Brian McCormick, Cindy Giffen and Thom Miles who graciously assisted in site selection, sample collection and the transportation and installation of flumes. Lab support was provided by Jim Garlitz, Geoff Frech, Cindy Giffen and Randy Richardson who helped me with sample processing and the laboratory analyses associated with the project. This research made use of the data and graphs generated by Tim Negley (Appalachian Laboratory) for which I am extremely grateful. I would also like to thank Mr. and Mrs. Paul Willison, Jenkins Development Company and the late Simon Mohr for allowing access to these field sites. I would like to thank Molly Taylor and Carole Diehl for their editorial comments and direction in writing this thesis. This thesis would not have been possible without the cooperation and funding from the Appalachian Laboratory, the Maryland Bureau of Mines, and the help of John Carey and Joe Mills. The majority of the funding for this project was provided by a grant from the A.W. Mellon Foundation as part of a much larger cooperative project promoting collaboration between the Appalachian Laboratory and the Appalachian College Association.

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Chapter I: INTRODUCTION

Coal mining has formed an integral part of the culture and economy for the people in hundreds of small towns in Appalachia since the mid 1800's. Many watersheds of the coal-producing region of Appalachia have been adversely impacted by coal mining. Prior to the 1940's, the typical method of extracting coal from the earth was by deep mining. The effects of deep mining are numerous, including acid mine drainage, water diversion, and groundwater contamination. There is a large body of literature (Brady et al. 1994, Taylor et al. 1984, Singer et al. 1970) documenting the environmental impacts resulting from the deep mining coal removal method.

Surface mining of coal began in 1866 in Danville, IL with the opening of a small-scale surface mine (Starnes 1983). Mining practices changed in the early 1940's from large-scale deep mining and small-scale surface mining to large-scale surface mining. Large-scale surface mining consists of activities that disturb hundreds of square meters to perhaps fifty square kilometers, the latter associated with the removal of entire mountain tops for coal extraction. The development of heavy machinery during World War II provided equipment with the capability of moving massive amounts of soil and overburden in a relatively short amount of time, thus rendering large scale surface mining both possible and more economical than other mining techniques. This machinery is used to remove the surface overlying the coal seam (termed "overburden"), which is then stockpiled adjacent to the mining area. After the coal is extracted, also via heavy machinery, the overburden is replaced over the mined area.

In 1977, the Surface Mining Control and Reclamation Act (PL 95-87) was enacted to address the environmental concerns of surface mining (Bonta et al. 1992). Under PL 95-87, it is required that surface mined land be returned to original grade and acceptable land use coverage (Negley 2000). To meet these standards, topsoil must be placed on top of the overburden, returned to original grade, and then revegetated (Chaney et al. 1995). Once soils have been stabilized and permanent vegetation has been established, the reclamation process is considered complete. Upon completion, the reclaimed mine site is evaluated by state and/or federal mining officials, and bond money, initially posted by the mining company, is returned if minimum reclamation requirements have been achieved.

Surface mined areas are subject to several manipulations that alter physical and hydrological properties of the area. In the eastern U.S., it is common to observe a change in vegetation of a mine site from forest to grassland. The standard procedure is to seed the reclamation site with fast growing grass and clover species to reduce erosion from the site. This manipulation however, alters the amount of precipitation that is intercepted and evapotranspired (Swift et al. 1975, Helvey 1967). Roughly two thirds of all precipitation that falls on a forested area returns to the atmosphere via evapotranspiration (Novotny and Olem 1994). However, it is shown that evapotranspiration of recently timbered areas may be 15-20% less than intact forests (Dunne and Leopold 1978). Similarly, evapotranspiration of forested areas is 20-30%

higher than grasslands under the same climate (Novotny and Olem 1994). Although mined areas clearly differ from logged areas and natural grasslands, it follows that evapotranspiration in surface mined areas is lower than native forests, meaning that mined watersheds must process an additional amount of “effective” precipitation.

Reclamation activities produce smooth, manicured appearances on mine sites, in contrast to the rocky, uneven, rough surfaces commonly present before mining. Thus the amount of precipitation that can be stored in depression storage is also reduced due to a decrease in surface roughness from the reclamation process (Novotny and Olem 1995). This process results in a further reduction in the amount of precipitation returning to the atmosphere via evapotranspiration. Perhaps the most dramatic impact of surface mining and subsequent reclamation is the change in the physical and hydrological properties of the surface soils of the mined area, primarily through compaction.

Heavy machinery (usually a bulldozer) is responsible for replacing the overburden and eventually replacing the topsoil in the reclamation process. During the reclamation process, the tracks of the heavy machinery compact the soil. According to Chong and Cowsert (1997), compaction increases soil bulk density, and reduces porosity, infiltration, and crop productivity. Compaction and the mixing of clay with the topsoil during reclamation have been shown to reduce infiltration capacities of the minesoils (Bussler et al. 1984). Ritter and Gardner (1993) found that infiltration rates of reclaimed minesoils can be up to an order of magnitude lower than undisturbed forested sites. In an Indiana study, it was hypothesized that soil compaction would lead to higher mean bulk densities on reclaimed surface mine areas compared to a reference forested site (Bussler et al. 1984). Physical soil properties were tested and compared between a reference watershed (undisturbed) and a reclaimed surface mine watershed that was otherwise similar in topography, soils, and vegetation prior to mining. Mean soil surface bulk density was 1.54 g/cmr^3 in the reclaimed watershed and 1.29 g/cm^3 in the non-mined reference site (Bussler et al.1984). The study also found bulk density to be higher on the reclaimed site not only on the surface, but at all depths from 0 to 120 centimeters (Bussler et al. 1984). Higher bulk densities in the rooting zone result in a reduction of root elongation, which leads to vegetation stress on reclaimed sites (Ritter and Gardner 1993). Root elongation by vegetation is also important in the development of the micro/macropore network, which increases infiltration rates as water penetrates the soil pore space (Bussler et al. 1984).

Several studies have attempted to quantify the differences in infiltration rates between surface mined areas and undisturbed forested sites. Pedersen et al. (1980) found infiltration rates of a surface-mined area to be 0.003-0.011cm/hr compared to 8-10 cm/hour on an undisturbed forested site. In a study performed in the Snowshoe Watershed in Central Pennsylvania, infiltration rates of newly reclaimed minesoils were 1-2 cm/hr, where pre-mined infiltration rates were 8-10 cm/hr (Guebert and Gardner 2000). In a similar study, also in Central Pennsylvania, Jorgensen and Gardner (1987) found infiltration rates of newly reclaimed soils to be 0.73 cm/hr compared to 8-10 cm/hour for undisturbed reference sites. Studies have found that infiltration capacities of minesoils increase with time; however, in no case did these increasing capacities approach infiltration capacities exhibited by pre-mined or undisturbed soils (Guebert and Gardner 2000, Jorgensen and Gardner 1987). In all cases, low infiltration rates of minesoils were attributed to high bulk density, high percent clay and silt content, and reduction or elimination of the micro/macropore network caused by the redistribution of soils and compaction of the surface by heavy machinery during the reclamation process.

Infiltration rates vary widely across the landscape and hillslope. As such, small-scale infiltration plots cannot easily account for variability across a larger scale (e.g. within a catchment), unless a large number of measurements are made. As such, studies at the small watershed scale require integration of infiltration rates that capture the range of spatial variability within an area. Watersheds represent the fundamental unit that can integrate hydrological changes; the average infiltration capacity of a watershed can then be derived from the stormflow response of a catchment, which integrates the spatial variability in the catchment (Dunne and Leopold 1978). The storm hydrograph of the stormflow response can be separated into stormflow and baseflow, that can be used to elucidate differences in infiltration between mined and un-mined watersheds. Stormflow can be further separated via techniques such as isotopic separation and specific conductivity signatures (Sklash et al. 1976).

The Horton theory (1933) postulates that stormflow is primarily derived from infiltration excess overland flow. The theory, however, does not account for the contribution of water stored within the watershed antecedent to a particular storm event. The isotopic method separates the time origin of stormflow by distinguishing “old” water from “new” water. “Old” water is water that was stored within the catchment (i.e. groundwater and soil moisture). “New” water is considered any water that is deposited by the precipitation event in which stormflow will be analyzed (Sklash et al. 1976).

Sklash et al. (1976) developed a technique to use hydrochemical or hydroisotopic data to separate storm discharge hydrographs into temporal components. Groundwater and precipitation have distinct isotopic (e.g. ^{18}O), and chemical signatures (e.g. silica and specific conductivity), which allows the separation of stormflow into pre-event (“old”) and event (“new”) water (Freeze and Cherry 1979). Instantaneous old and new water contributions to stormflow can be calculated at any time using the mass balance equations for the water and isotopic, chemical, and ionic fluxes in the stream:

$$Q_o = \left[(C_s - C_n)/(C_o - C_n)\right] * Q_s$$

$$Q_n = Q_s - Q_o$$

Where Q is discharge, C is the tracer concentration, and the subscripts s, o, and n correspond to the stream, old water, and new water, respectively.

Oxygen-18 (^{18}O) is a stable isotope of oxygen that occurs naturally in the environment. Using the ratio of ^{18}O to ^{16}O as a tracer, Sklash et al. (1976) found that "old" water contributed from 52 to 75% of the storm hydrograph of the seven stream gauges sampled. In a similar New Zealand study, only 3% of the storm runoff could be considered "new" water (Pearce et al. 1986). These findings cannot be explained by the traditional Hortonian overland flow theory (Dunne and Leopold 1978). However, both studies were conducted in watersheds with well-drained soils where it is likely that infiltration rates are very high (Pearce et al. 1986, Sklash et al. 1976). Sources and production of storm runoff in watersheds that have a large percentage of surface mine reclamation could be very different given the low infiltration capacities observed in several studies (e.g., Ritter and Gardner 1993, Negley 2000, Guebart and Gardner 2001).

Watersheds that have been subjected to intense surface mining can show different hydrological responses from unmined watersheds due to the changes in soil properties (Negley 2000). Different flow paths and runoff processes resulted in a surface mined watershed being more "flashy" compared to an unmined forest system. In watersheds where infiltration capacities are <3 cm/hr it has been shown that the dominant run-off process is infiltration-excess overland flow (Ritter and Gardner 1993). In watersheds draining surface mined areas, storm hydrographs can be characterized by increased peak and total runoff and decreased time to peak runoff (Ritter and Gardner 1993, Negley 2000, Guebart and Gardner 2001). In drainage basins where infiltration rates recover to more than 3 cm/hour, runoff is initially dominated by infiltration excess overland flow, but saturation overland flow becomes dominant with time (Ritter and Gardner 1993). The resulting changes in stormflow response in such watersheds include a decrease in peak runoff, combined with an increase in time to peak runoff (i.e., a lagged response of the saturation overland flow runoff process; Ritter and Gardner 1993).

In response to massive flooding in the George's Creek Watershed in 1996, a paired watershed study was performed in the watershed to compare hydrologic differences between a small surface mined watershed (45% reclaimed, 55% forested) and a small forested watershed (0% surface mined, 100% forested) (Negley 2000). Peak runoff rates for fifteen storms investigated were on average two times greater than an un-mined watershed in the surface mined watershed (Negley and Eshleman 2006). Negley and Eshleman (2006) also found that the mined watershed produced greater total storm runoff (3X) and higher runoff coefficients when compared with a reference watershed. In a central Pennsylvania study it was found that up to 55% of rainfall input to a surface mined watershed can leave as surface runoff (Ritter and Gardner 1993). In contrast, Dunne and Leopold (1978) estimated that 10-15% of rainfall onto forested watersheds is lost as surface runoff. These results are substantially different from the findings of Negley and Eshleman (2006) and Ritter and Gardner (1993).

Similar results have been reported on the impacts of surface mining on surface water hydrology in three Ohio watersheds (Bonta, 2000). Mining and reclamation activities resulted in an increase in daily flow volumes, peak flow rates, and runoff curve number, as well as the elimination of seasonal variation of stream flow in all three watersheds studied (Bonta, 2000, Bonta et al. 1997). The runoff curve number for the watersheds were 81, 71, and 75, respectively, before mining, but increased to 87, 91, and 88 following mining and reclamation (Bonta et al. 1997). Consequently, the runoff potential for each of the watersheds increased substantially from the pre-mining to the post-mining condition (Bonta et al. 1997). Surface mining and reclamation activities may significantly impact the hydrological responses of watersheds, particularly those with a large percentage of reclaimed surface mine land.

Surface mining and reclamation activities have been shown to significantly affect watershed hydrologic processes. The areas where large amounts of land have been affected by surface mining, such as the George's Creek Watershed in Western MD, have experienced catastrophic environmental impacts resulting in millions of dollars worth of damage (Paul Kale, personal communication). Studies have shown surface mining to decrease biomass, infiltration capacities of soils and biomass and increase erosion, stormflow and runoff. The processes affected by surface mining are interdependent, with changes in the components of the system impacting other watershed processes.

Many studies have found that the watershed as the preferred unit of study in examining the effects of land use and land cover (LULC) (Negley and Eshleman 2006). The watershed serves as a useful tool as boundaries can be delineated and hydrologic response characteristics such as runoff ratios, total runoff, new water volumes and peak stormflow can be quantified (and normalized) for comparative purposes. Several reclamation methods have been attempted since the Surface Mining Control and Reclamation Act (PL 95-87) was enacted in 1977 with varying degrees of success. Success (or lack thereof) of surface mining reclamation at the watershed scale, therefore, could be detected in the hydrologic response characteristics of a particular watershed. One possible way to determine reclamation success of a particular watershed is through quantification of differences in watershed scale stormflow response and associated runoff mechanisms.

Conventional hydrologic methods such as straight line and hydrochemical hydrograph separations, like those employed by Negley and Eshleman (2006) and Sklash et al. (1976), could be employed at the zero order watershed scale to measure the degree of reclamation success. For purposes of this study the definition of a zero order watershed is a watershed that is too small for the stream (which drains the watershed) to be present on a United States Geological Survey 7.5 minute topographic quadrangle. The results of the separations (i.e., the amount of direct runoff and/or the amount of new water) should reflect differences in watershed features such as soil properties and vegetation, which are affected by the success of reclamation activities. I hypothesize that sites that have been poorly reclaimed will likely exhibit increased new water and direct runoff, whereas well reclaimed sites would exhibit new water and direct runoff amounts similar to those of an undisturbed forested watershed. Ritter and Gardner (1993) found that in drainage basins where infiltration rates are poor (as a result of reclamation), runoff generation is dominated by infiltration excess overland flow. Conversely, in watersheds where infiltration capacities recover to greater than 3 cm/hr after reclamation, runoff is a result of shallow subsurface stormflow generation and, to a lesser degree, saturation overland flow. Therefore, I expect that poorly reclaimed sites are characterized by high new water percentages and increased direct runoff, with the primary runoff mechanism being infiltration excess overland flow. Moreover, I expect that sites of superior reclamation are characterized by low new water amounts, decreased direct runoff, and little overland flow; the primary runoff mechanism primarily should be shallow subsurface stormflow. Several studies have examined the affects of surface mining on the hydrologic response of a watershed (Negley and Eshleman 2006, Bonta et al. 1997). However, few studies have attempted to compare different reclamation sites of varying age and success. In fact, no other studies could be found that employed hydroisotopic (or chemical) hydrograph separation techniques as a method to compare mined watersheds and hence determine the success of post mining reclamation activities.

A. Goals and Objectives

This study examines surface mining and reclamation activities in the George's Creek drainage basin in Western Maryland (Figure 1). The primary goal of the study was to determine whether the hydroisotopic and straight line hydrograph separations could be used to assess success of reclamation at three zero order mined watersheds of various reclamation ages. The primary hypothesis of this study was that differences in watershed-scale stormflow responses and runoff mechanisms in zero order watersheds could be detected using conventional hydrologic methods. The differences in results from such separations should reflect differences in soil properties and vegetation establishment, as well as the overall success of reclamation at a particular site. Given this hypothesis, it was predicted that younger sites (more recently reclaimed) would produce larger new water amounts as would sites with a greater percentage of watershed mined due to the differences in soil properties and vegetation. The results from both the hydroisotopic and straight line separations would then be used to characterize and compare the hydrologic response of three surface-mined reclamation sites and one small, forested watershed. I hypothesized that mined watersheds would exhibit a different stormflow response when compared to a reference forested watershed. Greater direct runoff amounts, runoff ratios and an increase in peak stormflow were expected at the mined sites. The degree of impact on stormflow characteristics is expected to be a function of post mining watershed features (such as soil properties and vegetation), which in turn reflect the success of reclamation.

To achieve these goals, several objectives were developed. The first objective was to locate and select four watersheds that could be gauged and instrumented to compare and characterize stormflow responses to rainfall, as well as soil hydraulic properties. Comparisons for the four sites would include the "new" water portion of stormflow, soil infiltration capacities, stream discharge, response lag times and rainfall-runoff ratios. If possible, the selected sites would be comparable in location, slope, elevation, and climate characteristics, while differing only in age and percent of land impacted by mining within the watershed. A second objective was to collect time series data for three storms at each site in order to determine "new" water portions of stormflow. A third objective was to compare stormflow response at each site for a set of storms. The fourth objective was to measure and compare infiltration capacities of each site.

The evolution of these objectives stimulated several additional goals that were implicit to this project. Only a few other studies could be found that employed hydroisotopic (or chemical) hydrograph separation techniques at the zero order watershed scale (Weiler et al. 2003, McGlynn and McDonnell 2003). Both the McGlynn and McDonnell (2003) and Weiler et al. (2003) studies were performed in New Zealand, unfortunately no studies could be found employing such hydrologic techniques at the zero order water shed scale in the Appalachian Mountains or in the United States. Therefore, a secondary goal of this research project was to determine whether hydrograph separation techniques as described by Sklash et al. (1976) and

Eshleman et al. (1993) could be applied at the zero-order watershed scale in a manner comparable to the application at the river basin scale. A final goal of this study was to determine the effectiveness of the three natural tracers used to separate hydrographs. In this study I used $\delta^{18}O$, silica concentration, and specific conductance for hydroisotopically separating storm hydrographs. These tracers are influenced by different watershed processes, thus possessing the potential to produce unique new water and old water proportions. The data generated by these tracers were analyzed not only to generate new water contributions to the hydrograph but also to determine if and which tracers were capable of producing credible and reliable results.

Chapter II: METHODS

To investigate the hydrologic effects of surface mining and subsequent reclamation four watersheds I selected four small watersheds within the George's Creek Basin. More specifically, I investigated the differences in hydrologic response of four zero-order watersheds, which differed in percent of watershed affected by mining and the age of surface mine reclamation. The first component of this study involved separating stormflow into "new" and "old" water portions for each of the selected watersheds. In this study, I employed a variety of chemical and isotopic tracers and methods described in the Sklash et al. (1976) study. The second component of the study was to characterize and compare stormflow response of the selected watersheds for a set of storms. Ideally, the watersheds selected for comparison would be very similar in terms of size, slope, climate and other physical features. However, locating and gaining access to four such watersheds proved to be very difficult. The actual selection of the watersheds in this study involved a variety of other factors including: (1) proximity to the Appalachian Laboratory; (2) ability to gain landowner permission, and state environmental permits; (3) the suitability for stream gauging; (4) percent of the watershed affected by mining; and (5) age of reclamation. After reconnoitering a large number of potential sites, four zero order watersheds were selected for the study: (1) a 20 year old grassland site that was reclaimed in accordance with PL 95-87 of which about 50% of the watershed is reclaimed mineland; (2) a 2 year old grassland site that was reclaimed in accordance with PL 95-87 of which 100% of the watershed is reclaimed mineland; and (3) a 20-year old grassland site that was reclaimed in accordance with PL 95-87 of which 100% of the watershed is reclaimed mineland; and (4) a small un-mined forested watershed.

Physical characteristics such as elevation, slope, watershed boundaries, and watershed areas of the four watersheds were determined using a variety of tools. Watershed boundaries were delineated using a Trimble Pro XR Global Positioning System (GPS) Unit. The perimeter of each watershed was walked, recording GPS coordinates at 5-second intervals. The data were downloaded and differentially corrected using base station data from Allegany College, Cumberland, MD. Watershed slopes, were delineated from a 30m USGS digital elevation model (DEM) in ArcView 3.2.

B. Site Descriptions

The four watersheds selected for this study are located within the George's Creek watershed (Figure 1) in Allegany County, Maryland. The George's Creek basin (39 º 35'; 79 º 00'W) of western Maryland has been subjected to intensive surface mining and reclamation activities. The basin is approximately fifteen miles long draining an area of 187.5 km^2 (72.4 mi^2). Soils of the watershed belong to the Gilpin Dekalb-Cookport Association (U.S. Soil Conservation Service 1977). Characteristics of this association are gently sloping to very steep, well drained soils and moderately well drained soils. Soils of this association are mostly very stony and moderately deep over sandstone and shale. The average slope of the watershed is 9.5 degrees (Negley 2000).

Two watersheds used in the prior study by Negley (2000) research were selected for this study. The first watershed that was selected is a sub-watershed of Mathew Run (referred to hereafter as TMAT). TMAT is part of an on-going research project at the Appalachian Laboratory, Frostburg, MD and was previously equipped with a flume and other gauging equipment. Approximately 46% (12.4 ha) of the 27.1 ha watershed (Table 1) was mined and subsequently reclaimed in the early 1980's (Negley 2000). The area was backfilled, returned to original grade, and planted with a mix of grasses and clover species. In addition to the clover and grasses, locust (*Robinia pseudoacacia*) seedlings were planted at a density of 2500 stems/ha. Approximately 9100 kg/ha of $CaCO_3$ and 1100 kg/ha of 10-10-10 fertilizer were added during the backfill operation to enhance plant growth and neutralize acidic mine soils mixed with the backfill. The reclamation plan for the TMAT site called for the post mining land use to be 100% woodland. At present, the site remains covered mostly by herbaceous vegetation, however, as a result of poor soil quality due to mining and reclamation. Prior to mining activity the soils were mapped as Cookport silt loam (0-10% slopes) and Cookport very stony silt loam (10-30%) (USDA Soil Conservation Service 1977). Following reclamation, TMAT slopes are northwest facing and are an average of 4.5 degrees (Table 2). The unmined, forested section of the watershed is covered with typical second-growth deciduous forest composed of black birch (*Betula lenta*), chestnut oak (*Quercus prinus*), and red maple (*Acer rubrum*).

The second watershed used in this study was also part of the Negley (2000) study. This watershed is drained by a tributary to the east branch of Neff Run (referred to hereafter as TNEF). TNEF is approximately two km from the TMAT watershed (Figure 1) and has never been disturbed by surface mining activities. The site is a typical second growth, uneven aged stand consisting primarily of sugar maple (*Acer saccharum*), black birch (*Betula lenta*), and black cherry (*Prunus serotina*). The TNEF forest was selectively timbered approximately 25 years ago (Negley 2000). In a 1977 survey, the soils were mapped as Cookport very stony silt loam with 10-30% slopes (USDA Soil Conservation Service 1977). Like TMAT, the slopes are northwest facing but are slightly steeper with the average slope of 9.5 degrees. The TNEF watershed is the smallest of the four watersheds at approximately 3.0 ha.

The third watershed selected, the Seldom Seen reclaimed site (TSSR), is found within the Seldom Seen Run sub-watershed approximately one km south of Lonaconing, Maryland (Figure 1). According to Bureau of Mines reports (and personal knowledge), reclamation of the Seldom Seen site began in the fall of 2002 (Table 1). Reclamation activities resumed in the fall of 2004 and included grading of the watershed surface, removal of temporary diversion channels, and planting of several types of seedling trees. During reclamation activities, diversion ditches were installed to ensure that upslope runoff would not drain onto the reclaimed site. Installing such diversion ditches is common practice during mineland reclamation throughout the Mid-Atlantic States. This activity resulted in the TSSR watersed being entirely of one land use – reclaimed mineland. This site presented the unique opportunity to examine a watershed of only one land use.

The initial reclaimed Seldom Seen watershed (referred to hereafter as TSSR[1]) drained approximately 5.13 hectares of reclaimed mine land (Table 1). Reclamation activities continued at TSSR[1] in fall of 2004, which included the re-grading of some heavily eroded sections of the watershed and the planting of tree seedlings. Tree species included white pine (*Pinus stubus*), (*Pinus strobus*), scotch pine (*Pinus sylvestris*), black locust (*Robinia psuedoacacia*), fir (*Abies spp*.), and norway spruce (*Picea abies*). Approximately 1500 trees/ha were planted with 2.5m by 2.5m spacing. Like the TMAT site, the reclamation plan was for the post-mining land use to be 100% woodland. The reclamation plan does not mention the use of any fertilizer or lime during the backfill operation. At present, the site is in poor condition with respect to both herbaceous and woody vegetation. Large areas of bare soil are present throughout the site, particularly on the south facing slope near the northern boundary of the watershed. Post mining soils are high in clay and sand content, whereas pre-mining soils of TSSR[1] were mapped as a mixture of Cookport very stony silt loam, stony, rolling land, and Buchanan very stony loam. The slopes are steeper at TSSR[1] (Table 2) than the TMAT and TNEF watersheds, ranging from 10% to 20% (USDA Soil Conservation Service 1977). Post-reclamation slopes of TSSR[1] are southeast facing.

The runoff ratios observed at TSSR[1] (discussed later, Tables 17 and 20) were extremely high throughout the first year of the study (2004-2005), but were credible.

However, a November 29, 2005, event generated a runoff ratio of 1.03, indicating that there was more runoff than rainfall. Although possible (rain on snow event), it is highly unlikely that a runoff ratio be greater one. Therefore, the additional water (causing the runoff ratio to be greater than one) had to be explained to justify such a calculation. Because this storm occurred in late November, a rain on snow event was one possible explanation to account for this additional water. In fact, 7 days prior to this event, a depth of 20 cm of snow fell in the George's Creek Watershed. Most of this snow melted, however, prior to the November 29 event, as was evident from stage levels noted on the days leading up to the event. There is no doubt that some lingering snow patches may have increased runoff levels, but based on runoff ratios of storms prior to this event, lingering snow patches alone would not have caused the runoff ratio to be greater than one. Another possible explanation for this runoff ratio was the areal variation in rainfall depths. Although variability in rainfall depths is likely, the small differences that may have occurred in the eight km that separate the TSSR site from the TMAT site (where the precipitation gauge is located) is not likely to explain a runoff ratio of greater than one. In addition, the November 29 was not an isolated storm system, but rather was a large storm that dropped precipitation over a 15 hour period. This led to the conclusion that the additional water flowing through the flume at TSSR was coming from beyond watershed boundaries.

United Energy, Inc. (the mining company responsible for the mining and reclaiming TSSR[1]) planned additional reclamation activities in the years following 2004, but went bankrupt and reclamation activities ceased. During this time, the diversion ditches that surrounded the original TSSR[1] site deteriorated as a result of several extreme precipitation events and lack of maintenance, ultimately resulting in a breach in a diversion ditch. The breach occurred in the diversion ditch bordering the eastern watershed boundary of TSSR[1], which allowed upslope runoff onto the TSSR[1] site thus changing watershed boundaries and size. Data from a May 14, 2006 event further supported this interpretation, as the runoff ratio for this event at TSSR[1] was 1.22. The fact that no snow was present at the onset of the May 14, 2006 at the TSSR site and because wedge gauge rainfall depths at TSSR were similar to rainfall depths of the Belfort gauges at TMAT it was determined that the additional water had to be coming from beyond the TSSR watershed boundaries.

To resolve this issue, the TSSR watershed was surveyed for sources of additional water. During this survey, a breach in the diversion ditch bordering the eastern watershed boundary of TSSR[1] was identified. Upon further examination of runoff ratios of storms prior to and after the November 29, 2006 event, it was determined that the November 29 event was, indeed, the event that caused the breach in the diversion ditch. Once located, the breach was inspected in detail to determine if it was allowing water onto the TSSR site. Surface erosion and a small gully were observed just down slope of the breach indicating that it did indeed allow additional water into the TSSR watershed. The flow path of water entering through the breach was tracked to determine its final destination. Due to wide gentle slopes in this region of the TSSR watershed, flow became diffuse and no single flow path was followed. To further complicate matters, the breach itself and the water flowing through it, were extremely close to the southwestern edge of the TSSR^{1} watershed boundary. The final destination of waters entering through this breach, therefore, could not be determined entirely. After the breach in the diversion ditch was discovered, new watershed boundaries were delineated. It was decided that runoff data for the TSSR site be reported for two watersheds of different areas, TSSR^{1}, which was 5.1 ha, and TSSR^{2}, which measured 12.4 ha. Because reclamation is an ongoing process, it is common that the size of a drainage basin changes with the removal of diversion ditches and holding ponds. Bonta et al. (1997) experienced the same problems during a study examining the impacts of coal mining on surface-water hydrology in three watersheds in Ohio. This study examined watersheds at three different phases of reclamation, where each phase had a different watershed area and shape. Similar to this study, Bonta et al. (1997) computed and reported their data based on the differing watershed areas.

The "new" 12.5 ha watershed is referred to hereafter as TSSR^{2} (Table 1). Like the original 5.1 ha, the additional 7.4 ha of TSSR^{2} is also reclaimed mineland, where pre-mined soils were mapped as Dekalb very stony sandy loam. The slopes of the additional 7.4 ha of TSSR^{2} are more gentle than the slopes found at TSSR^{1} ranging from 5% to 10% (Table 2). The additional lands of TSSR^{2} differ from TSSR^{1} in age of reclamation and vegetation type. According to aerial photos and Bureau of Mines reports, the additional 7.4 ha of TSSR^{2} were reclaimed in 1978-1979 and were planted with a variety of coniferous tree species. Tree species include white pine (*Pinus strobus*), Norway spruce (*Picea abies*), scotch pine (*Pinus sylvestris*), and black locust (*Robonia pseudoacacia*). However, striped maple (*Acer pennsylvanicum*) and black cherry (*Prunus serotina*) are present at very low densities.

The fourth watershed selected for this study is located approximately two km north of Lonaconing, Maryland at the base of Big Savage Mountain within the Squirrel Neck Run sub-watershed (referred to hereafter as TSNR). This site is just east of Squirrel Neck Run Road with a watershed area of 11.1 ha (Table 1). Like the TSSR[1] site, the entire TSNR watershed has been mined and reclaimed. However, this site differs from TSSR[1] in that it was mined and reclaimed in the early 1980's and is similar in age to the TMAT site. During backfill operations, 9100 kg of $CaCO_3$ and 1100 kg of 10-10-10 fertilizer were added per hectare. Like the TSSR and TMAT sites, this site was reclaimed in accordance with PL 95-87 and was seeded with the normal grass, clover, and fescue mix but with no planting of woody vegetation. The reclamation plan for TSNR also required that the seed bed for the grasses and clover mix be prepared by discing, harrowing and/or backblading along the contour where impermeable areas were to be ripped with a dozer blade to prevent soil compaction. At present, the site is covered with a variety of grass and clover species and is used for grazing cattle. Revegetation of herbaceous plants has been so successful at the TSNR site that it is mowed annually for the production of hay. Prior to mining and reclamation activities, the soils were mapped as a mixture of Gilpin silt loam (0-10%), Cavode silt loam, and Shelocta shaly silt loam (0-8%). Post-reclamation, the slopes are northwest facing and range from 10 to 20% grade.

C. Field Hydrologic Measurements

Each of the watersheds selected for the study was equipped with instrumentation to measure continuous stream stage and discharge and allow for periodic event sampling. Two of the four small watersheds, TMAT and TNEF, lack natural bedrock controls and had previously been equipped with pre-fabricated, pre-calibrated "Montana" flumes as part of the ongoing ROCA research project (Negley 2000). The two additional sites chosen for this project, TSSR and TSNR, also lacked natural bedrock controls in the stream channel and, therefore, also were equipped with "Montana" flumes.

Negley (2000) selected flume size based on the rational runoff method, where the flumes could accommodate runoff generated by rain events with a 10-year return period. The same rationale was used when choosing the flume size for the TSSR and TSNR sites (Table 3). In early spring of 2004, the perimeters of the TSSR and TSNR watersheds were delineated and recorded using a Trimble Pro GPS Unit. Coordinates generated from these perimeters were then used to generate watershed areas via ArcView 3.2 Software. Once watershed areas were obtained, the runoff amount for a ten year event was calculated for each watershed using the methods described by Hornberger et al. (1998) and flume size was selected accordingly.

All of the flumes in this study are made of ruggedized 9mm thick fiberglass. The flumes are anchored to 15 cm x 15 cm pressure treated timbers with the wingwalls buried in the streambed and streambank (Negley 2000). To measure stage height and, subsequently, discharge, each flume is manufactured with a stilling well. Unidata Model 6541 digital stage recorders (equipped with a copper float and counterweight) were used to continuously record stage at each of the sites. The recorders can detect water level fluctuations greater than 3mm (Negley 2000). Stage records were downloaded from the digital stage recorders on a quarterly basis throughout the study. Stage was converted into instantaneous discharge (Table 3) using rating curves obtained from Free Flow, Inc., the flume manufacturer. (Negley 2000).

Hourly precipitation was measured using two Belfort universal weighing type precipitation gauges manufactured by Belfort Instrument Company. Both of the precipitation gauges were placed in the TMAT watershed on top of Dan's Mountain. One gauge was located adjacent to the TMAT flume in a clearing (29° 35' 31.5" N, 78° 53' 48.9" W), while the second gauge was located in a clearing near the eastern watershed boundary of TMAT. The gauges were deployed in the fall of 1999 and have been collecting rainfall data since December 1999 (Negley 2000). To prevent sampling error from ground splashing, the instruments were fastened to wooden platforms approximately 1 m above the ground. The Belfort gauges used in this study were set to detect precipitation depths greater than 1 mm on 8-day, hourly charts. A major limitation of this study is the location of the two Belfort gauges in relation to the TSSR and TSNR watersheds. Given the proximity of TMAT to TNEF, there is likely little difference in rainfall depths between the two sites. However, TSNR and TSSR are located approximately 10 km southwest of TMAT (Figure 1), differing in aspect and elevation. Because of these physical and geographic differences, it is possible that rainfall depths differed between the sites for a particular storm. Although I was aware of this problem throughout the study, funding for an additional Belfort gauge was not available and the timing of rainfall data was available only from the gauges located at the TMAT watershed. The most affordable solution to remedy this problem was to place wedge gauge precipitation collectors at the TSSR site. Rainfall levels from these gauges were compared to Belfort levels on a storm to storm basis and although small differences did occur, they were not large enough to impact the study. A photograph showing the field instrumentation at TMAT is provided in Figure 2.

Soil infiltration capacity measurements followed the methodology described in Negley (2000) thesis. In fact, infiltration measurements at the TMAT and TNEF sites were used with permission in this study. At TMAT and TNEF, measurements of soil infiltration capacity were recorded at three randomly located plots on each watershed (Negley 2000). Likewise, at TMAT and TNEF infiltration measurements were made at five randomly located plots on each watershed. In both studies, infiltration measurements were performed by installing double ring cylinder infiltrometers (Figure 3). Installing double ring infiltrometers, however, requires relatively level and stone free soils. On several occasions, the randomly selected location was on or near a large rock or tree. When this occurred, a location where the infiltrometer could be installed was identified with the goal of keeping it as close as possible to the original, randomly selected location. The double ring infiltrometers were constructed of 16 gauge sheet metal, with one side sharpened for installation purposes. Installing the infiltrometer required driving the instrument into the soil via a sledge hammer and a installation tool constructed of heavy metal. Once installed, a water supply reservoir was placed on top of the infiltrometer, adding water to the inner ring of the infiltrometer. The reservoir consists of two tubes at the bottom end, with the longer of the two tubes allowing water to pass through, while the shorter permits air back into the infiltrometer. This design makes it possible to keep a constant head in the inner ring of the infiltrometer. The reservoir was constructed from 45 cm a length of cylindrical PVC pipe, where each end of the reservoir is capped with a piece of 0.03 cm plexi-glass. Once the reservoir was in place, water was manually added to the outer ring of the infiltrometer to match the level of the inner ring to avoid differential pressure heads (Negley 2000). The reservoir was also equipped with a graduated tube to allow one to measurement of the amount of water leaving the reservoir to replace the water infiltrating into the soil over time. Infiltration capacity was considered the rate at which water leaves the reservoir to maintain a constant head level in the inner ring of the infiltrometer. One assumption of the infiltration measurements was that soils of each watershed were relatively homogenous and infiltration measurements were representative of the entire watershed.

D. Event Sampling

Storm runoff was sampled at each of the four sites by deploying Isco and/or Sigma automatic event samplers near the gauging site. At the beginning of each precipitation event, the samplers were deployed and programmed to sample ~ 0.9 L for subsequent laboratory measurements of specific conductance, silica concentration, and water $\delta^{18}O$ of water on each sample. For both the September 2004 and April 2006 event, the automatic water samplers were programmed to sample on an hourly interval and could thus sample continuously for an entire day (for a total capacity of 24 samples). As a result of storm duration and watershed response for both events, the initial sampling bottles were collected and then replaced with an additional carousel of empty bottles thus allowing a maximum sample time of 48 hours. Using the field experience gained in my first two sampling events, I chose to program the automatic samplers to sample at 2 hour intervals for the May 2006 event. Although this sacrificed hourly resolution, I found it much more efficient and reduced the chance for programming error and human mistake. Programming the automatic sampler to sample at 2 hour intervals also allows a maximum sampling time of 48 hours. In all three events sampled, 48 hours was enough time to sample the rising limb, peak, and recession limb of the storm hydrograph.

Precipitation samples were also collected during each storm event at the TSSR site. A metal post was equipped with a funnel and collection bottle was installed adjacent to the flume at TSSR. The 1 L sample bottle and large collecting funnel were attached to a post approximately 1 m above the ground. A tube approximately 60 cm long was attached to the base of the funnel and was then looped before being attached to the top of the sample bottle. Because this study used the isotopic tracer ^{18}O, it was important to collect the precipitation in a manner that prevented isotopic fractionation due to evaporation. For each storm event, a clean funnel and 1 L sample bottle were installed at the same time and precipitation was collected for 48 hours. The precipitation sample was collected with the stream samples and transported immediately back to the Appalachian Laboratory where it was stored at 4° C along with the stream samples.

E. Laboratory Analysis

Stream and precipitation samples from all three events sampled were brought back to the Appalachian Laboratory and stored in a refrigerated room at 4° C. Within 7 days of collection, approximately 500 ml of each stream and the precipitation sample was filtered using a two micron water filter and partitioned into 100ml bottles for ^{18}O and silica analyses. The partitioned samples and the remainder of the unfiltered sample were saved and again refrigerated at 4° C. The remainder of the unfiltered sample was saved for later specific conductance measurements.

Silica concentrations were determined by segmented flow analysis on the Lachat Quickchem FIA (Flow Injected Analysis) 8000 instrument. This method is commonly used to determine silica concentrations in surface, domestic and industrial waters and has an applicable range from 0.1 to 60 mg/L. The flow injected analysis determines silica in solution as silicic acid. Silicilate reacts with molybdate reagent in acid media to form β-molybdosilicic acid. The complex is then reduced by ascorbic acid to form molybdenum blue and the absorbance is measured at the wavelength of

660 nm.

Because a mass spectrometer was not available at the Appalachian Laboratory, samples were sent to the Environmental Isotope Laboratory (EIL) at Waterloo University for $\delta^{18}O$ isotope analysis. The mass spectrometer at EIL is a VG MM 903 and has a triple Faraday bucket collector that uses a 90°, 9 cm radius magnet for precise and simultaneous determinations of isotope ratios of ^{18}O in CO_2 gas (Drimmie and Heemskerk 1993). The EIL uses standard procedures for oxygen isotopes. These procedures entail equilibration of CO_2 with liquid water in a controlled bath, with continuous shaking. The shaking occurs for no less than 3 hours, but is usually carried out overnight. The preparation and extraction of the CO_2 is done on a fully automated system of 30 – 30 ml vessels attached to the mass spectrometer (Moser 1977).

Specific conductance was measured to indicate the total ionic content of the water samples for each of the three storm events analyzed. To measure specific conductance, the remainder of the unfiltered stream or precipitation sample was warmed to room temperature (~25°C) using a warm water bath before the analysis. The samples were measured using a conductance meter and conductivity cell. The meter and cell were checked periodically using potassium chloride standards of known conductivity to ensure accurate measurements. Between each sample, the conductance meter and the conductivity cell were rinsed profusely with deionized water to prevent sample to sample contamination. A laboratory duplicate was measured every 15 samples for quality assurance. Temperatures of each sample were recorded, and specific conductance measurements were then corrected manually to room temperature (25°C) using a temperature correction table.

F. Hydrograph Separation

Water samples were obtained for three storm events at each of the four watersheds. After transporting the event samples to the Appalachian Lab, they were filtered and partitioned for $\delta^{18}O$, silica, and specific conductance analyses. Natural isotopic tracers such as ^{18}O and chemical tracers such as conductance and silica are commonly used for hydrograph separation to determine sources of stormflow (Pearce et al. 1986, Wels et al. 1991, McGlynn and McDonnell 2003). All natural waters contain a unique amount of ^{18}O, or naturally occurring solutes such as silica and ions contributing to specific conductance. As such, measurements of ^{18}O, silica, and specific conductance in stream water and rainwater serve as suitable tracers of stormflow sources (Sklash et al. 1976). ^{18}O in particular has proven to be an excellent tracer as areal variations in $\delta^{18}O$ in precipitation are minor across small catchments (Pearce et al. 1986). Hence, stormflow can be separated into "old" (soil and groundwater) and "new" (precipitation) water as both have distinct isotopic and chemical signatures. ^{18}O concentrations are given in conventional δ-notation where:

$$1)\ \delta^{18}O = \left[({}^{18}O / O^{16}\ \text{sample}) / ({}^{18}O / O^{16}\ \text{standard}) - 1\right] * 1000$$

(where $\delta^{18}O$ is measured in per mil units)

The ^{18}O / O^{16} standard is taken to be that of Standard Mean Oceanic Water (SMOW), which by definition has a zero $\delta^{18}O$ value, thus waters depleted in ^{18}O with respect to SMOW have negative delta values and waters enriched in ^{18}O will have positive delta values (Sklash et al. 1979).

Old and new water contributions to stormflow can be calculated at any time using the mass balance equations for the water and isotopic, chemical, and/or ionic fluxes in the stream:

$$2)\quad Q_o = \left[(C_s - C_n)/(C_o - C_n)\right] * Q_s$$
$$Q_n = Q_s - Q_o$$

where Q is discharge, C expresses tracer concentration (e.g. $\delta^{18}O$), and the subscripts s, o, and n correspond to the stream, old water, and new water, respectively. As mentioned above, natural chemical tracers can be used in this very same manner to generate old water and new water components. In this study, data from ^{18}O concentrations, silica concentrations, and specific conductances were used to separate stormflow hydrographs into new and old water components using the mass balance equation.

One of the major limitations of the hydroisotopic (and hydrochemical) separation technique is the inability to determine geographic source components or runoff generation mechanisms (Sklash et al. 1976). Sklash and Farvolden (1979) stated the two major assumptions of the hydroisotopic separation technique: (1) the isotopic contents of groundwater and vadose zone water are equivalent; and (2) surface storage is minimal and does not contribute to the hydrograph. Other assumptions of the hydroisotopic separation technique are: 1) isotopic (and chemical) concentrations of precipitation are constant and do not vary temporally or spatially for a particular event; and 2) precipitation ("new") and groundwater ("old") have distinct, different isotopic (and chemical) concentrations.

Another major limitation of this particular study is the lack of baseflow between storm events to obtain baseline information required for completing the mass balance equation. As mentioned in the site descriptions, all four watersheds in this study are zero order watersheds and flow only seasonally and following precipitation events. Because there is normally no antecedent baseflow to sample, one cannot easily determine baseline ("old" water) isotopic (and chemical) concentrations of stream water. Other potential baseline or old water sampling sources such as natural springs, seeps and wells were not present at any of the sites and therefore could not be sampled. One method that was attempted in hopes of obtaining "old water" values was the installation and subsequent sampling of soil lysimeters at each of the four watersheds. Upon installing the lysimeters in the 2004, samples were collected and analyzed monthly. Silica and specific conductance data were highly variable and it was determined that this method would not accurately indicate true old water measurements for the two tracers. Since it was not possible to obtain this data as suggested by the hydroisotopic hydrograph separation technique, I used isotopic (and chemical) concentrations from a sample at either the beginning of the rising limb or at the end of the recession limb of the hydrograph. The assumption that such a sample is representative of "old water" is one that is unique to this study and could not be avoided. To my knowledge, no other studies have used the hydroisotopic hydrograph separation technique at the zero order watershed scale and therefore a previous methodology could not be followed to remedy such problems. The implications of this assumption are addressed and discussed in the following chapters.

The much simpler straight line hydrograph separation technique was also used in this study to separate stormflow and baseflow for 13 different storms. In this method, storm hydrographs are separated into stormflow and baseflow components by using the steps described in detail by Dunne and Leopold (1978). An analyst draws a straight line from the "time of rise" to the "end of stormflow" of the stormflow hydrograph. The "time of rise" is determined by the first observed increase in stream height after the beginning of the precipitation event. The "end of stormflow" is more difficult to determine and requires that the hydrograph be plotted on a semi-log plot. Once plotted, the "end of stormflow" is then determined as the point at which the recession limb of the hydrograph becomes linear. Negley (2000) used this method to obtain stormflow measurements such as runoff ratio, total direct runoff and peak runoff rate for a two-year period for the TMAT and TNEF sites. Because this study builds to some degree on the Negley (2000) research, the same straight line method was also used in this study to separate stormflow hydrographs from 13 events during the period September 1, 2004 to June 1, 2006 for each of the four sites.

G. Data Analysis

Stormflow hydrographs were separated into baseflow ("old" water) and stormflow ("new" water) by two different techniques, the hydroisotopic (chemical) technique and the straight line method (Sklash et al. 1976, Dunne and Black 1978). Hourly discharge and runoff values for a particular storm were computed from stage heights and, in the case of runoff, were normalized to watershed area. Both of the hydrograph separation techniques used the instantaneous hourly data to produce total contributions of both "old" water and "new" water to the storm hydrograph.

The hydroisotopic method of separation used concentrations/measurements of ^{18}O, silica, and specific conductance to detect a dilution or concentration in stream water at a given point in time throughout the hydrograph. Old and new water contributions to stormflow were calculated by using the mass balance equation:

$$3)\quad Q_o = \left[(C_s - C_n)/(C_o - C_n)\right] * Q_s$$

Using Equation 3, old water and new water contributions were calculated for each data point available for ^{18}O, silica, and specific conductance values throughout the events of September 17, 2004, April 22, 2006 and May 14, 2006. Upon calculating these values at each data point for each of the three analytes, graphs were constructed illustrating total stormflow, old water portion of stormflow and new water portion of stormflow (discussed later, Figures 23-34) for each of the three events for all four watersheds.

The time series data for ^{18}O, silica, and specific conductance for the events of September 17, 2004, April 22, 2006 and May 14, 2006 were used to calculate total contributions of old water and new water using a numerical time integration of the separated hydrographs. In addition to the old water and new water contributions, percent new water at peak runoff and total percentage of new water were calculated for all watersheds for each of the three storms (Tables 4-8).

To be consistent with Negley (2000), watershed response characteristics for each watershed were calculated from hydrographs separated using the straight line method. Peak stormflow, centroid lag, total surface runoff, direct runoff and runoff ratio were computed for 13 different storm events from September 1, 2004 to June 1, 2006. A complete data set (data from all four watersheds for a particular storm) is only available for 8 of the 13 storms due to a variety of equipment problems. Winter freezing and malfunctioning stage recorders were two of the most common problems throughout the study. Given the scope of this project, equipment problems and the small size of the data set, no inferential statistical tests were performed on the data set. Although the data set from this project is qualitative, obvious patterns were present and generalizations about the stormflow response of each watershed are made and discussed.

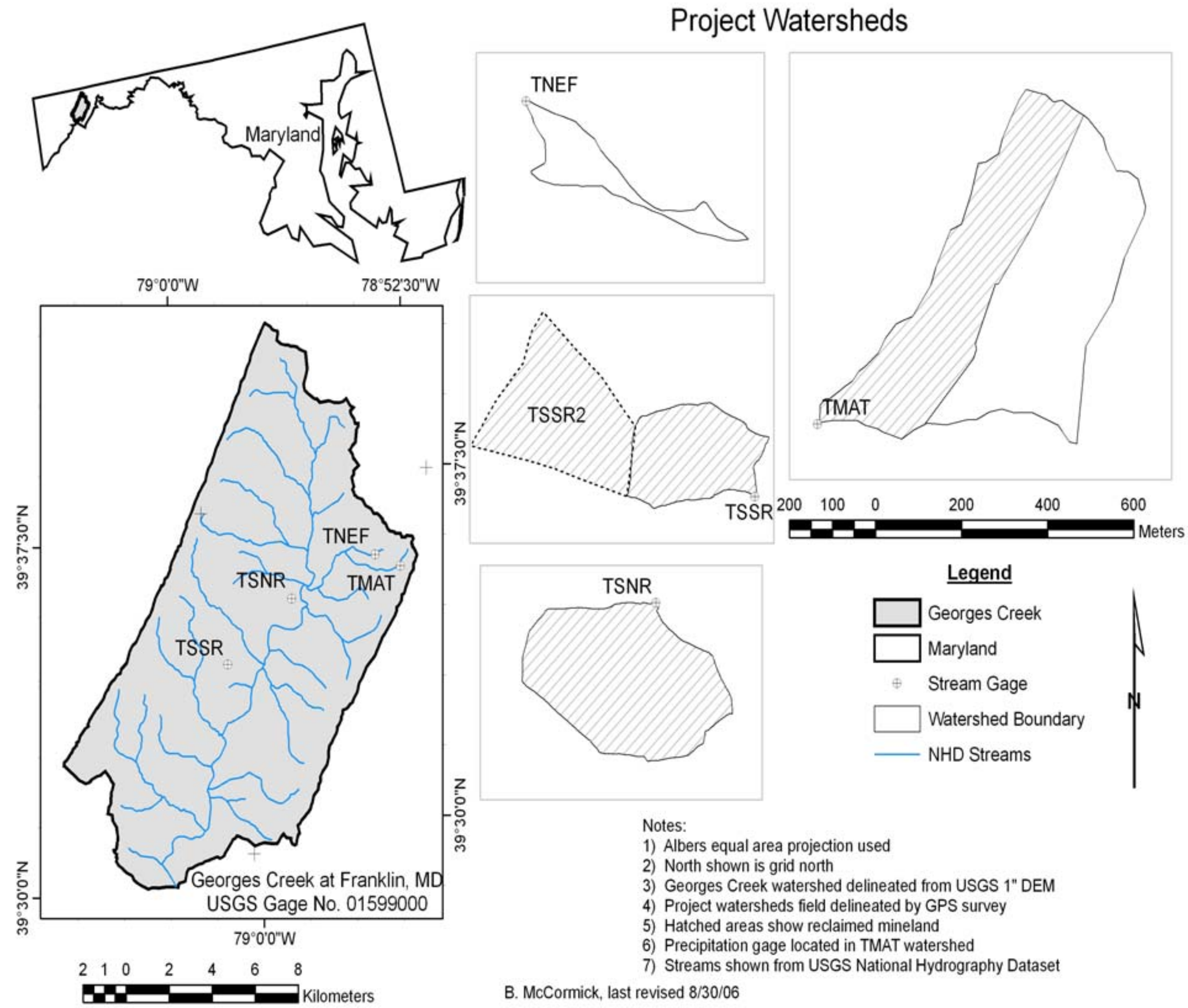


Figure 1. Locations of stream gauges, watershed boundaries, major tributaries and the location of the four watersheds of interest within the George's Creek Watershed, Allegany, Maryland.

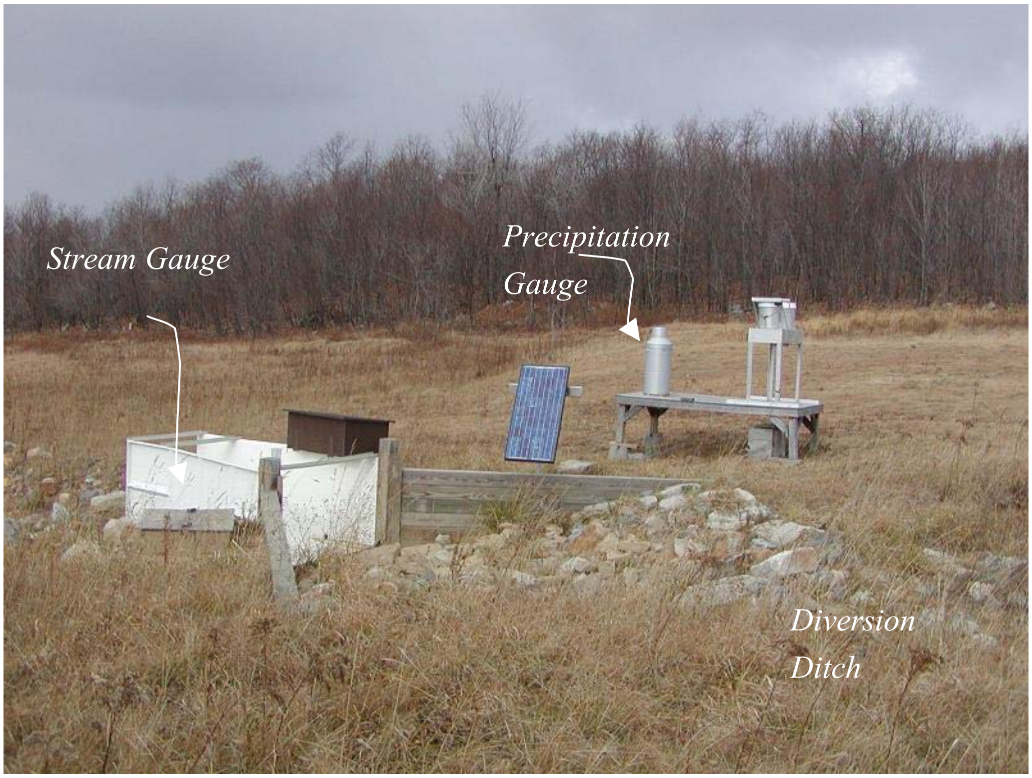
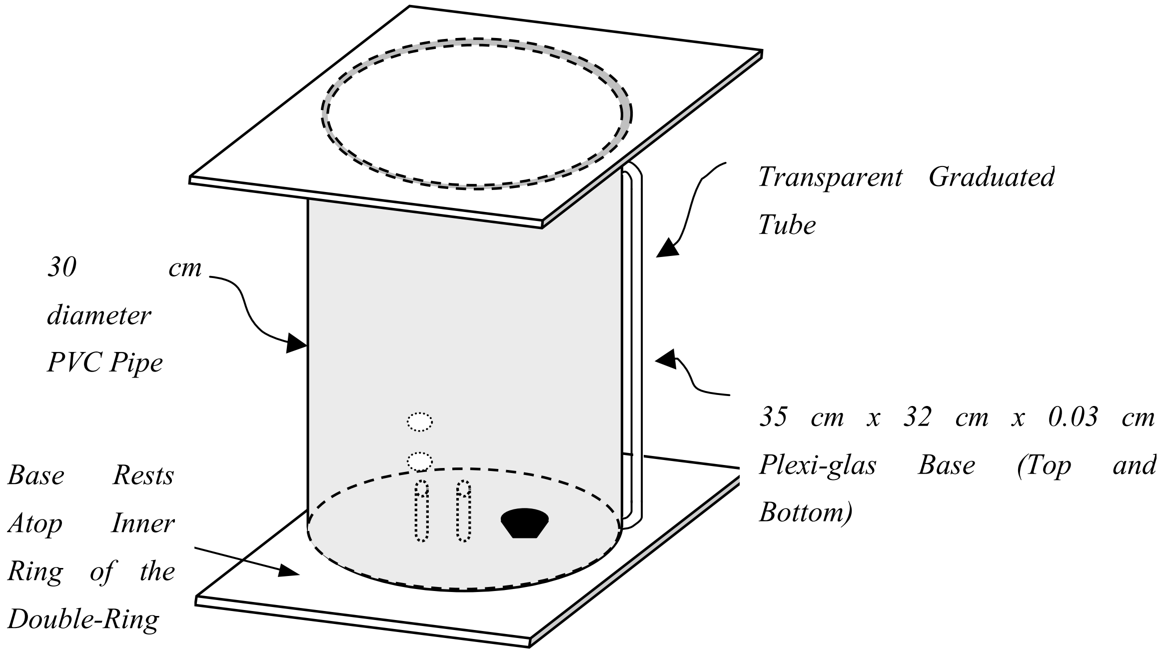


Figure 2. Equipment installed at gauging station at TMAT for monitoring catchment inflow and outflow. Stream gauge ("Montana Flume") is similar to that installed at TNEF, TSNR, and TSSR. (Used with permission – Negley 2000)



Reservoir for double-ring infiltrometer

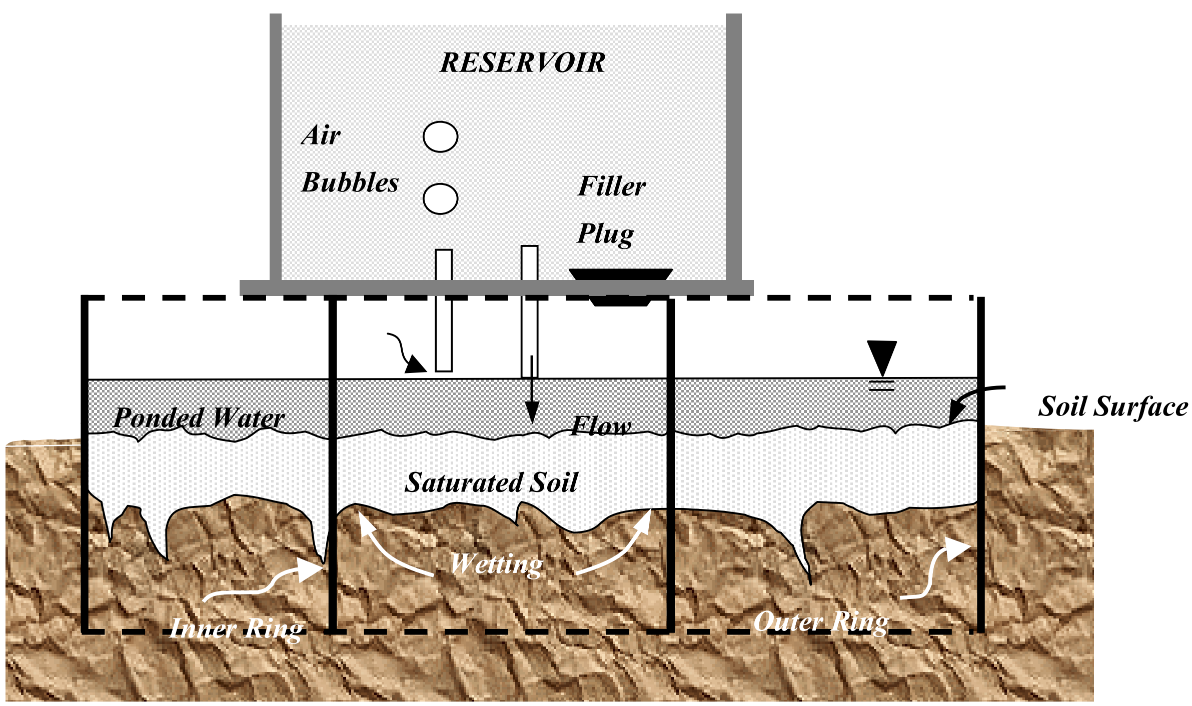


Figure 3. Schematic of double-ring infiltrometer and water reservoir used to measure infiltration capacity (adapted from Eshleman 1985)

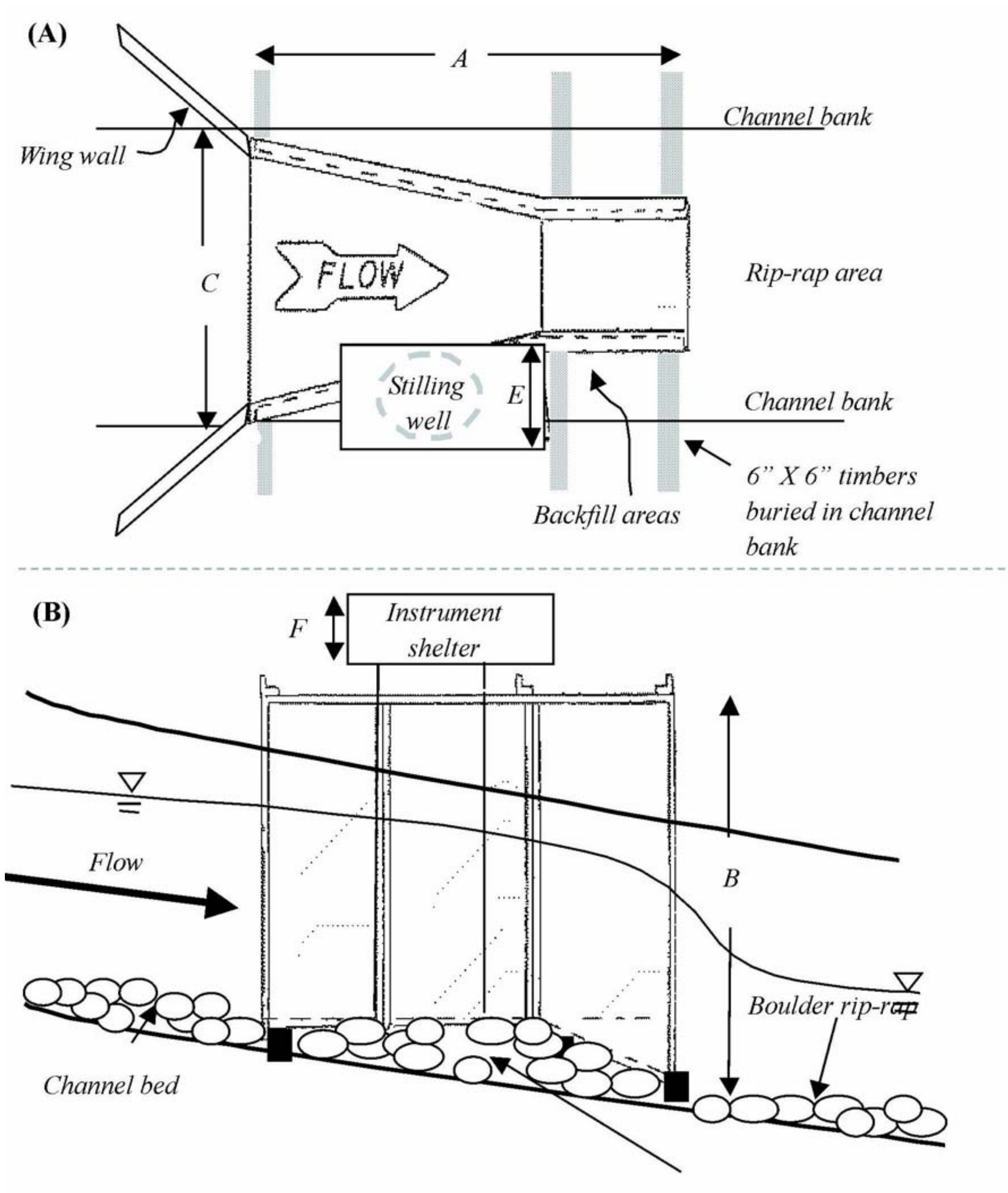


Figure 4. Plan view (A) and side view (B) of Montana flumes installed at sites TMAT, TNEF, TSNR, and TSSR. (Used with permission – Negley 2000)

Table 1. Acronym, drainage area, % of watershed mined, reclamation type, year reclaimed, andadditional comments on the watersheds examined in this study.

Site Name	**Acronym**	**Area (ha)**	**% Mined**	**Reclamation Type**	**Year Reclaimed**	**Comments**
Tributary Mathew Run	TMAT	27.1	47%	Grassland (PL95-87)	1982	Flume, infiltration experiments, ^{18}O, silica and sp. cond.
Tributary Neff Run	TNEF	3.0	0%	Not mined	N/A	Flume, infiltration experiments, ^{18}O, silica, and sp.cond.
Tributary Squirrel Neck Run	TSNR	11.1	100%	Grassland (PL95-87)	1982	Flume, infiltration experiments, ^{18}O, silica and sp. cond.
Tributary Seldom Seen Run 1	TSSR[1]	5.1	100%	Grassland (PL95-87)	2002	Flume, infiltration experiments, ^{18}O, silica and sp. cond.
Tributary Seldom Seen Run 2	TSSR[2]	12.5	41%	Grassland (PL95-87)	2002	Breach in diversion ditch changed watershed area

Table 2. Drainage area, slope, and elevation of watersheds examined in this study.

Name	Area (ha)	Slope (degrees)			Elevation (meters)		
		Min	Max	Mean	Min	Max	Mean
TMAT	27.1	0	15	5	783	851	825
TNEF	3.0	6	13	10	689	778	727
TSNR	11.1	0	13	5	570	605	587
TSSR[1]	5.1	0	40	9	605	641	623
TSSR[2]	12.5	0	40	8	605	679	641

Table 3. Stage discharge relationships for the four flumes used in the comparative catchment study.

#	**Watershed**	**Throat Width (in)**	**Rating Curve**
1	TMAT	36	$Q_{(cfs)} = 12\ H_a^{\ 1.5561}$
2	TNEF	12	$Q_{(cfs)} = 4W\ H_a^{\ (1.522\ W\ \hat{}\ 0.026)}$
3	TSNR	24	$Q_{(cfs)} = 8\ H_a^{\ 1.5497}$
4	TSSR	24	$Q_{(cfs)} = 8\ H_a^{\ 1.5497}$

Q = discharge, H_a = head (depth) in feet, W = flume throat width in feet

Chapter III: RESULTS

This study found several compelling results suggesting that watersheds subjected to surface mining (and reclamation activities) exhibited very different stormflow responses in comparison to the hydrologic response of an entirely forested watershed. Not only were hydrologic differences observed between mined and forested sites, but also among the different mined watersheds used in the study. The watersheds TSSR^1 (and/or TSSR^2 after breach) and TMAT tended to have a more flashy hydrologic response than TSNR and TNEF. TMAT and TSSR produced the greatest runoff ratios for all of the storms analyzed and the greatest peak stormflows for all but one of the storms. Despite the flashy behavior of both TMAT and TSSR, lag times varied greatly among and between watersheds and no consistent pattern could be detected. For the three storms analyzed, several trends were also apparent in the isotopic and chemical data. From the isotopic and chemical data, TSSR and TMAT exhibited the greatest total new water runoff depths and the highest percentages of total new water (per storm event) and new water at peak flow for the majority of the events analyzed.

Runoff hydrographs were created to compare general characteristics of the hydrologic response of each watershed. Four storms were selected from the 13 available in the data set based on several simple criteria: (1) stage data were available from each site; and (2) rainfall data were available. The only four storms that met these criteria were: May 20, 2005, November 29, 2005, January 2, 2006 and May 14, 2006 were. The runoff hydrographs (of the four sites) in response to approximately 31.8 mm of precipitation (maximum rainfall intensity of 5.1 mm/hr) can be found in Figure 17. The November 29, 2005 storm dropped 41.9 mm of precipitation with a maximum rainfall intensity of 7.62 mm/hr. Runoff hydrographs in response to this storm can be found in Figure 18. Runoff hydrographs in response to 26.7 mm of precipitation on January 2, 2006 (maximum rainfall intensity of 3.8 mm/hr) can be found in Figure 19. Approximately 46.4 mm of precipitation fell during the May 14, 2006 event (maximum rainfall intensity of 7.6 mm/hr). Runoff hydrographs of the four sites can be found in Figure 20. For all four events, the TSSR watershed exhibited the highest peak runoff. TMAT and TSSR exhibited very similar hydrographs for all four storms, as did TNEF and TSNR. TNEF and TSNR produced much lower peaks than TMAT and TSSR. TSNR did not respond at all to 3.2 cm of rain on May 20, 2005.

Peak runoff for TSSR[1] (5.1 ha watershed) was twice that of any other watershed. In response to 4.19 cm of rain on November 29, 2005, TSSR responded with a peak runoff of 8.2 mm/hr, which was three times greater than TMAT, TNEF and TSNR. According to the straight line separation results, the runoff ratio for this storm was 1.03 when computed for the watershed area of 5.1 acres. It rained a total of 4.19 cm and the total runoff was 4.30 cm, which indicated that the watershed was receiving water from unknown sources or beyond the watershed boundary. It is hypothesized that the November 29, 2005 event was the event that resulted in a breach in the eastern diversion ditch, explaining runoff ratio greater than 1. At the end of the data collection, it was determined that the additional 7.4 ha was affecting the stormflow response and total runoff of the TSSR site. As a result, stormflow characteristics for storms occurring prior to the November 29, 2005 event are reported for TSSR[1] (5.1 ha) and results for this event and all events after it are reported for TSSR[2], which has a watershed area of 12.5 ha.

Hydrologic response characteristics generated by the straight line hydrograph separation method were quite different from site to site. Hydrologic response characteristics for this study include total direct runoff, runoff ratio and peak direct runoff. No inferential statistics were calculated due to the small data set, as well as the large amount of missing data. Descriptive statistics, however, were generated for each site for comparative purposes and to characterize the response of each watershed.

The average direct runoff from the four watersheds for events occurring during this study was 12.15 (s.e.= 4.02, n=11) mm at TMAT, 5.25 (s.e.= 2.69, n=13) mm at TNEF, 2.82 (s.e.= 1.92, n=10) mm at TSNR and 12.28 (s.e.= 2.79, n=11) mm at the TSSR watershed (Table 4). Interestingly, the TSNR watershed, a mined watershed, exhibited the lowest total direct runoff of all of the sites, even less than the reference forested site, TNEF. TMAT and the TSSR sites exceeded TNEF and the TMAT sites in total runoff in all but two storms in this data set. Similarly, runoff ratios were much higher at TMAT and the TSSR site. The average runoff ratios at TMAT and TSSR were 0.24 (s.e.= 0.44, n=11) and 0.30

(s.e.= 0.50, n=11), respectively. Likewise, TSNR had the lowest average runoff ratio at 0.07 (s.e.= 0.27, n=10) where TNEF had a 0.09 (s.e.= 0.29, n=13) runoff ratio (Table 4). It is no surprise that the peak stormflow values followed a similar trend, where average peak stormflow was highest at TSSR at 2.36 mm/hr (s.e.= 1.27, n=11), followed by 1.70 mm/hr (s.e.= 1.61, n=11) at TMAT (Table 5). The peak average stormflow values at TNEF and TSNR were 0.85 mm/hr (s.e.= 1.19, n=13) and 0.67 mm/hr (s.e.= 0.96, n=10) respectively. The hydrologic response statistics suggest that the TMAT and TSSR have a similar flashy behavior when compared to the TNEF and TSNR, which exhibit a more dampened hydrologic response.

Soil infiltration capacity influences stormflow response and the amount of new water produced in a storm event. Soil infiltration capacity is the maximum infiltration rate of the soil assuming ponded water conditions on the soil surface (Negley 2000). At all sites, soil infiltration rates were highly variable from plot to plot. TNEF, the forested watershed, had by far the greatest infiltration capacity. All three mined sites (TSNR, TMAT and TSSR) exhibited much lower infiltration capacities than TNEF. At TMAT, all three of the infiltration plots had a cumulative depth of water infiltrated of less than 3 mm in one hour. TSNR exceeded both TMAT and TSSR in cumulative depth of infiltration, where two of the three plots were above 20 mm. Two of the three plots on TSSR had a cumulative depth of water infiltrated of less than 9 mm in one hour (Figures 21 and 22).

Steady-state soil infiltration capacity was estimated by the point at which the infiltration curve (cumulative depth of water infiltrated vs. time) becomes linear. Steady state soil infiltration capacities were again similar at TMAT and TSSR, exhibiting steady state infiltration capacities of less than 1 cm/hr (n=3). As expected, infiltration plots at TNEF yielded steady state infiltration capacities of nearly 50 cm/hr (n=3) (Negley 2000). The three infiltration experiments at TSNR yielded an average steady state infiltration capacity of approximately 3 cm/hr (n=3). For the 13 storms occurring between September 1, 2004 and June 1, 2006, rainfall intensity (maximum hourly rainfall, Tables 4 and 5) exceeded the infiltration capacities of TMAT and TSSR (Figures 21 and 22) in all 13 events. In contrast, at no point in any storm did rainfall intensity exceed the soil infiltration capacity of TNEF. The highest recorded rainfall intensity for the data set occurred on September 17, 2006 where it rained 2.28 cm in one hour, and even this amount did not exceed the soil infiltration capacity of TSNR.

The first storm in which the automatic samplers were deployed at each of the sites was on September 17, 2004. This storm was the remnants of Hurricane Ivan, and was the largest storm during the data collection period. The storm dropped 106.7 mm of rain on the gauge at TMAT in approximately 36 hours. Approximately 48 hourly samples were taken at each site and samples were selected for analysis of $\delta^{18}O$, silica concentrations and specific conductance levels. Results for this precipitation event provide very strong evidence of stormflow dilution/concentration according to $\delta^{18}O$, silica concentrations and specific conductance levels measured in the watersheds. The sampling effort appears to have provided adequate temporal coverage of this storm hydrograph with one exception. The sample set at $TSSR^1$ was incomplete, as the intake tube of the automatic sample was washed ashore and was not corrected until 18 hours later when fresh sample bottles were deployed for the second half of the sampling. Despite missing the hydrograph peak and the samples surrounding the peak, dilution at $TSSR^1$ during this event was still evident from those samples that were collected (Figure 8). It also should be mentioned that there was no stage recorder in place at TSNR for the September 17, 2006 event and the data series for ^{18}O, silica and specific conductance were all graphed using the TNEF hydrograph (Figure 7). After analyzing and comparing hydrographs throughout the study, it were determined that TNEF and TSNR, in most cases, had very similar hydrographs, therefore the TNEF hydrograph data was used for the lack of TSNR data.

Isotopic separation using ^{18}O employed samples from both ends (rising and recession limb) of the hydrograph to obtain the ^{18}O value that would be most representative of base flow. This approach assumes that samples from the rising or recession limb are appreciably different from the rainfall ^{18}O value for a particular storm. For the September 17, 2004 event, the rainfall ^{18}O value was -8.09 per mil. For this event, samples from the rising limb of TMAT, TSNR and $TSSR^1$ were very different from the rainfall value, measuring -6.3, -4.69, and -

4.56 per mil, respectively. Hence, separation was possible at these watersheds as the "baseflow/prestorm" values were noticeably different from the rainfall ^{18}O value. Several samples throughout the TNEF data series were noticeably different from the rainfall ^{18}O value, but the differences were greater towards the peak of the storm (Figure 6) indicating that dilution of $\delta^{18}O$ had in fact occurred. Another problem which occurred at all sites was that ^{18}O values of stream samples at peak flow were more dilute than the rainfall ^{18}O values. This discrepancy most likely resulted from having only one precipitation sample for the entire event, which was obtained at the $TSSR^1$ site. To remedy this problem, the samples with values more dilute than the rainfall ^{18}O values were considered to be 100% new water.

Using the isotopic separation technique and the ^{18}O data, it was determined that the new water at peak discharge for TMAT, TNEF and TSNR for the September 17, 2004 event was 100%, 52.6% and 100%, respectively (Table 7). Despite the sampling problem at $TSSR^1$, percent new water peak stormflow was assumed to be 100% new water because stream water ^{18}O values were more dilute than the ^{18}O precipitation value approximately six hours past peak discharge for the event. TSNR had the highest percentage of new water at 97.2% for this event. TMAT followed at 83.9% and TNEF at 51.1% new water. Total new water runoff depth for this same storm is available for only TMAT and TNEF as the TSNR was not equipped with a stage recorder at this time and because of sampling problems at TSSR. At TMAT and TSNR the total new water runoff depths were 53.9 mm and 18.5 mm respectively (Table 5).

The second hydrochemical tracer used for hydrograph separation was silica. As with the ^{18}O data series, silica concentrations of samples from both ends (rising and recession limb) of the hydrograph were examined to obtain a value that would be most representative of baseflow and to determine if hydrograph separation was possible with the silica data. Silica concentrations of samples from both the rising limb and recession limb at all sites were appreciably different from the of rainfall sample (0.12 mg/L). When examining the silica data set, it was obvious that a dilution of stream water silica concentrations occurred near peak flow at all sites where data were available (Figures 5-8). At all sites, samples from the rising limb were most different from the rainfall silica concentrations. Silica concentration of samples from the rising limbs at TMAT, TNEF, and TSNR measured 2.79, 6.84, and 9.06 mg/L respectively. At TSSR[1], a sample on the recession limb that had a silica concentration of 4.70 mg/L was most different from the rainfall silica concentration. Unlike the ^{18}O data set, no stream silica concentrations were more dilute than rainfall silica concentrations, thus suggesting that streamflow was always a mix of new and old water.

Using the silica data set to separate the hydrograph resulted in different new water percentages than the ^{18}O data. According to the silica data, TNEF had the highest percent of new water at peak discharge at 53.9%, followed by TMAT at 50.5% and finally TSNR at 27.7% (Table 8). These results are in stark contrast to the ^{18}O data, in which TMAT and TSNR had 100% new water at peak discharge.

Despite the differences between sites in percent new water at peak discharge for the silica data, the total percentages of new water for the entire storm were very similar for each of the sites. Interestingly, the percent of new water of total storm runoff was 28.1% at TMAT, 29.6% at TNEF, and 28.9% at TSNR, which is essentially the same for each watershed (Table 7). Because of the problems mentioned earlier about TSSR[1] and TSNR, total new water runoff depth could only be computed for TMAT and TNEF and were 18.0 mm and 10.7 mm respectively (Table 6). After observing such differences in the new water statistic between ^{18}O and silica data, the specific conductance data were useful for comparison purposes.

The time series of specific conductance data for the September 17, 2004 event was also used to separate stormflow into new and old water. Sklash (1976) found specific conductance a useful measurement in detecting stream water dilution from a precipitation event (Figures 5-8). The specific conductance is a quick, easy and accurate laboratory analyses; therefore, it was also used in this study. Upon examination of the conductance data set for the September 17th event, it was obvious that dilution occurred throughout the storm. Rainfall conductance was measured and found to be 5.6 µs/cm. At TSSR[1] and TSNR, recession limb conductance values were found to have the greatest difference from rainfall at 57.8 and 513.2 µs/cm respectively. Although conductance values at both ends of the hydrograph were very similar at TMAT and TNEF, the rising limb offered the values with the greatest difference at 69.7 and 44.4 µs/cm respectively.

Despite having trends similar to the ^{18}O data, the new water estimates for the specific conductance time series were quite different for the September 2004 event. Like the ^{18}O data series, TMAT and TSNR had the greatest percent new water at peak discharge at 69.6 %, and 67.5 % respectively followed by 19.8% at TNEF (Table 8). Total new water percent of total stormflow and the total new water runoff depth followed similar patterns to the ^{18}O data as well. The new water percent of total stormflow was greatest at TNSR at 59.2 %, compared to 56.4 % at TMAT and 13.8 % at TNEF (Table 7). Total new water runoff depths were calculated for only TMAT and TNEF watersheds and were found to be 36.2 mm and 5.0 mm respectively. The ^{18}O, silica and specific conductance data series showed obvious dilutions in stormflow making separation possible for this event. However, new water estimations generated by these three different data sets differed and no clear conclusions could be made about each watershed from this one storm event.

The April 22, 2006 storm event dropped approximately 39.4 mm of rain in an 18-hour period with the maximum intensity of 5.08 mm/hr. The magnitude and intensity of this storm was much less than the September 17, 2004 event. The shapes of the hydrographs for each site were also different from the first event in that there were three distinct peaks recorded at each site. Again, automatic samplers were deployed and were programmed to take hourly samples for a continuous 48-hour period. This sampling method again required that additional bottles be placed in at each site after the initial 24 bottles were filled to capacity. To prevent the sampling mishap that occurred at $TSSR^2$ on the September 17, 2006 event, the intake tube (of the automatic water sampler) was anchored down at each site with large rocks to ensure that the tube would stay submerged in the stream water throughout the storm. Unlike the first event, no samples were missed at any site during the entire 48-hour sampling period, although the stage recorders at $TSSR^2$ and TSNR stopped recording stage levels on April 14, 2006 due to memory problems. The hydrographs for $TSSR^2$ and TSNR were therefore unavailable for data analysis and interpretation for this event. After analyzing the entire 13 storm data set from September 1, 2004 to June 1, 2006, it was decided that TMAT and $TSSR^2$ showed similar stormflow responses to these storms. Likewise, TNEF and TSNR showed similar stormflow responses. Because of these results, the time series data for $TSSR^2$ was plotted with the TMAT hydrograph, whereas TSNR was plotted over the TNEF stormflow hydrograph (Figures 9-12). Hence, the new water statistics calculated for the watersheds $TSSR^2$ and TSNR were based upon the stormflow discharge levels of TMAT and TNEF, respectively.

Obvious dilution (or concentration) trends were apparent in the data and graphs for ^{18}O, silica and specific conductance data series for the April 22, 2006 event at each site. (Figures 9-12). The ^{18}O time series data were analyzed to determine if stream water ^{18}O values were considerably different enough from the rainfall ^{18}O

value so that the isotopic separation technique could be used. Stream water values at TMAT, TSNR and TSSR^2 were all greater than the rainfall ^{18}O value of -6.64 per mil. At all sites, stream water values became more dilute, thus making separation possible. At TNEF, pre-storm ^{18}O stream water values were more dilute than that of precipitation values. Because of this result, stream water ^{18}O values became more concentrated around peak flow indicating that the precipitation enriched stream water ^{18}O values, thus making separation with this data possible. Timing of greatest dilution in stream water ^{18}O values corresponded to the last of the three hydrograph peaks at TMAT, TSNR and TSSR^2, while timing of concentration in stream water ^{18}O values corresponded to the second peak at TNEF (Figures 9-12). Although dilution and/or concentration of stream water ^{18}O values were not obvious, at all of the hydrograph peaks, a general dilution/concentration in ^{18}O values was obvious making hydrograph separation possible.

The ^{18}O data for the April 22, 2006 event followed similar trends to the September 17, 2004 storm. TMAT and TSNR again had greater percent new water at peak discharge than TNEF. At peak discharge, new water at TMAT was 53.6%, compared to 48.8% at TSNR and 23.9% at TNEF (Table 8). TSSR^2 was an impressive 80.5% new water at peak discharge. As mentioned earlier, the April 22, 2006 event produced hydrographs with three distinct peaks. The timing of peak discharge differed among sites, so the greatest peak at each watershed (and the associated ^{18}O, silica and specific conductance value) reported here corresponds to the site specific peak discharge rather than a common peak. Despite the differences among sites, the percent new water of total runoff at $TSSR^2$ of 58.8% was similar to TMAT at 61.0%. The new water percent of total runoff was again lowest for TNEF at 21.5% and was 45.2% at TSNR (Table 7). Total new water runoff depth could only be reported for TMAT and TNEF, due to the problems with the stage recorders at TSNR and $TSSR^2$. The total new water runoff depth was again greater at TMAT with 8.83 mm than the 2.8 mm at TNEF.

Silica time series data for the April 22, 2006 event showed obvious stream water dilution of silica concentrations around the peak discharge of the event. The silica concentration of rainfall for this event measured 0.0156 mg/L. Stream water values ranged from 0.635 to 1.38 mg/L at TMAT, 0.80 to 2.34 mg/L at TNEF, 3.25 to 4.85 mg/L at TSNR and 0.10 to 2.64 mg/L at $TSSR^2$. For TNEF, TSNR and T $TSSR^2$, silica concentrations were greatest during the recession limb and hence "old water" values were taken from the recession limb. However, at TMAT, the rising limb offered the greatest silica values. The timing of dilutions in stream water silica concentrations was very similar for all of the sites. For the silica time series, stream water silica concentrations became dilute by the first of the three hydrograph peaks and remained dilute for the following two peaks and increased with time during the recession limb. The trends and timing of the silica time series data again made hydrograph separation possible.

New water statistics generated by the silica data were quite different for the April

22, 2006 event compared to the September 17, 2004 event. TMAT and TSSR^{2} exhibited the greatest percent of new water at peak discharge at 83.7% and 85.6%, respectively. The TNEF watershed had the highest percent of new water at peak discharge for the first event (47.6%) for the April 22, 2006. Like the first storm, the lowest percent new water at peak discharge of the four sites occurred at TSNR, which had 33.2% new water at peak discharge (Table 8). For the silica data set, the percent of total runoff being new water was an astonishing 93.2% at TMAT. The other sites had much lower results, with the percent new water of total runoff at TNEF, TSNR and TSSR^{2} measured as 44.4%, 20.1% and 59.0%, respectively (Table 7). The new water runoff depth for the silica data series was 13.5 mm at TMAT and 6.26 mm at TNEF.

The specific conductance data series for the April 22, 2006 event also exhibited stream water dilution around peak discharge. Conductance values ranged from 52.33 to 102.52 μs/cm at TMAT, 40.06 to 55.56 μs/cm at TNEF, 193.51 to 339.92 μs/cm at TSNR and 28.70 to 71.37 μs/cm at TSSR. All of these values are very different from the rainfall conductance value of 13.67 μs/cm. At TMAT and TNEF the lowest specific conductance value (greatest dilution) corresponded to the second hydrograph peak while at TSNR and TSSR^{2}, the lowest conductance value, corresponded to the third peak. Regardless of which peak, it was apparent that dilution of total ions in stream water occurred. The highest specific conductance values occurred during the recession limb at TNEF, TSNR and TSSR^{2}. At TMAT, the greatest stream water conductance value occurred during the rising limb of the hydrograph.

New water statistics for April 22, 2006 followed similar trends of those from the September 17, 2004 event for the specific conductance data set. $TSSR^2$ and TMAT exhibited the greatest percent new water at peak discharge at 68.1% and 56.5%, respectively (Table 8). TNEF and TSNR again responded with similar peak percentages and were much lower than the peak percentages at TMAT and TSNR. Percent new water at peak discharge was lowest at TNEF at 34.5% and was 42.4% at TSNR. The new water percentages of total runoff were again similar, higher at TMAT and $TSSR^2$, substantially lower at TNEF and TSNR. New water percentages of total runoff were 50.8% at TMAT, 47.8% at $TSSR^2$, 27.6% at TSNR and, again lowest, 14.5% at TNEF (Table 7). Total new water depths were computed for the TMAT and TNEF watersheds and were 7.35 mm and 2.05 mm respectively for the specific conductance data set. The data sets for ^{18}O, silica and specific conductance for the April 22, 2006 event, like the stormflow response statistics, suggested that TMAT and $TSSR^2$ sites responded similarly, as did the TNEF and TSNR sites.

The final storm event that was sampled for hydroisotopic and hydrochemical separation occurred on May 14, 2006. This storm event dropped approximately 4.63 cm of rain over a 15-hour period with a maximum rainfall intensity of 7.62 mm/hr. Unlike the first two events, no sampling or stage recorder problems occurred during this event. Hence, a complete new water data set was generated for this storm. The majority of precipitation for this event occurred in one large 4 hour pulse, thus generating one peak in the hydrograph of each site. As a consequence, interpretation and analysis of the hydrochemical and hydroisotopic data sets were much more straightforward than the previous storms. For this storm, the automatic water samplers were programmed to sample every two hours. Although hourly resolution was sacrificed, the length of sampling time was not and remained 48 hours, which was sufficient to capture the rising limbs, peaks and recession limbs of the hydrographs at all sites. We determined from this study that two hour samples were adequate and efficient for zero order watersheds.

The time series of stream water ^{18}O values were analyzed at each site for dilution and/or concentration trends for the May 14, 2006 event. At TMAT, TSNR and TSSR^2 dilution of stream water ^{18}O values was apparent and corresponded to the time of the peak discharge. At TNEF, a concentration in ^{18}O values occurred around the peak, where rising limb and recession limb values were lower than the rainfall ^{18}O value of -7.44 per mil. Like the September 17, 2006 event, ^{18}O stream water values became more dilute than the rainfall ^{18}O value. Again, when the rainfall ^{18}O value was exceeded, the new water portion of streamflow was assumed to be 100%. Old water ^{18}O values were taken from the rising limb of the storm hydrograph at TNEF, TSNR and TSSR^2 with old water ^{18}O values of -9.03, -6.24 and -5.94 per mil, respectively. The old water ^{18}O value at TMAT was taken from the recession limb and measured -7.21 per mil. Despite the problem of a few stream water ^{18}O values being more dilute than rainfall, the hydroisotopic hydrograph separation technique was again used to generate new water statistics from the ^{18}O data set for each of the four sites.

^{18}O new water data for the May 14, 2006 event followed a much different pattern than the previous storms. The TNEF watershed had a much higher percentage of new water at peak flow than the preceeding two storms. Percent new water at peak discharge was 87.8% at TNEF for this event, compared to 52.6% and 23.9% for the September 17, 2004 and April 22, 2006 events (Table 8). Notably, TNEF had the highest percent new water at peak discharge of any of the four sites. The percent new water at peak discharge at TMAT also differed substantially from the first two events with 35.2% new water at peak flow. TSNR and TSSR^2 responded very similarly in both percent new water at peak discharge and percent new water of total runoff. Percent new water at peak discharge was 60.8% at TNSR and 57.6% at TSSR^2 (Table 8). Despite the large percentage of new water at peak discharge at the TNEF site, the percent new water of total runoff at TNEF was 52.2%. TSNR had the greatest percent new water of total runoff at 60.8%, followed by TSSR^2 at 57.7% and finally TMAT at 31.2% (Table 7). The runoff depths at the TSSR site were found to be higher than the rest of the sites for the four storm data set mentioned above (Figure 17-20). TNEF was next at 8.3 mm of total new water runoff, followed by 4.95 mm at TMAT and, finally, 3.07 mm at TSNR. Unfortunately, this is the only storm that total new water runoff depth is available for all stations, thus no comparison can be made to the other storms.

Stream water dilution was observed in the silica data set for the May 14, 2006 event, but was not as pronounced as the previous storms. However, the time series data for silica did exhibit a substantial difference between rainfall silica concentrations and stream water silica values to allow the hydrochemical separation. Stream water silica values ranged from 0.12 to 2.87 mg/L at TMAT, 0.05 to 2.41 mg/L at TNEF, 0.20 to 4.26 mg/L at TSNR, and 0.09 to 3.66 mg/L at $TSSR^2$. Precipitation from the May 14, 2006 event had a silica concentration of 0.006 mg/L. Old water silica values (highest silica concentrations) occurred after peak discharge and during the recession limb at TNEF, TSNR and TSSR. Conversely, highest silica concentrations were found during the rising limb of the storm hydrograph. At TMAT, TNEF and $TSSR^2$ the most dilute silica concentrations corresponded to the time of peak discharge, thus suggesting dilution. At TSNR, the most dilute sample occurred during a small peak in the rising limb, however, a dilution trend occurred again at the peak discharge for the event.

Like the ^{18}O new water data for the May 14, 2006 event, the silica new water results differed from the trends apparent in the first two storms. Again, TNEF showed the most notable change from other storms, where the new water percent at peak flow was 81.3% for this event as compared to 53.4% and 47.6% for the first two events (Table 8). The silica data for the TMAT watershed produced a drastically different new water percentage at peak discharge from the ^{18}O time series. For the silica data the new water percentage at peak discharge at TMAT was 93.6% as compared to the 35.1% for the ^{18}O time series for the May 14, 2006 event. $TSSR^2$ also produced a very high new water percentage at peak discharge at 97.8% while TSNR again produced the lowest percentage at 29.5%. The percent new water of total discharge, like the previous event for the silica tracer, was highest at TMAT and $TSSR^2$ at 94.1% and 82.9%, respectively (Table 7). Despite the large new water percentage at peak discharge for TNEF, the percent new water of total discharge was much lower and more comparable to the first two storms at 58.8%. Again, TSNR exhibited the lowest percent new water of total discharge at 23.5%. Total new water runoff depth was again much higher at $TSSR^2$ due to the comparably higher total runoff amounts. At $TSSR^2$, the total new runoff depth was 22.83 mm, which was still 8 mm greater than any other watershed. Total new water runoff depths were 14.9 mm at TMAT, 9.32 mm at TNEF and finally 1.19 mm at TSNR for the silica time series (Table 6). The discrepancies in new water statistics between the ^{18}O time series and the silica time series for the May 14, 2006 event were alarming and interesting and are addressed later in the paper.

The specific conductance time series data for the May 14, 2006 event again exhibited both dilution and/or concentration trends sufficient for hydrograph separation. At TMAT, TSNR and $TSSR^2$ dilution trends were apparent in the specific conductance data, being most dilute at peak discharge. At TNEF, a concentration occurred in the specific conductance time series where stream water had the greatest conductance value at peak flow. Specific conductance values ranged from 51.0 to 137.5 µs/cm at TMAT, 46.3 to 56.9 µs/cm at TNEF, 183.1 to 324.3 µs/cm at TSNR and 18.9 to 87.8 µs/cm at TSSR[2]. The conductance value of rainfall for the May 14, 2006 event was 12.9 µs/cm, and was markedly different enough from all of the stream water samples for separation purposes. Samples used to represent baseflow occurred during the rising limb at TMAT and TNEF and during the recession limb at TSNR and TSSR.

Despite the many ion sources that could affect specific conductance within a watershed, this data set produced the most consistent results for the three storm data set. That is, for both new water percentage at peak discharge and new water percentages of total runoff, TMAT and TSSR[2] exhibited the highest percentages, TNEF consistently had the lowest percentages and TSNR fell in between. The new water percentage at peak discharge was 63.4% at TMAT, 16.6% at TNEF, 56.9% at TSNR and 91.9% at TSSR for the specific conductance time series (Table 8). The new water percentage of total runoff followed similar trends. TMAT and TSSR[2], which seemed to respond similarly throughout the study, again had the greatest percent new water of total runoff at 65.1% and 75.0%, respectively. As stated earlier, TNEF had the lowest percent new water of total runoff at 11.4% compared to 40.0% at TSNR (Table 7). Total new runoff depth was again higher at the TSSR[2] site for the May 14, 2006 event measuring 20.4 mm. Total new water runoff depths at the TMAT, TNEF and TSNR were 10.3 mm, 1.8 mm and 2.0 mm, respectively (Table 6). Data trends and discrepancies are summarized and discussed in the following chapter.

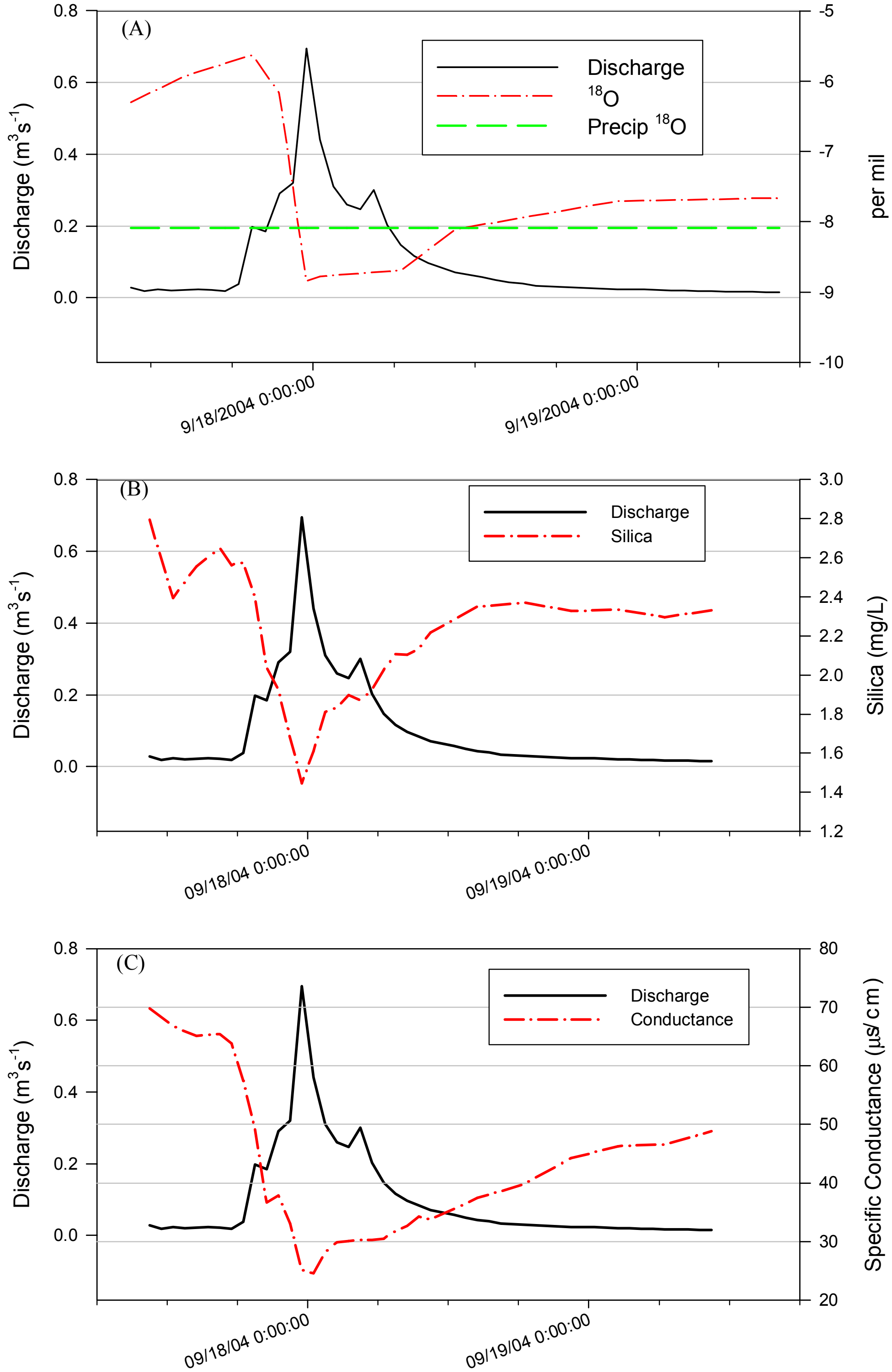


Figure 5. TMAT hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the September 17, 2004 storm event.

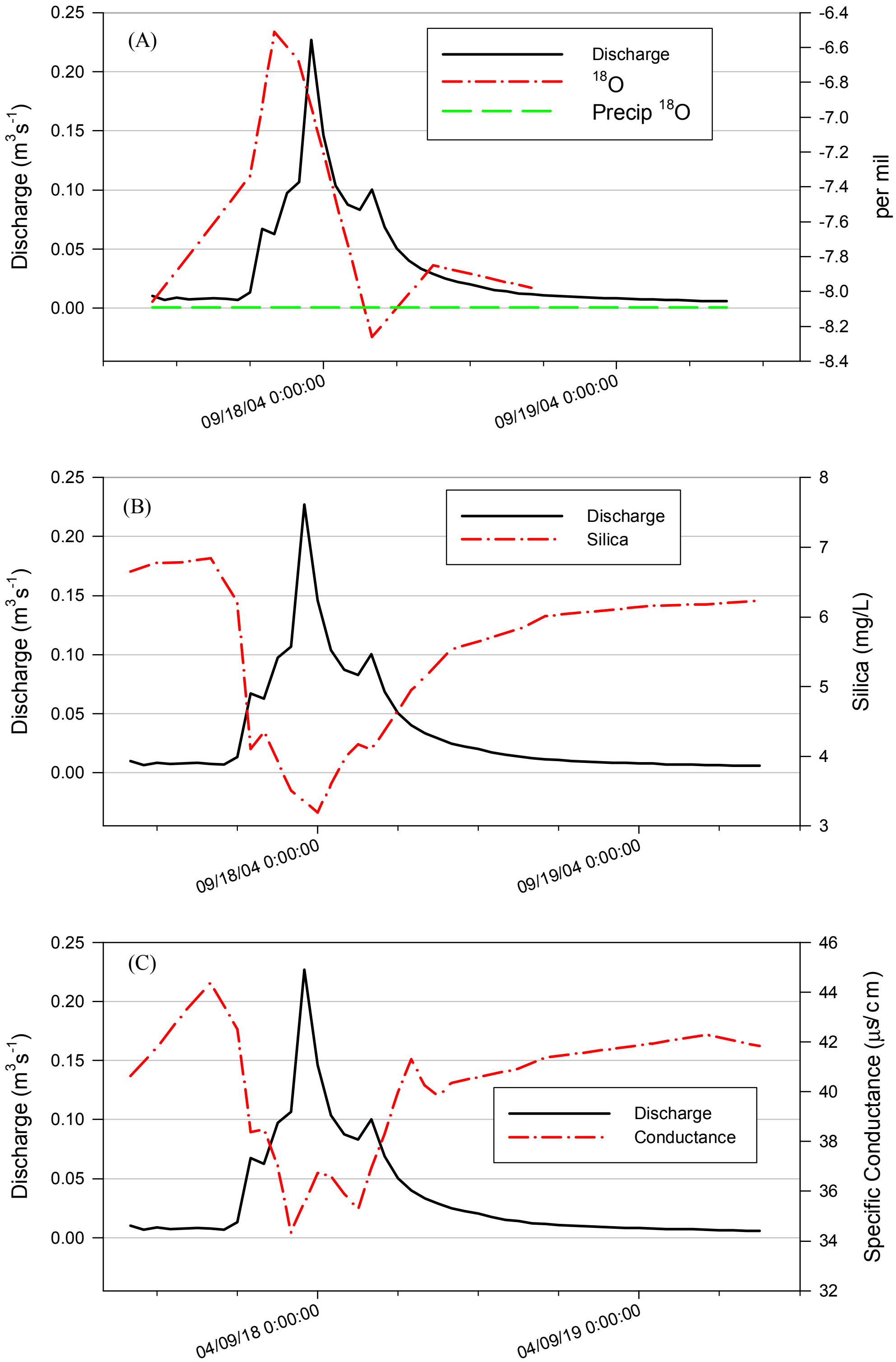


Figure 6. TNEF hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the September 17, 2004 storm event.

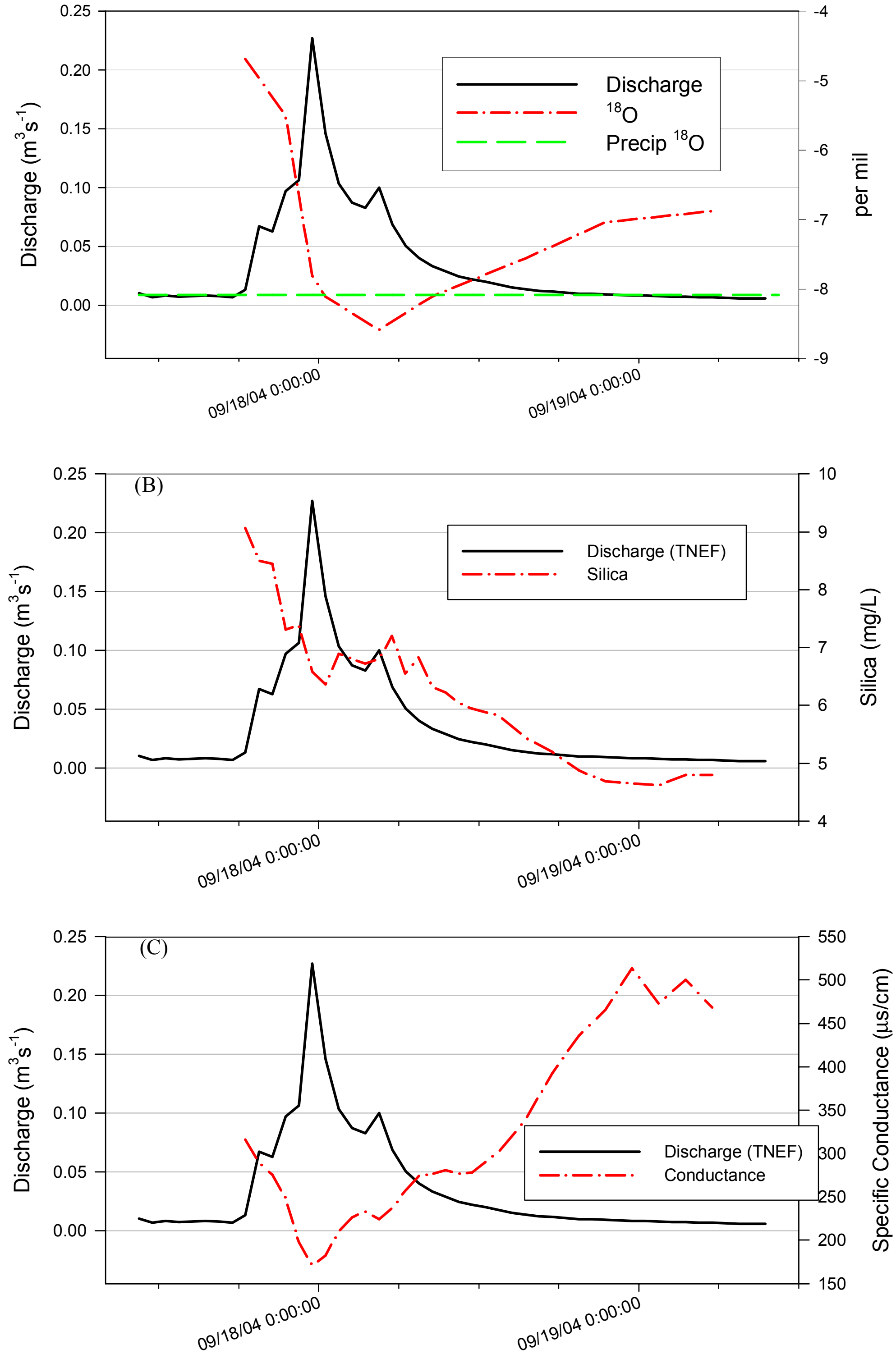


Figure 7. TSNR stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the September 17, 2004 storm event. (TNEF hydrograph is graphed as no flume was in place at TSNR at this date and TNEF and TSNR generally exhibit similar stormflow response).

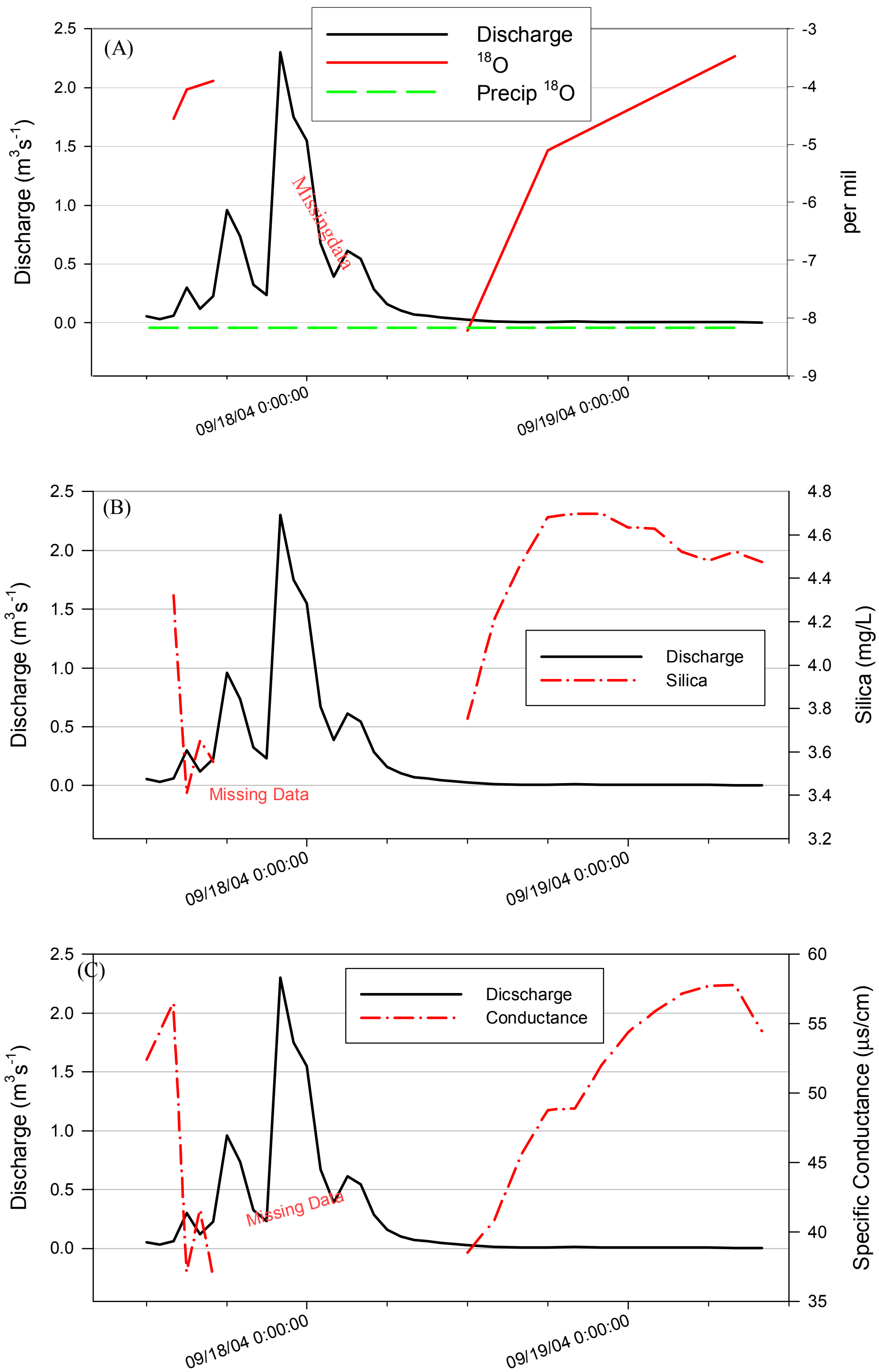


Figure 8. TSSR hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the September 17, 2004 storm event.

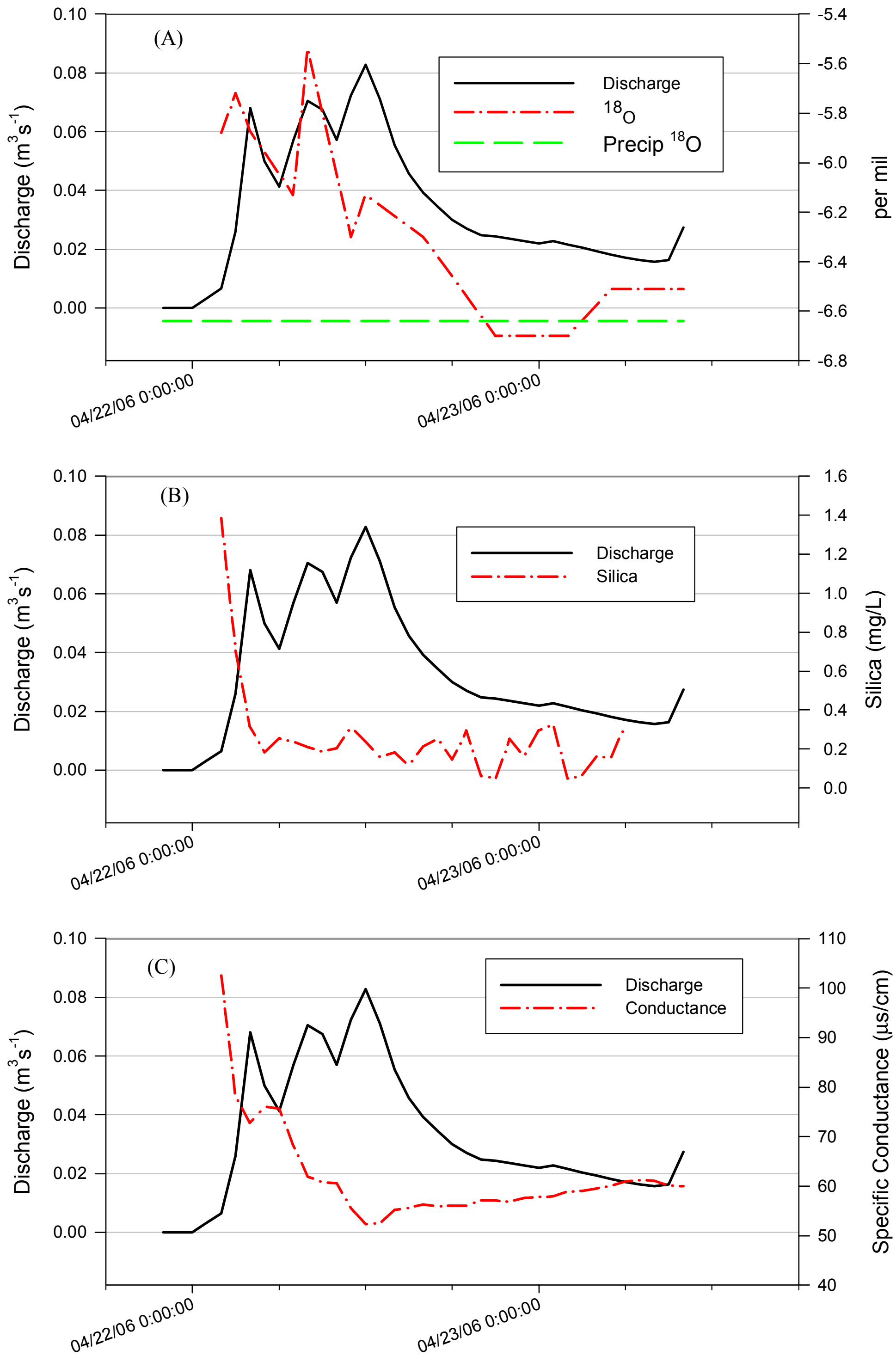


Figure 9. TMAT hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the April 22, 2006 storm event.

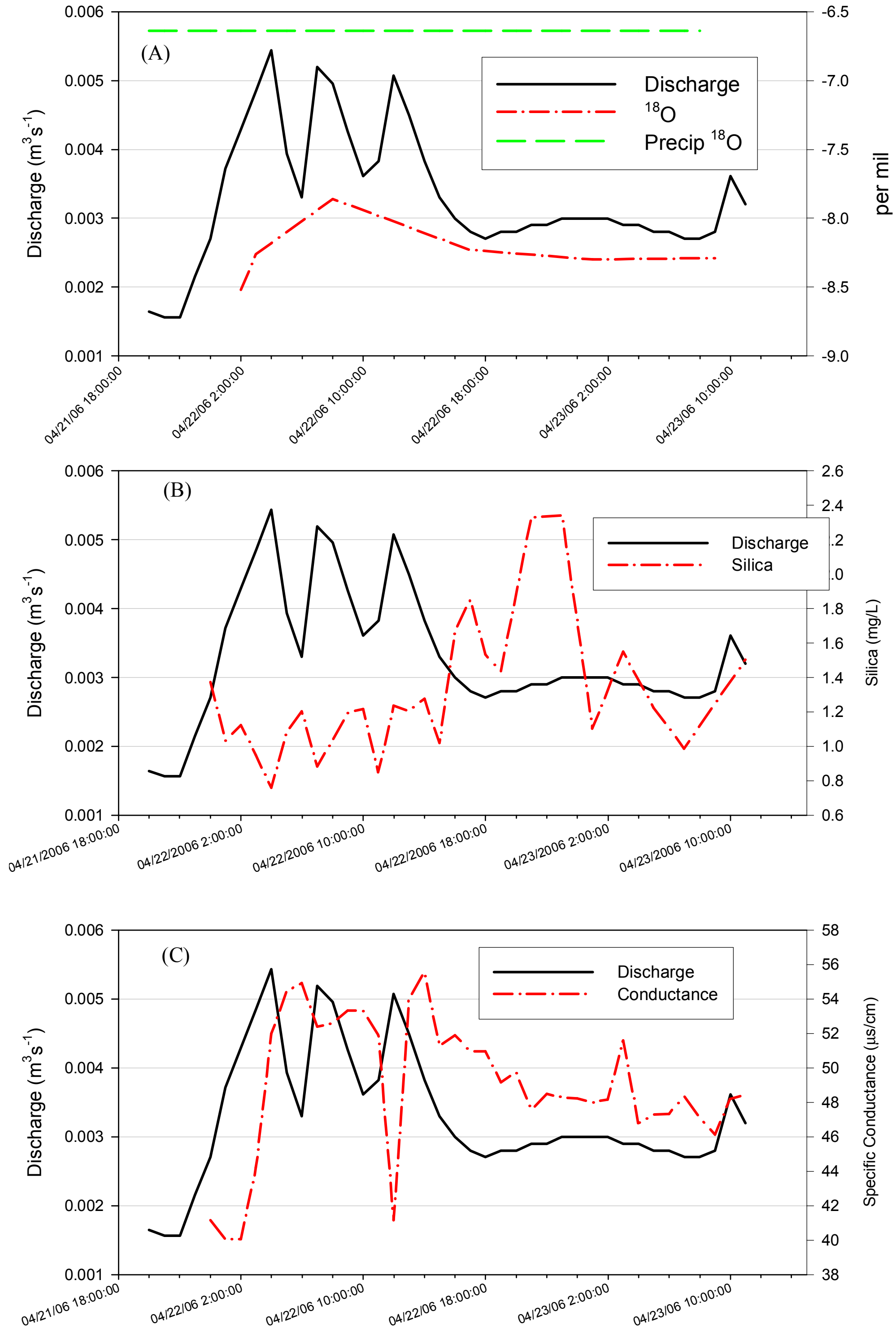


Figure 10. TNEF hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the April 22, 2006 storm event.

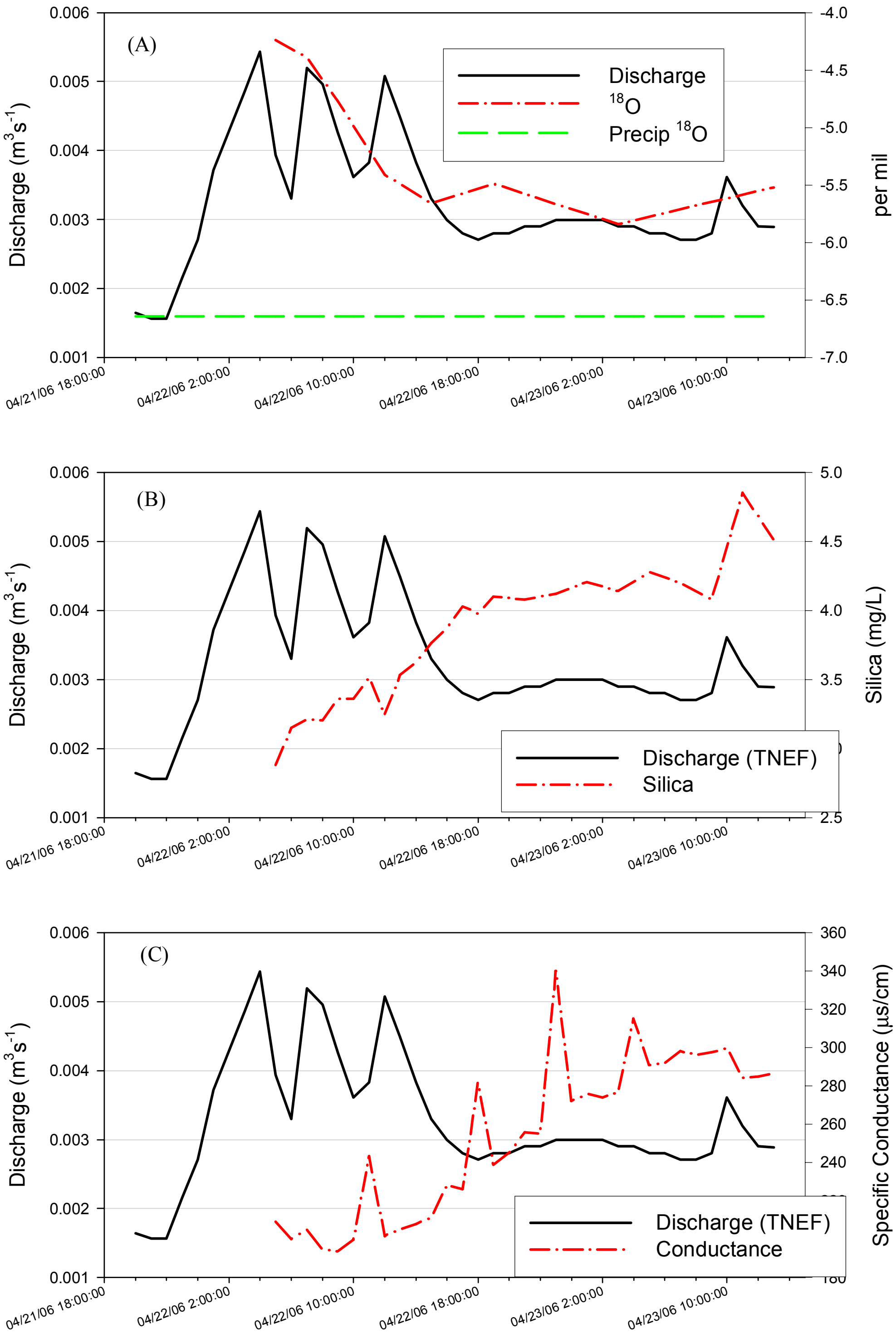


Figure 11. TSNR stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C), for the April 22, 2006 storm event. (TNEF hydrograph is graphed due to equipment problems at TSNR and TNEF and TSNR generally exhibit similar stormflow response).

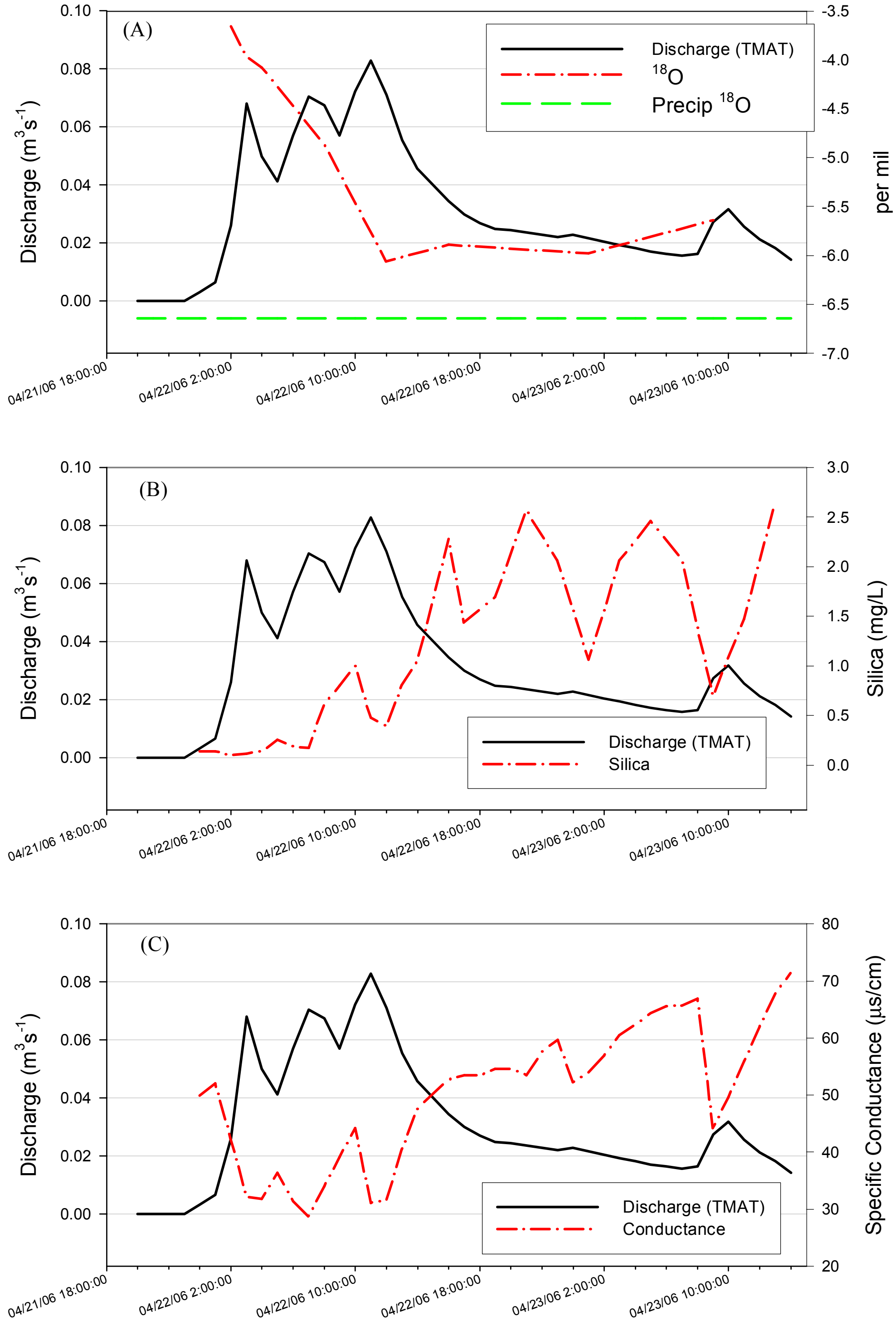


Figure 12. TSSR stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C), for the April 22, 2006 storm event. (TMAT hydrograph is graphed due to equipment problems at TSSR where TMAT and TSSR generally exhibit similar stormflow response).

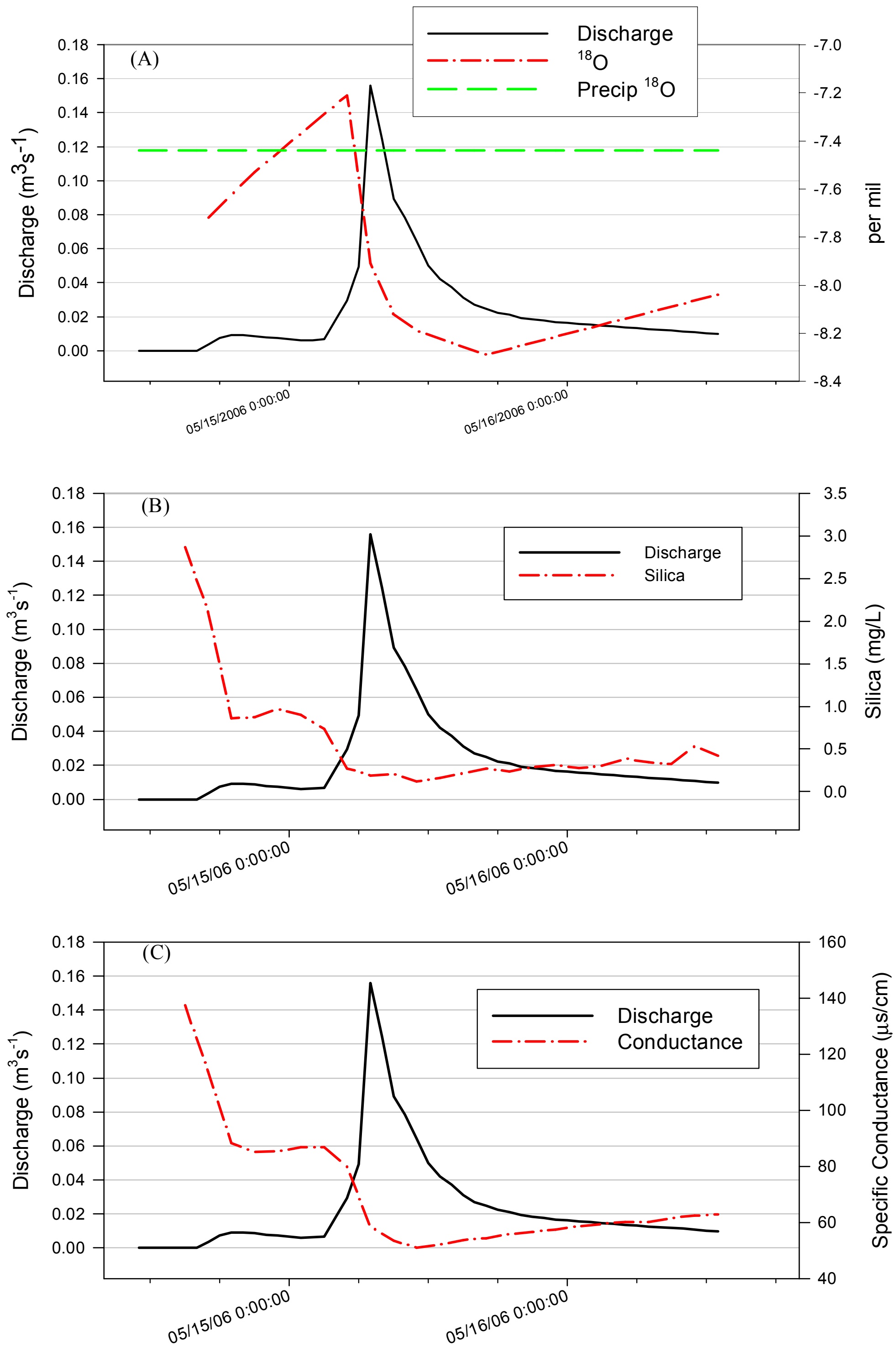


Figure 13. TMAT hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the May 14, 2006 storm event.

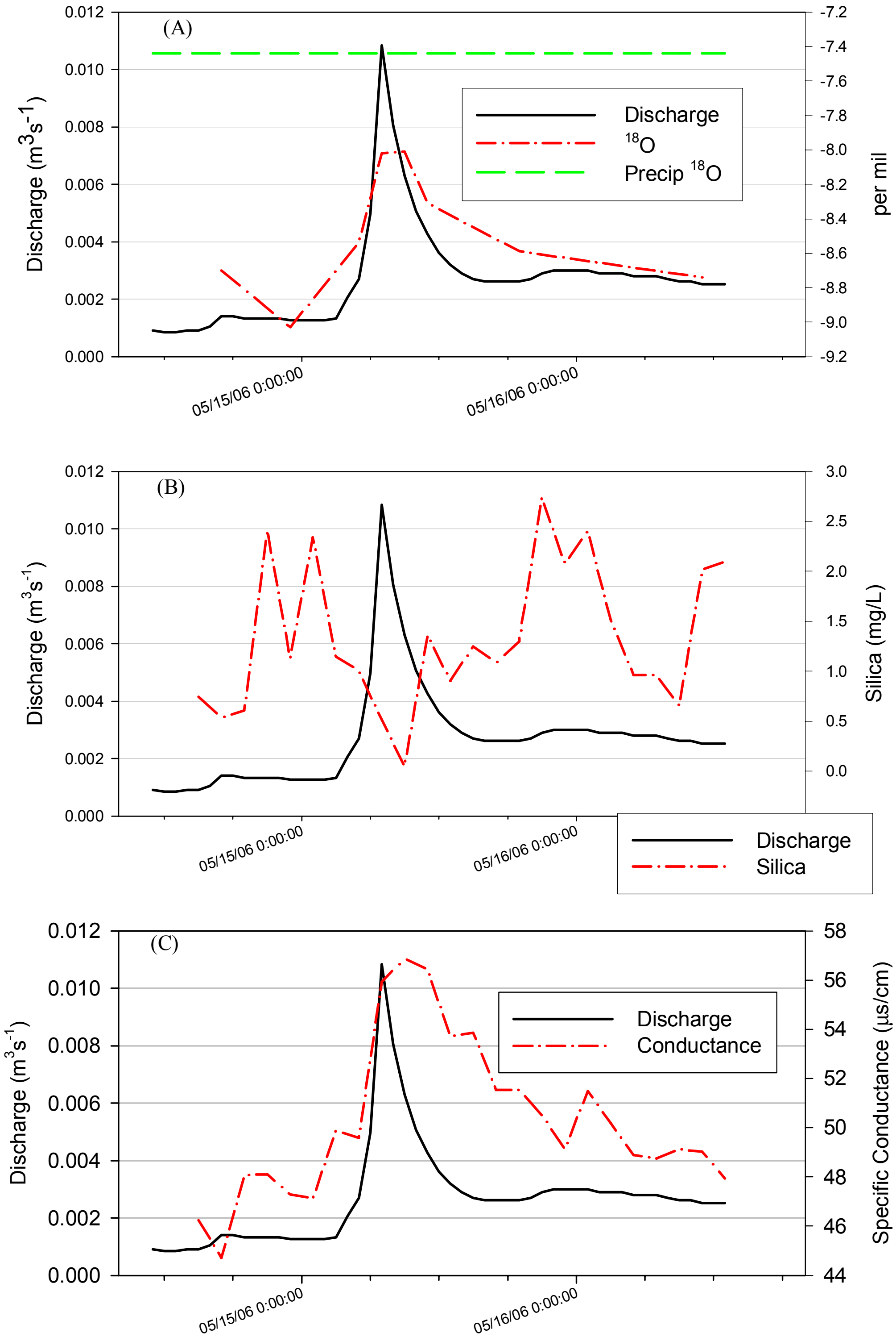


Figure 14. TNEF hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the May 14, 2006 storm event.

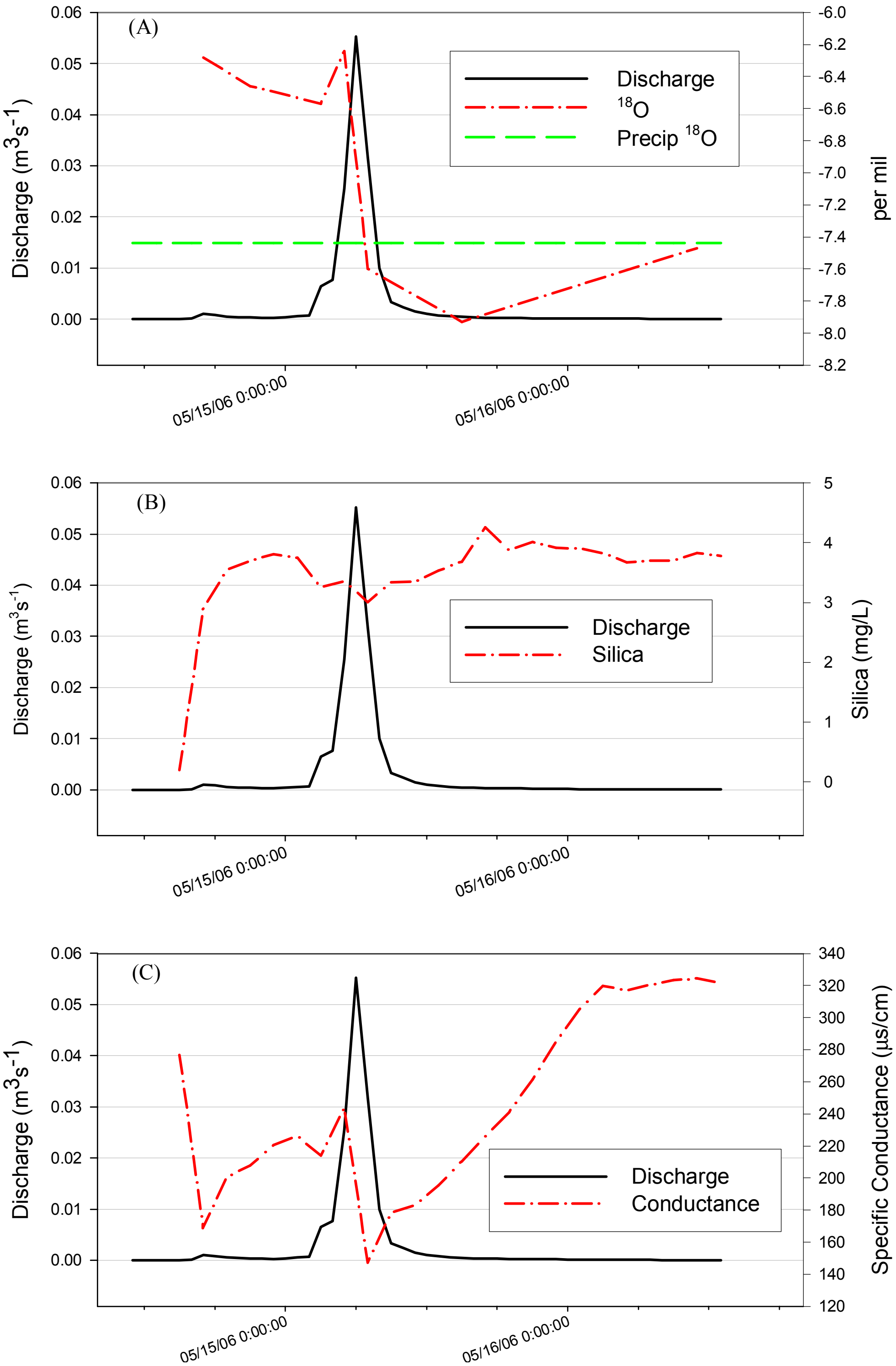


Figure 15. TSNR hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the May 14, 2006 storm event.

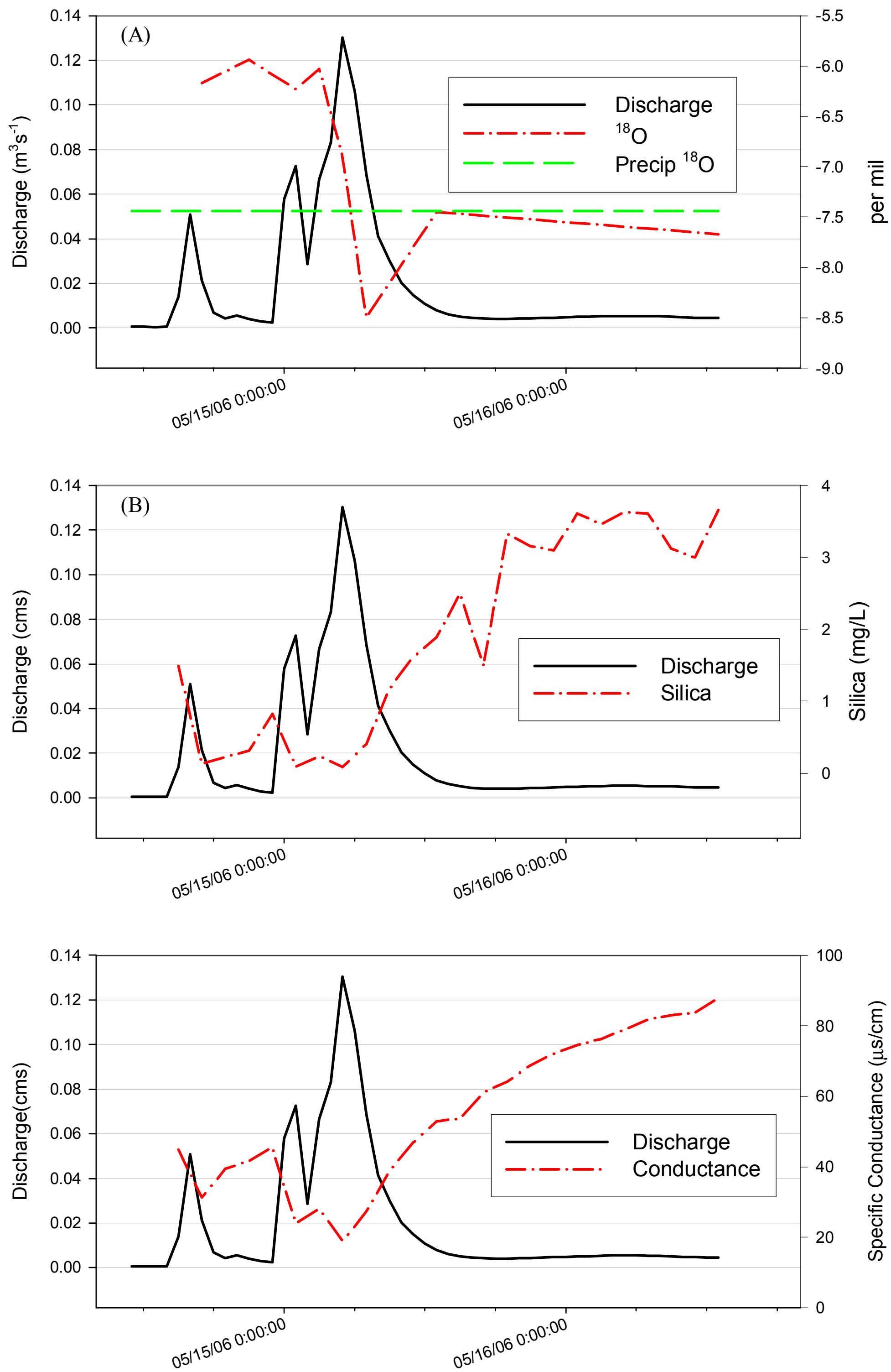


Figure 16. TSSR hydrograph and stream water values for ^{18}O isotope (A), silica (B) and specific conductance (C) for the May 14, 2006 storm event.

May 20, 2005 Runoff Hydrograph

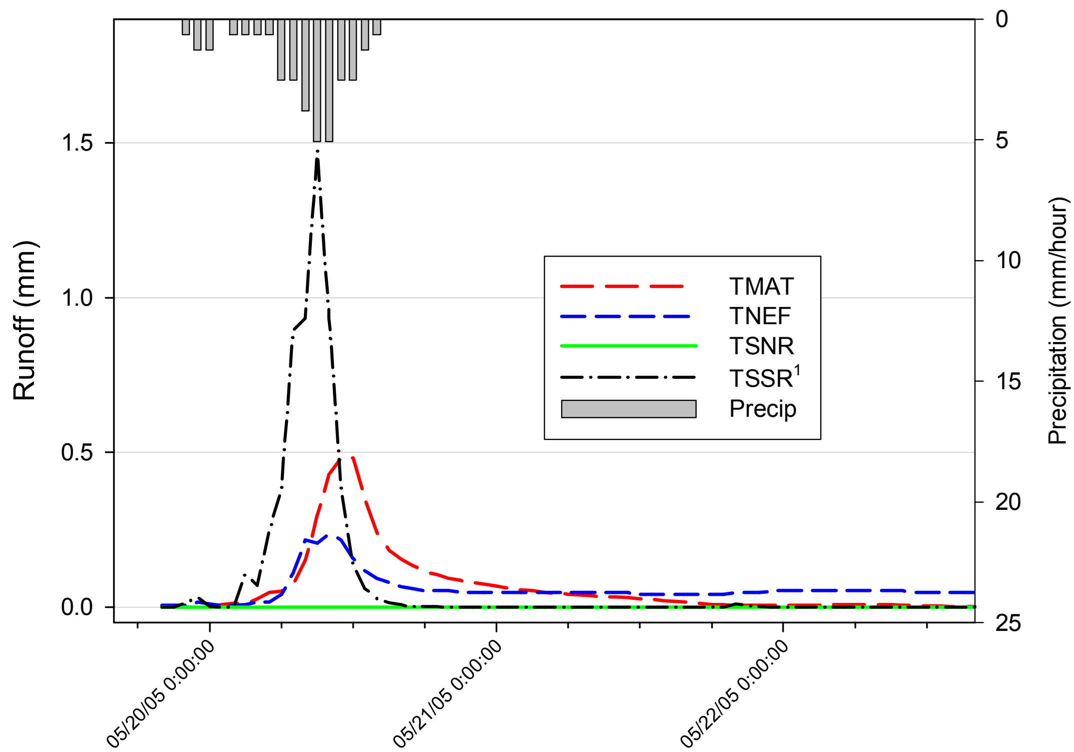


Figure 17. Runoff hydrographs (normalized by area) and hourly precipitation for the May 20, 2005 storm event at TMAT, TNEF, TSNR and TSSR[1].

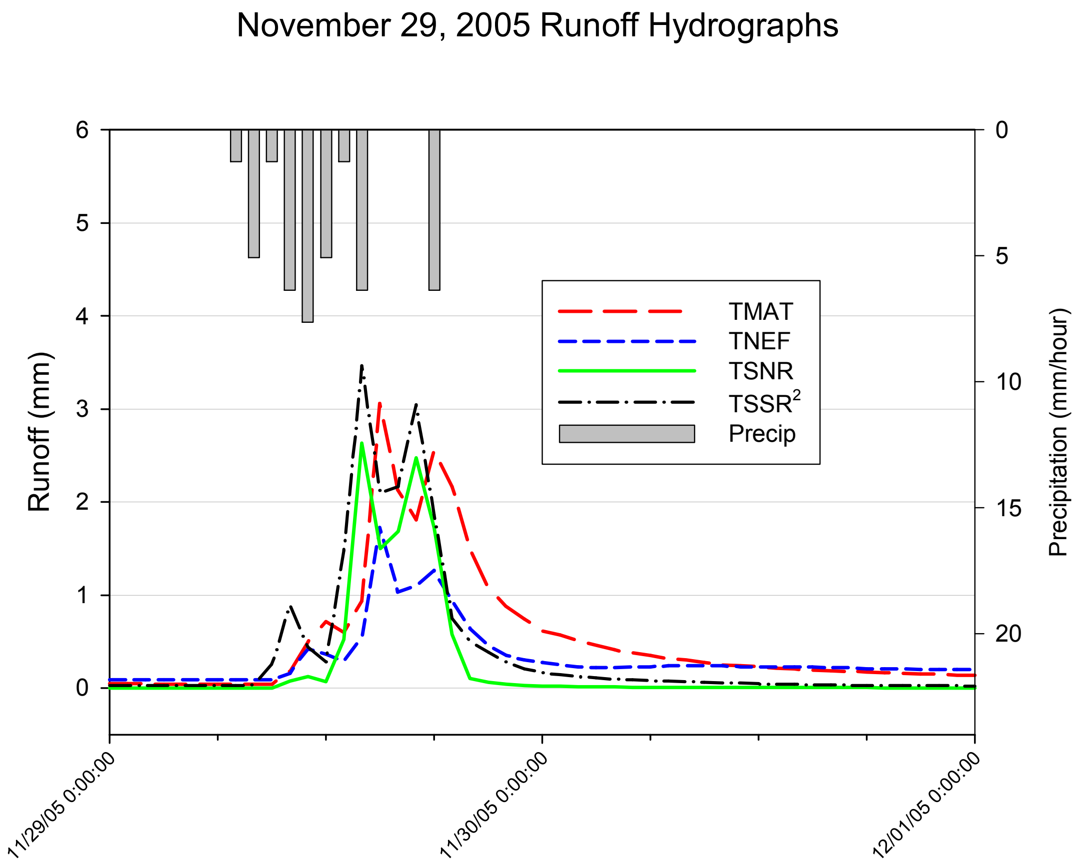


Figure 18. Runoff hydrographs (normalized by area) and hourly precipitation for the November 29, 2005 storm event at TMAT, TNEF, TSNR and TSSR^2.

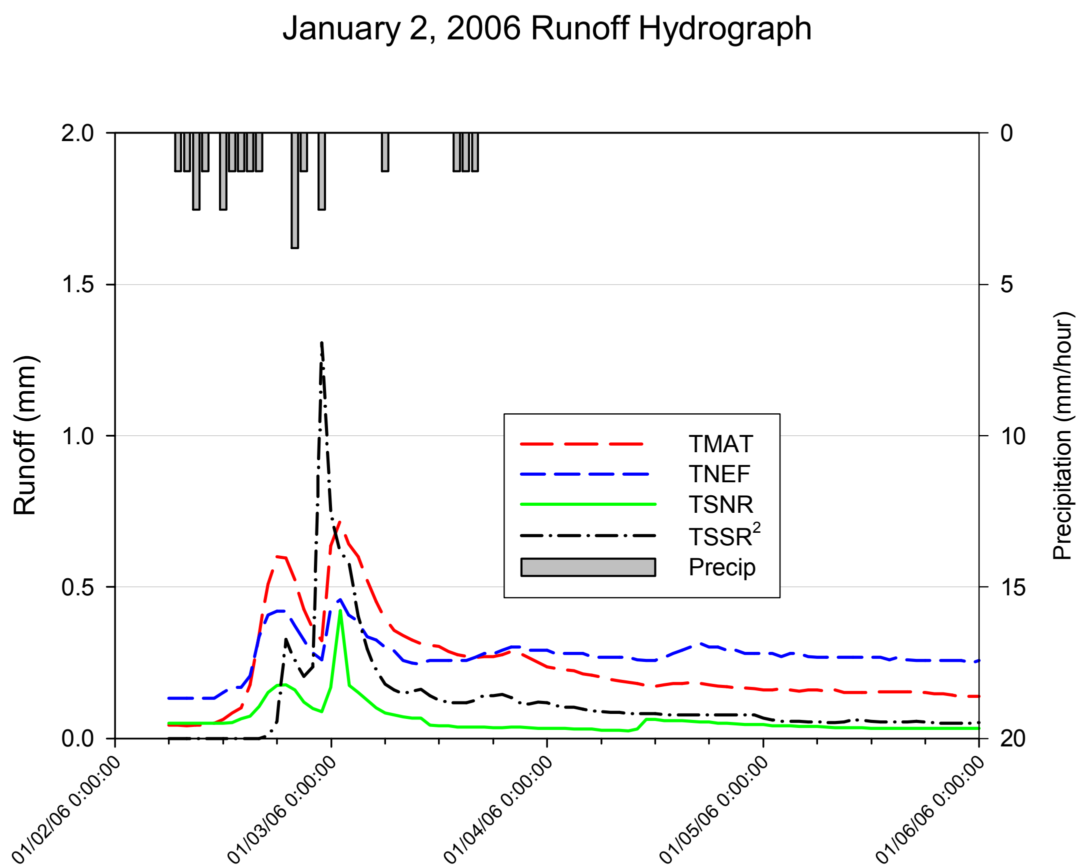


Figure 19. Runoff hydrographs (normalized by area) and hourly precipitation for the January 2, 2006 storm event at TMAT, TNEF, TSNR and $TSSR^2$.

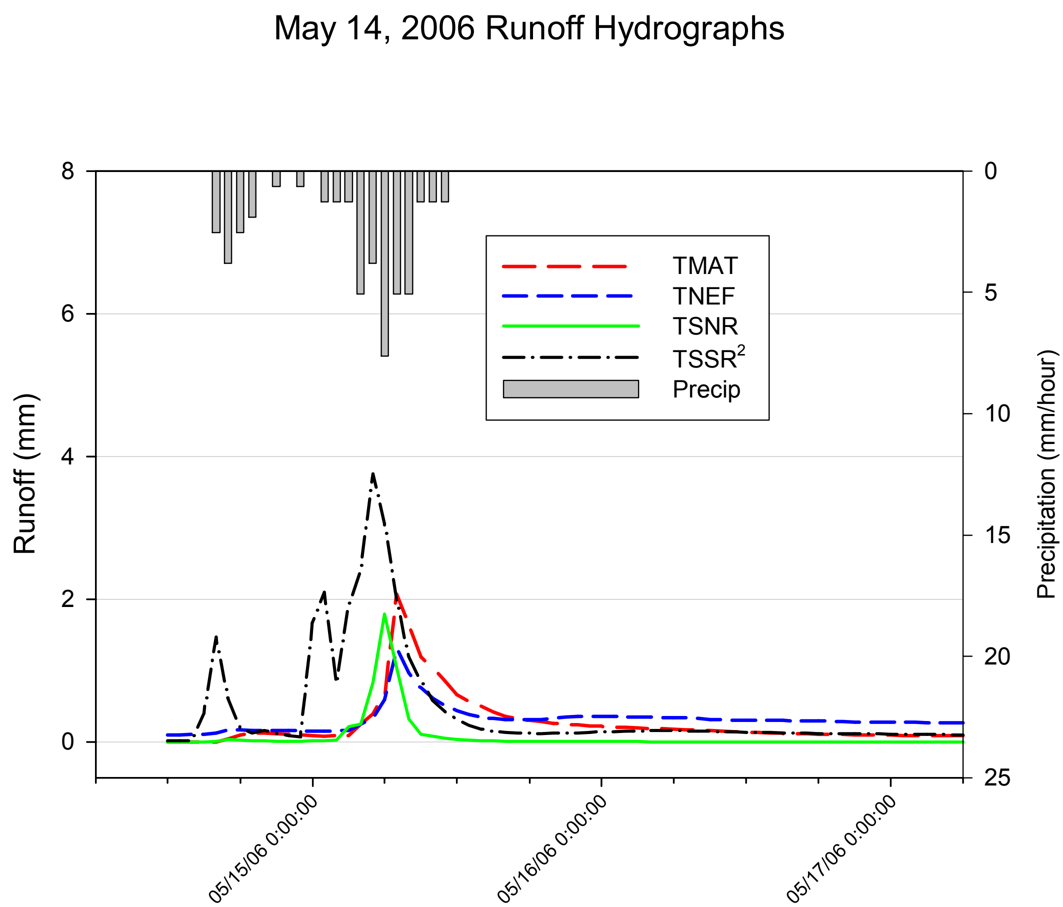


Figure 20. Runoff hydrographs (normalized by area) and hourly precipitation for the May 14, 2006 storm event at TMAT, TNEF, TSNR and $TSSR^2$.

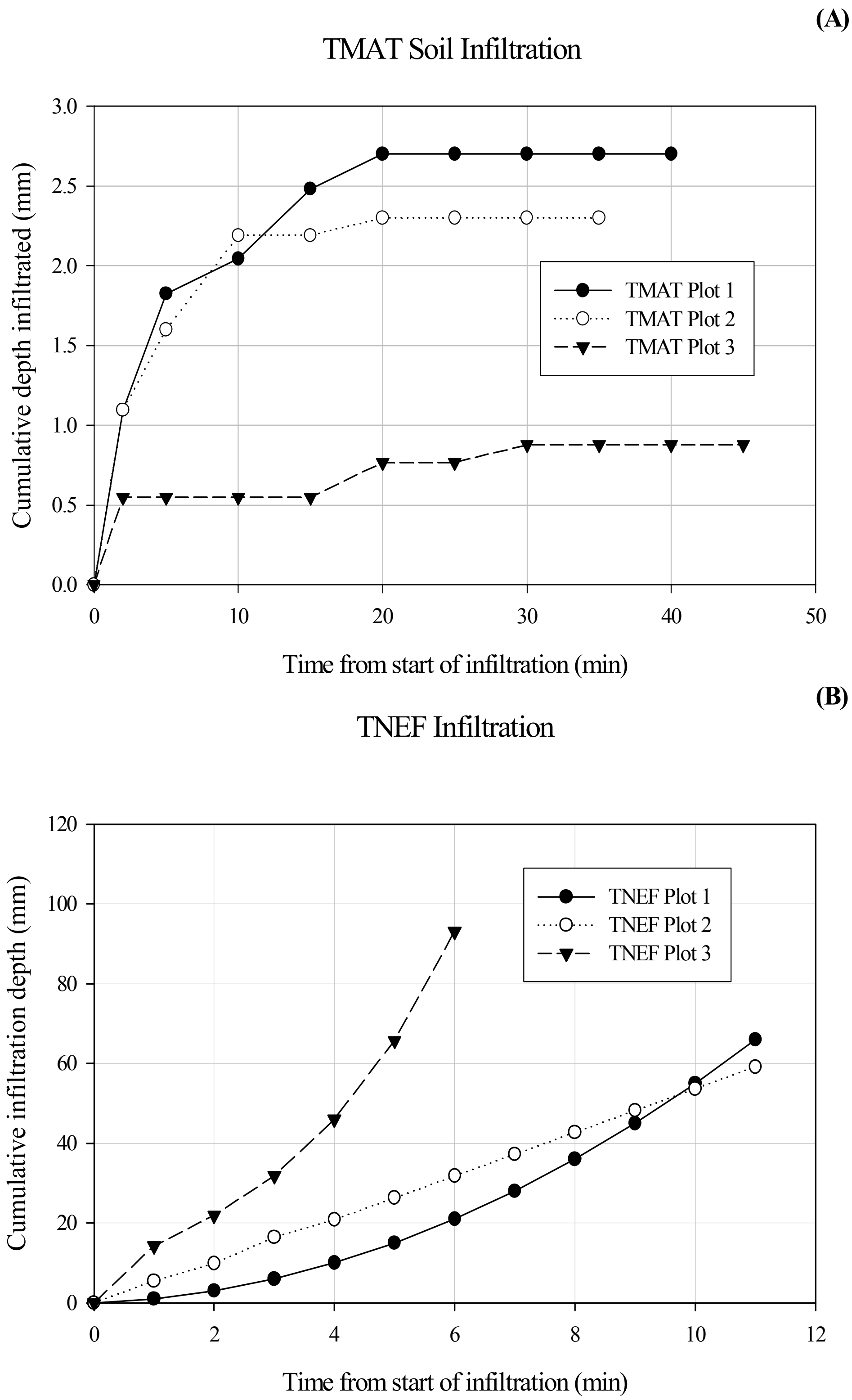
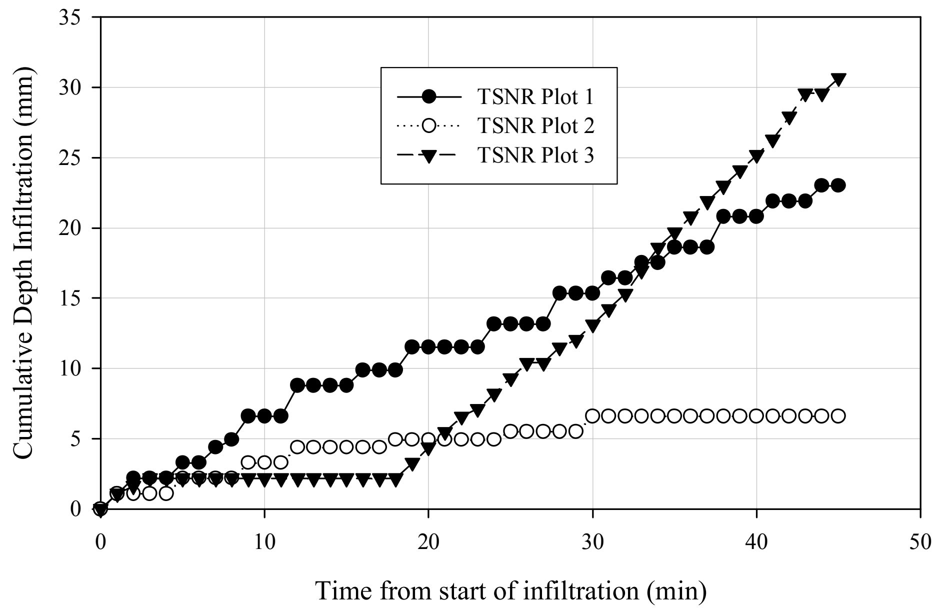


Figure 21. Cumulative depth of water infiltrated at three plots at TNEF (A), and TMAT (B). (Used with permission – Negley 2000).

(A)

TSNR Infiltration



(B)

TSSR Infiltration

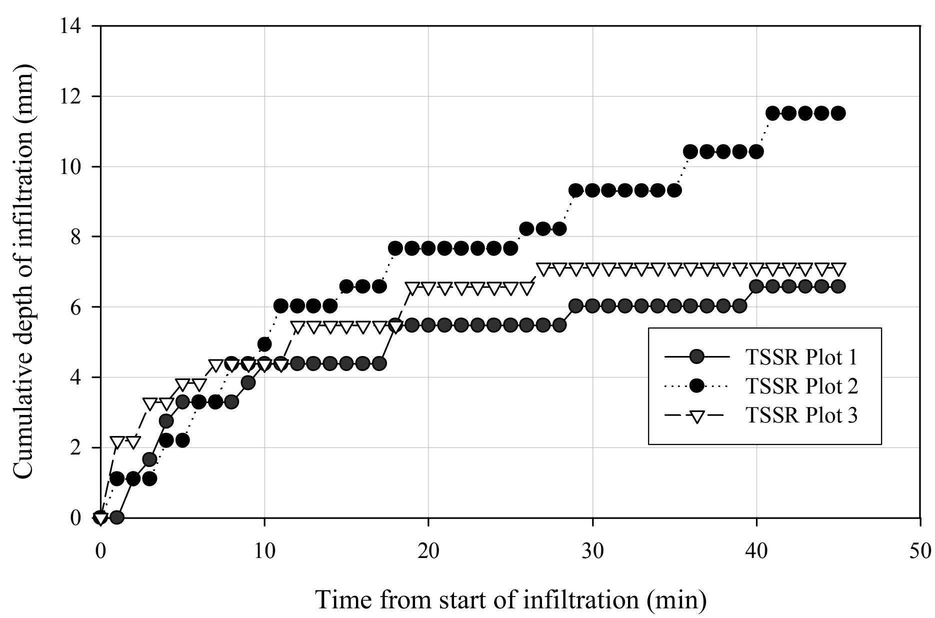


Figure 22. Cumulative depth of water infiltrated at three plots at TSNR (A), and TSSR (B).

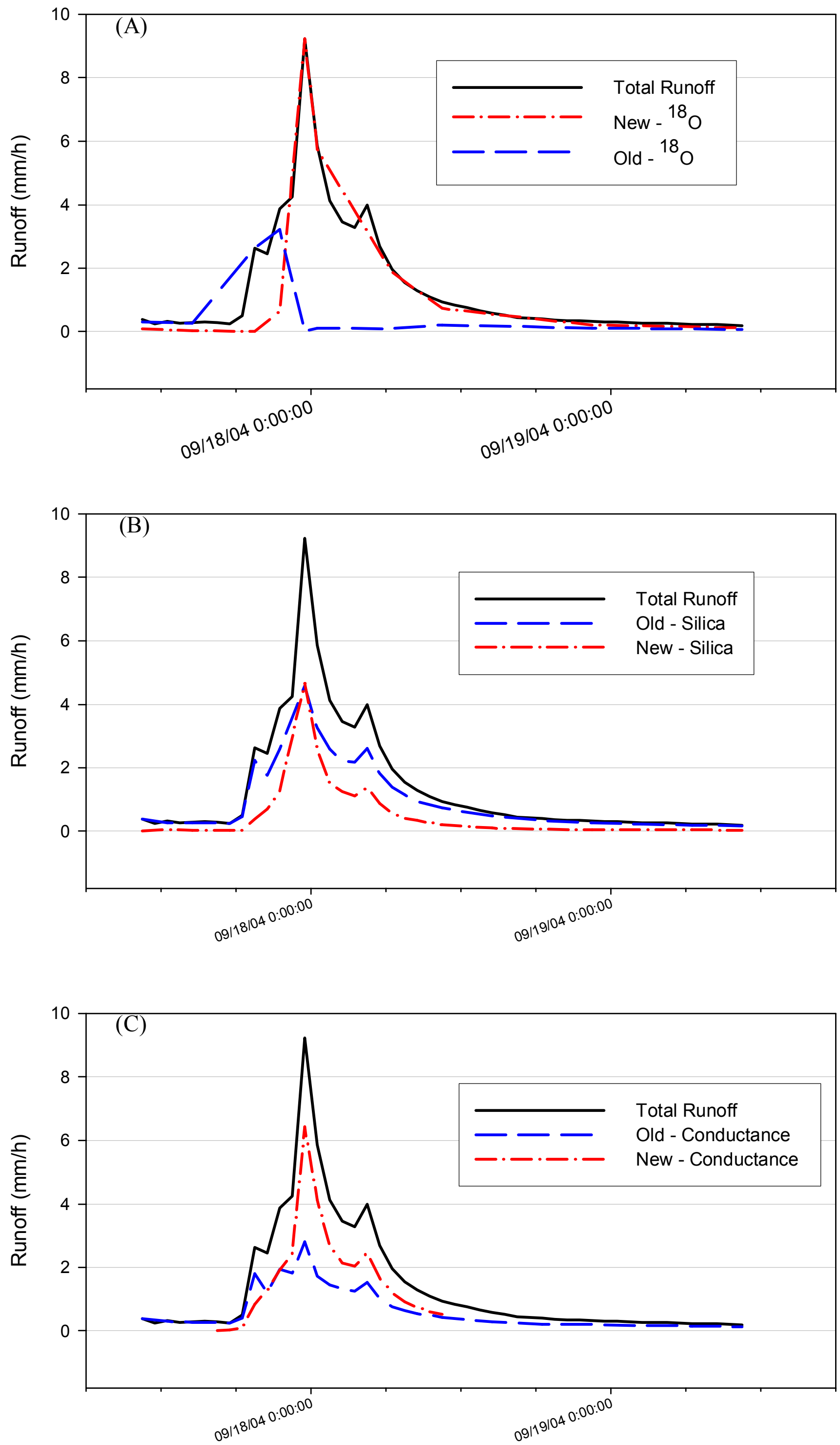


Figure 23. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the September 17, 2004 storm event at the TMAT watershed.

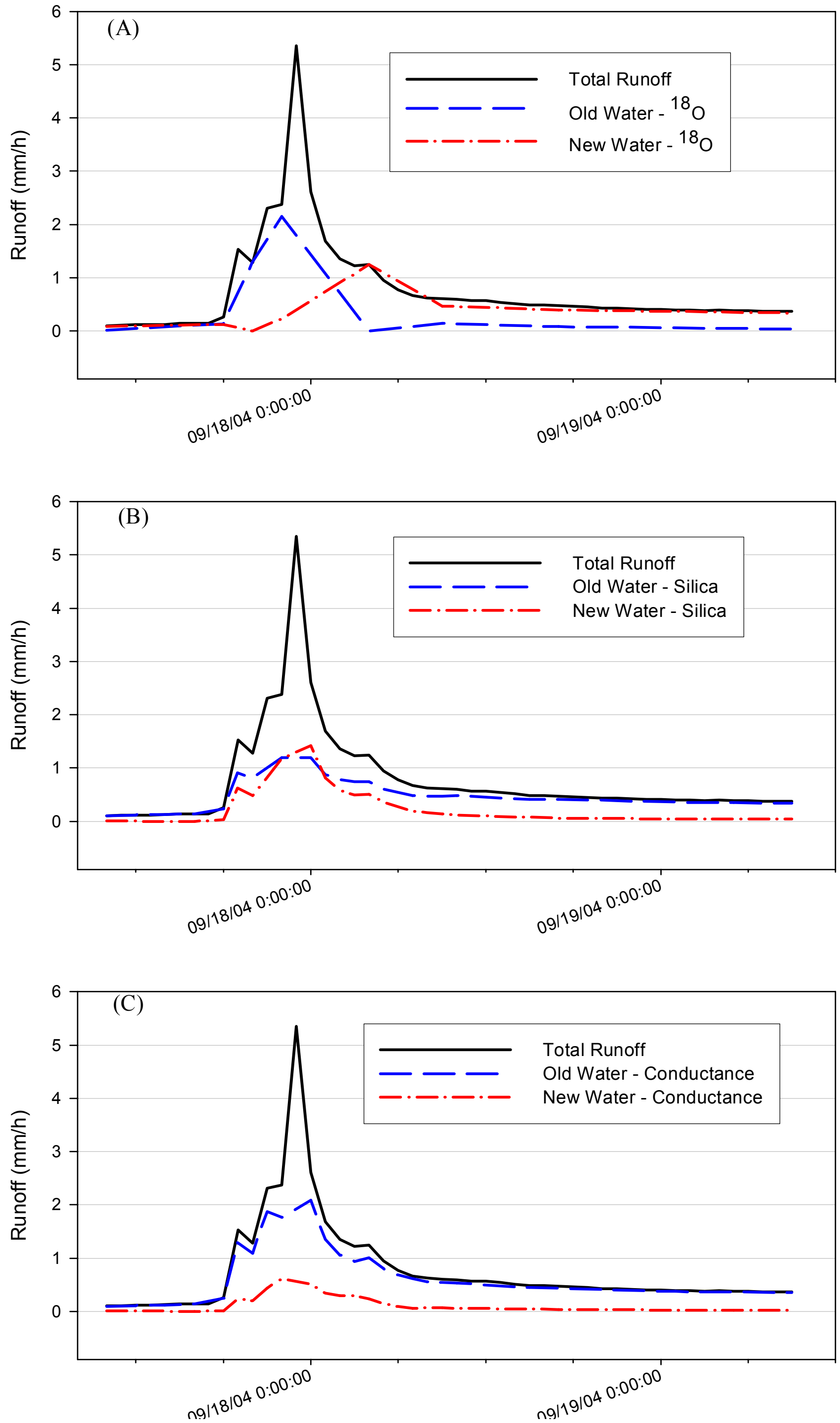


Figure 24. Chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the September 17, 2004 storm event at the TNEF watershed.

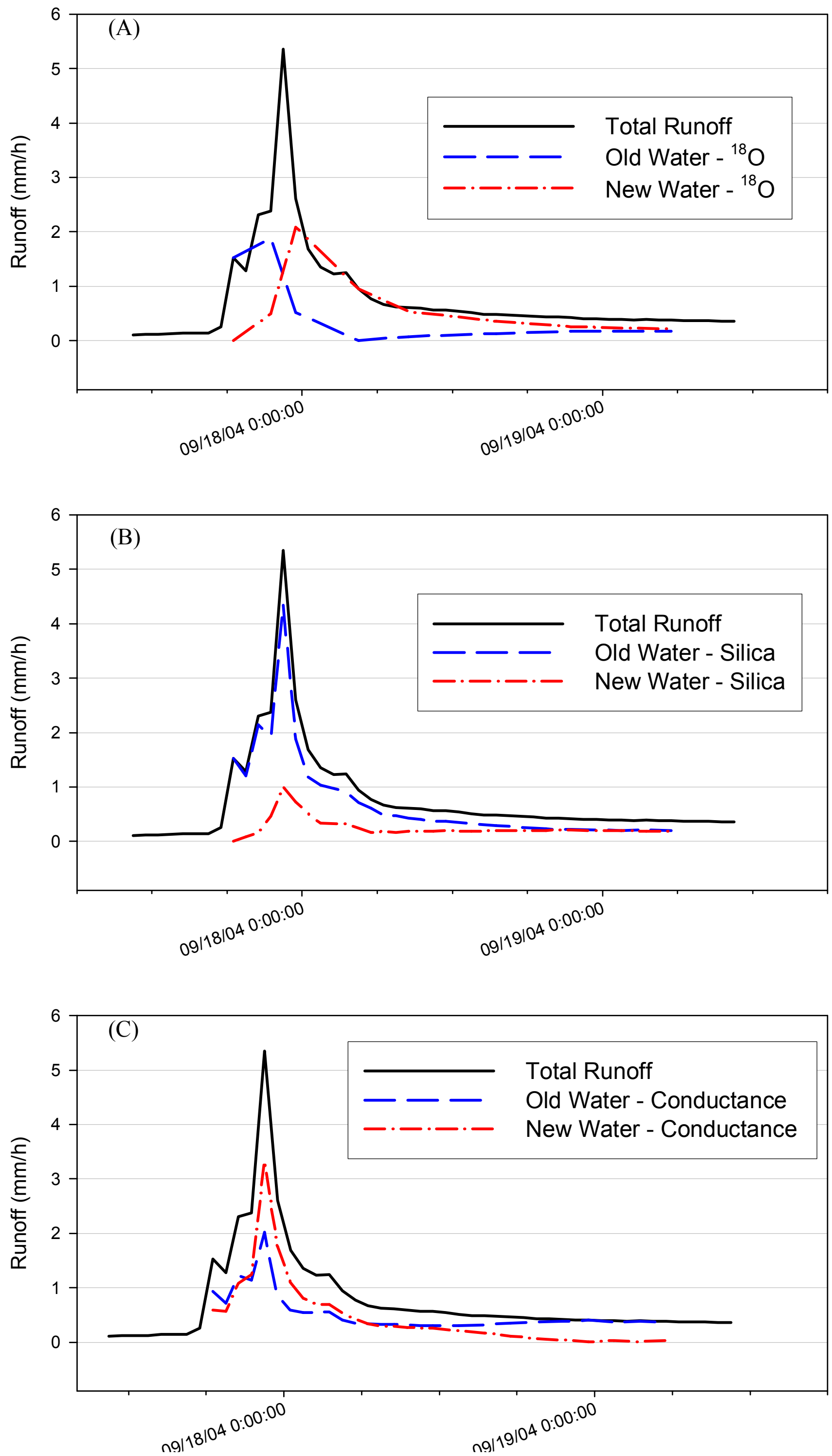


Figure 25. Runoff hydrograph (TNEF) and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the September 17, 2004 storm event at the TSNR watershed. (TNEF runoff hydrograph used as no flume was in place at this time and TSNR and TNEF generally exhibit similar stormflow).

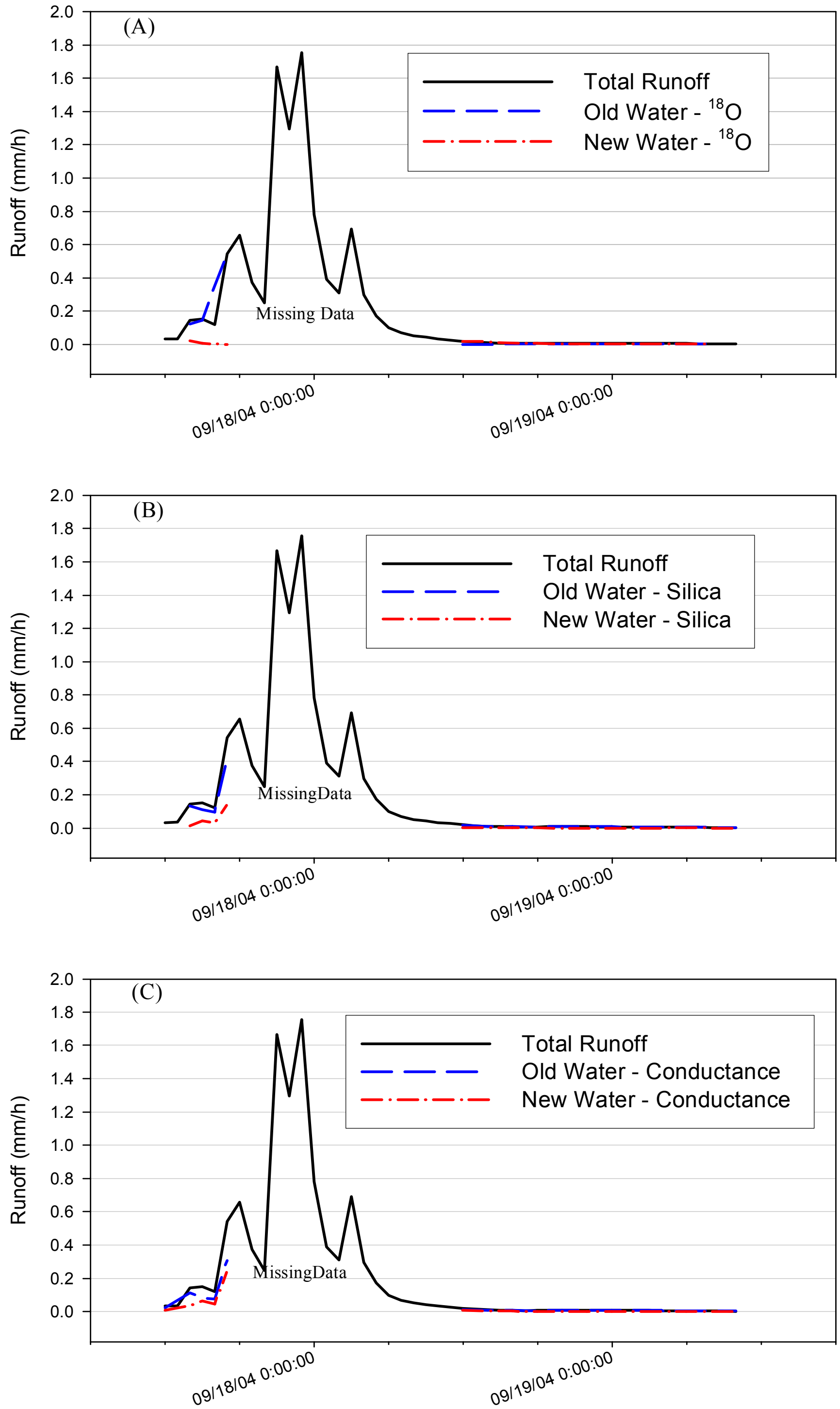


Figure 26. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the September 17, 2004 storm event at the TSSR[1] watershed. (Missing data from 18:00 11/17/04 to 11:00 11/18/04 are a result of equipment problems).

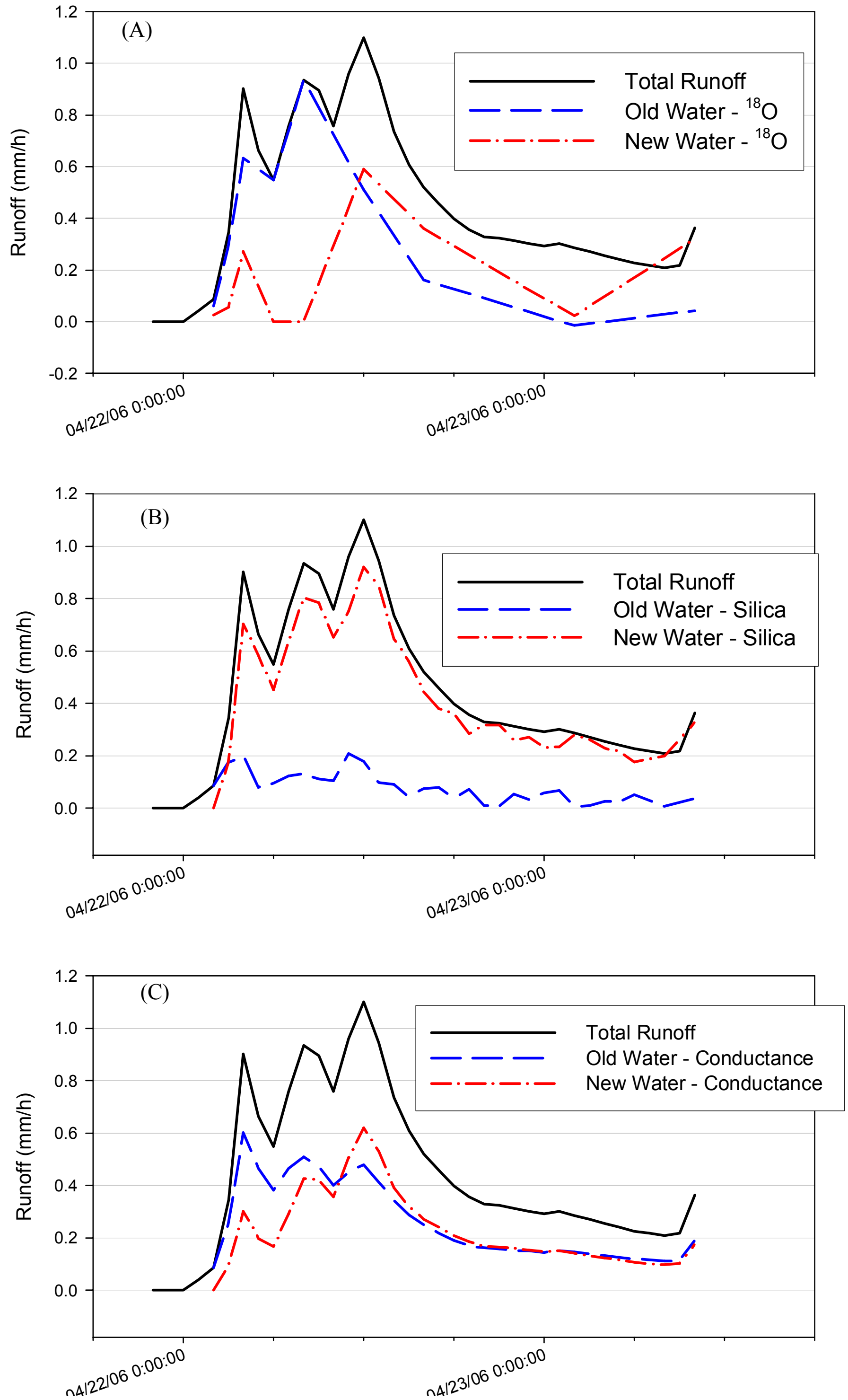


Figure 27. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the April 22, 2006 storm event at the TMAT watershed.

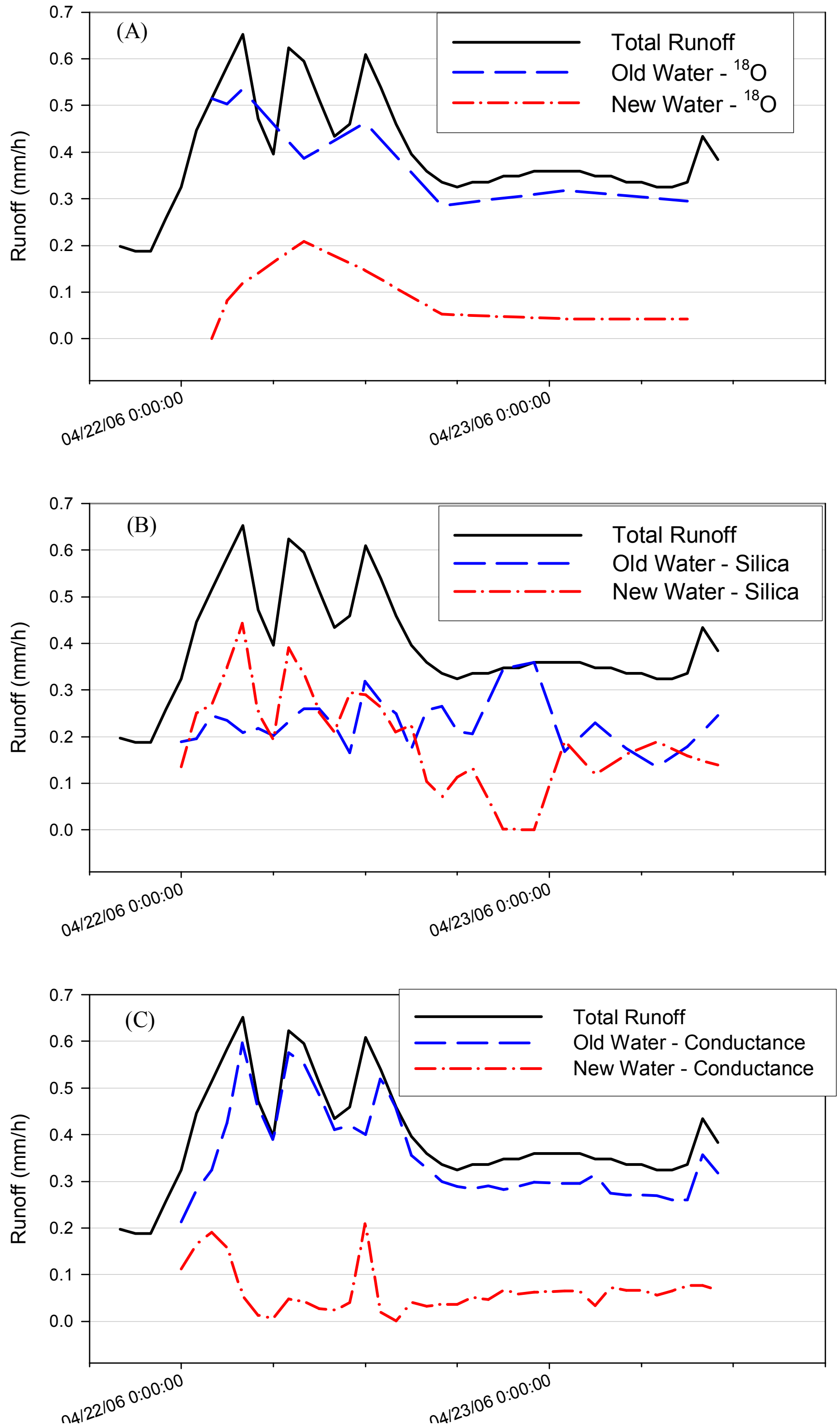


Figure 28. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the April 22, 2006 storm event at the TNEF watershed.

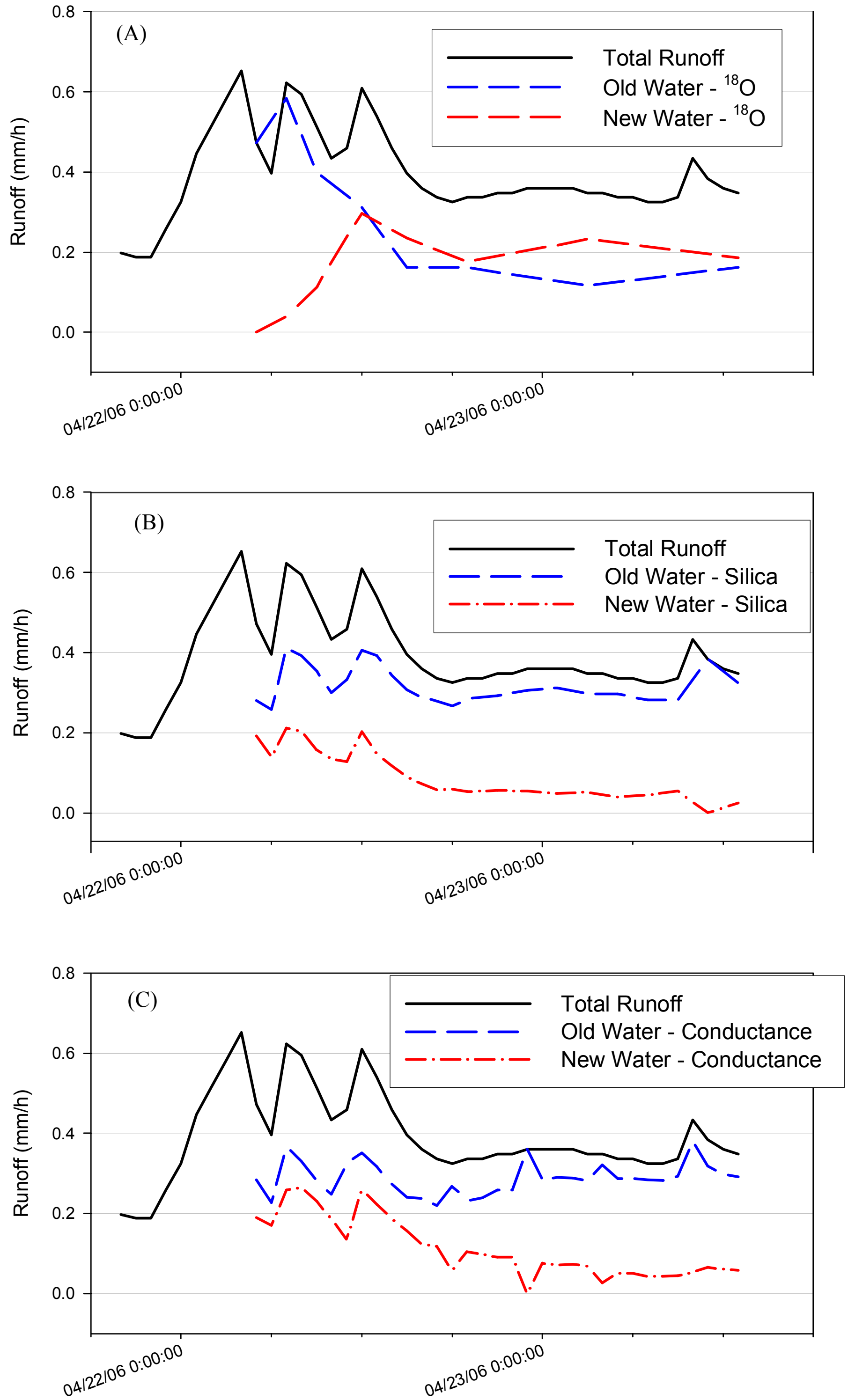


Figure 29. Runoff hydrograph (TNEF) and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the April 22, 2006 storm event at the TSNR watershed. (TNEF runoff hydrograph was used as TSNR equipment failed and no data were available and TSNR and TNEF generally exhibit similar stormflow).

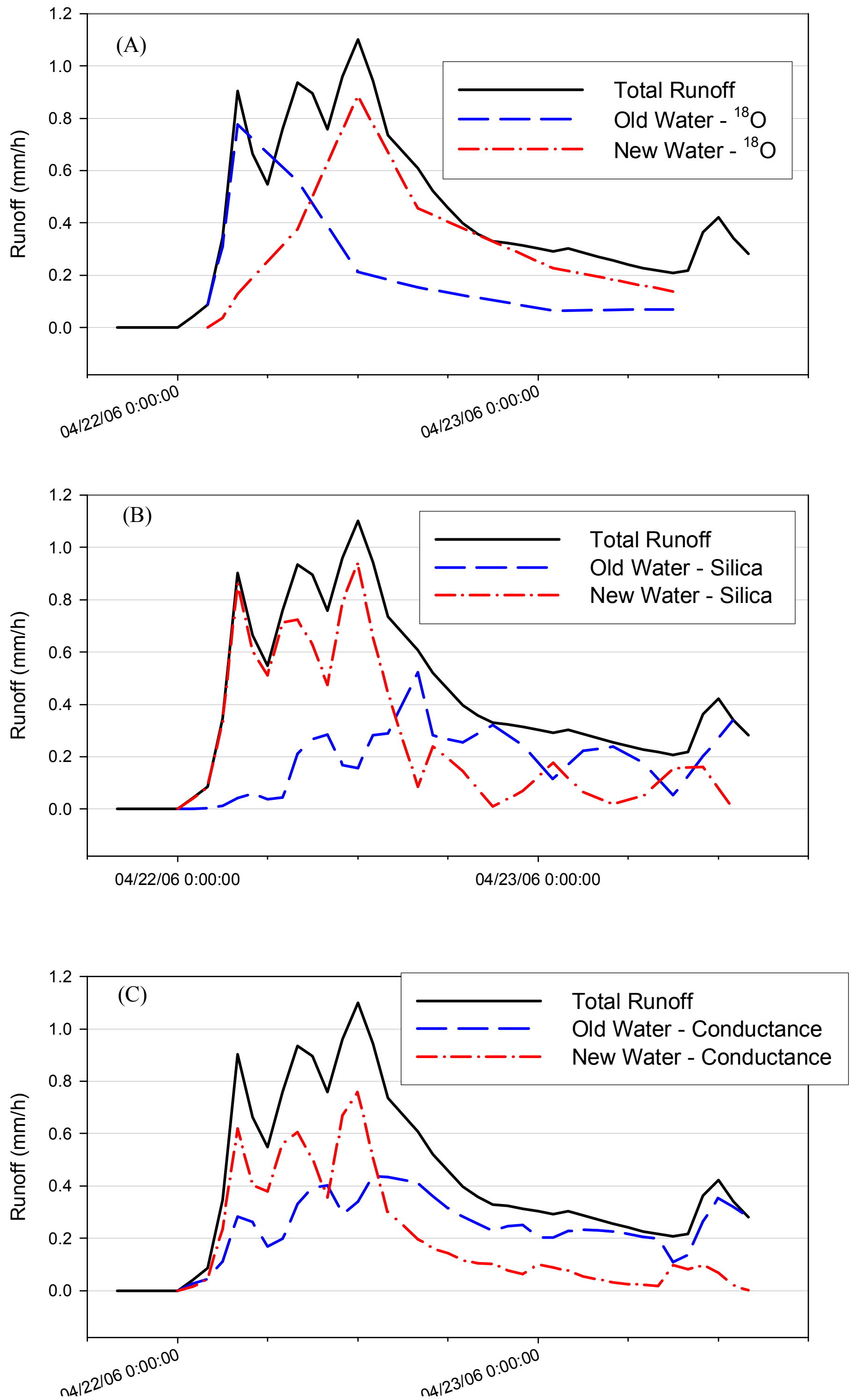


Figure 30. Runoff hydrograph (TMAT) and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the April 22, 2006 storm event at the TSSR watershed. (TMAT runoff hydrograph was used as TSSR equipment failed and no data were available and TSSR and TMAT generally exhibit similar stormflow).

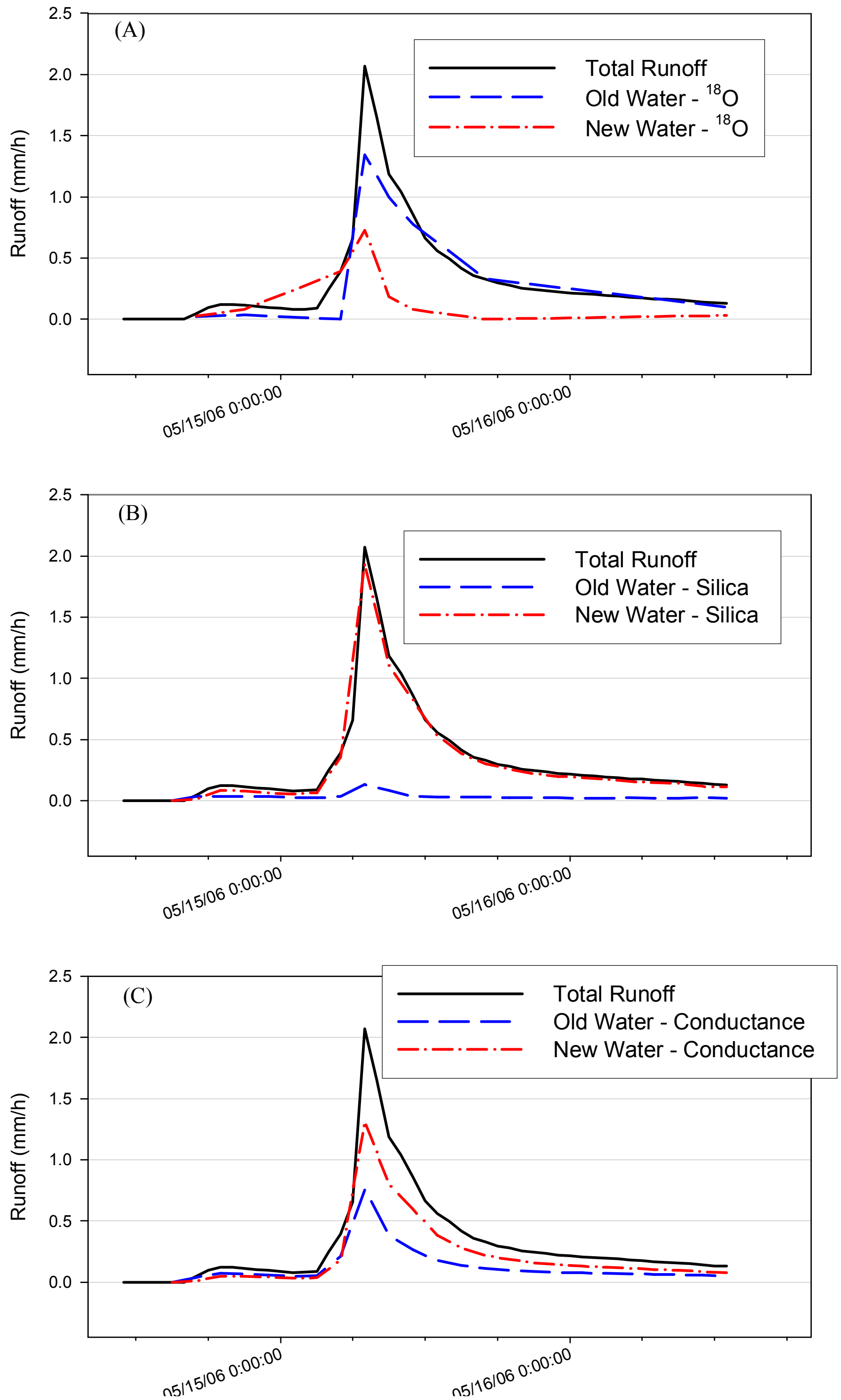


Figure 31. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the May 14, 2006 storm event at the TMAT watershed.

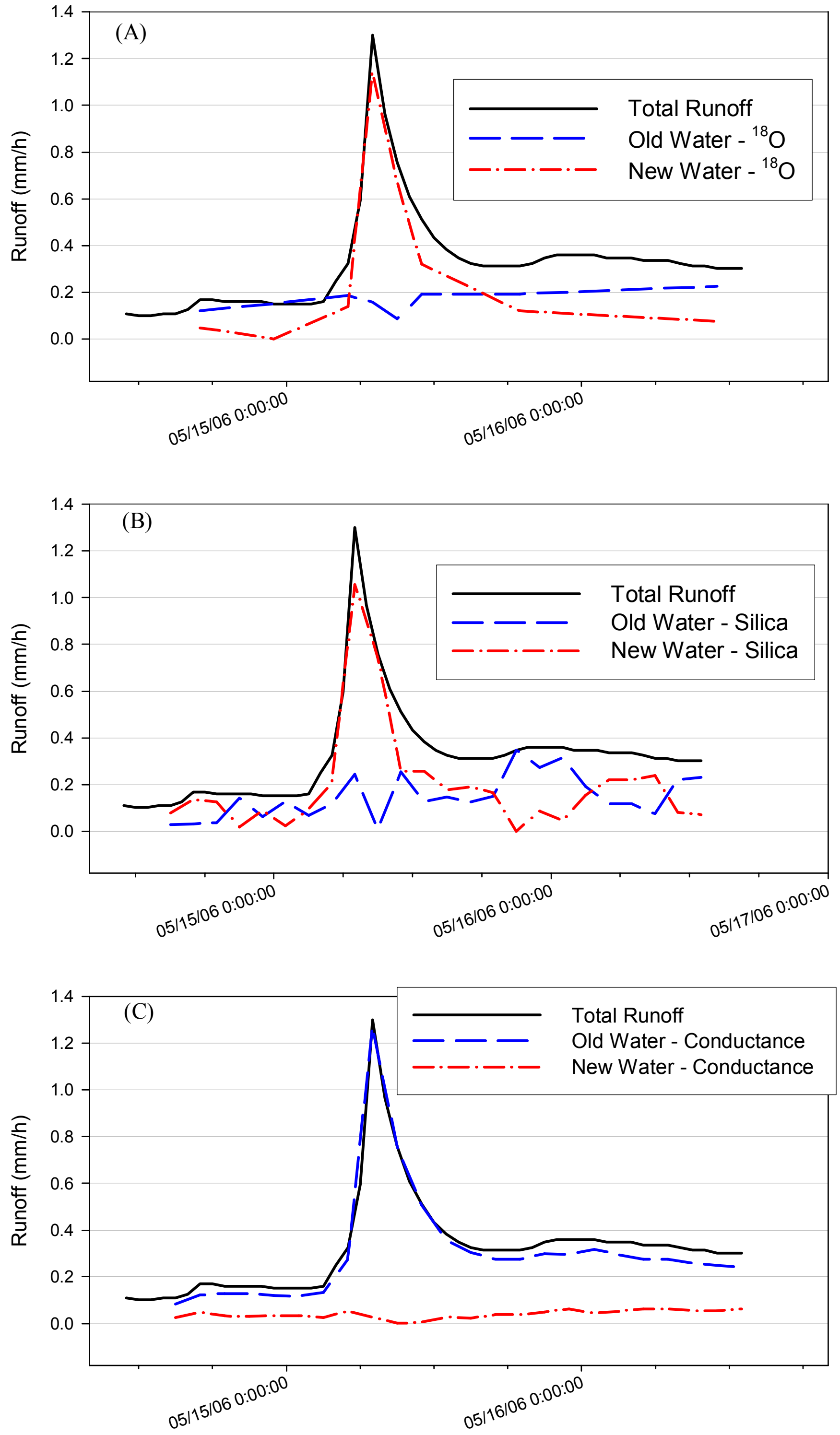


Figure 32. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the May 14, 2006 storm event at the TMAT watershed.

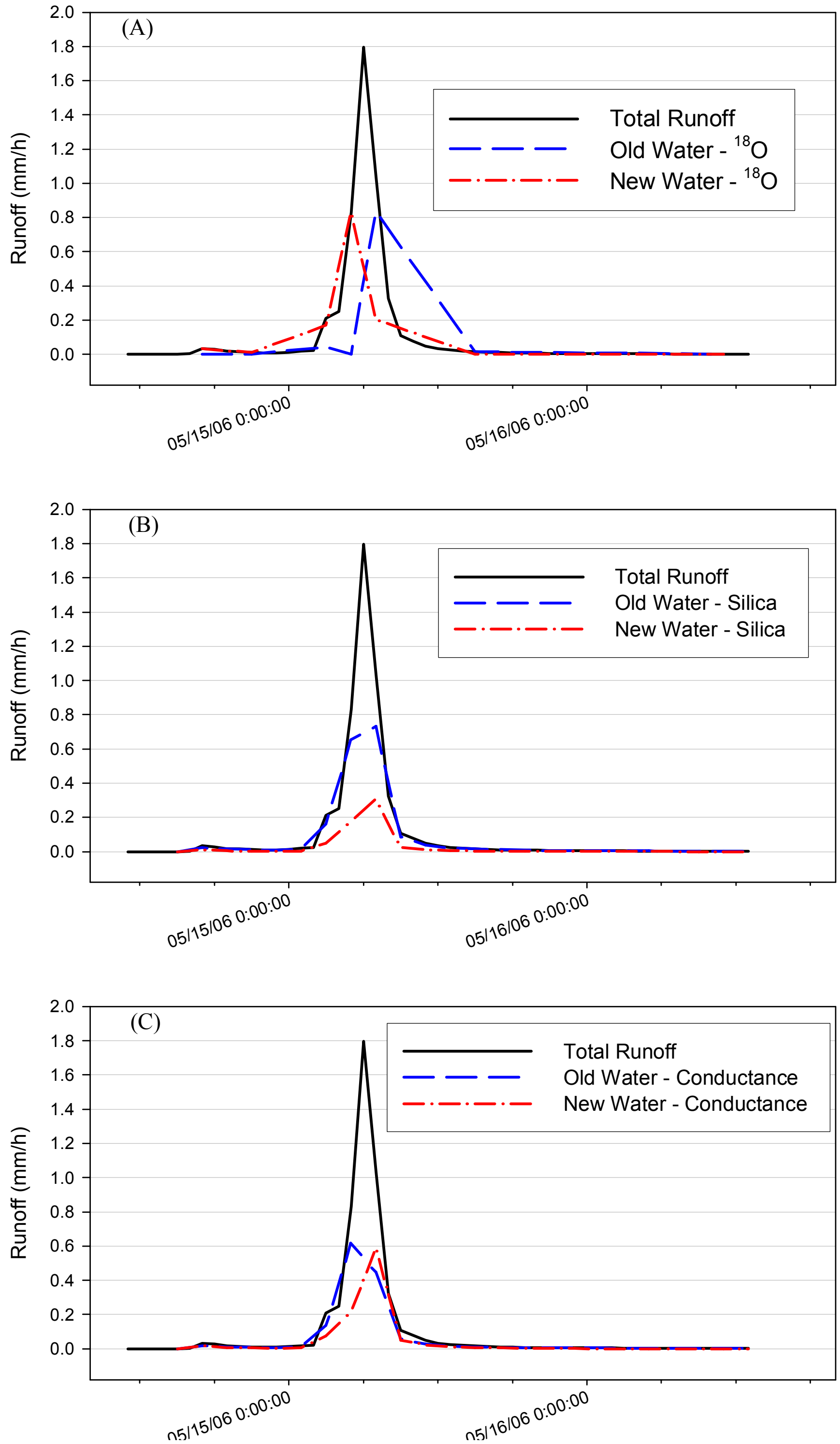


Figure 33. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the May 14, 2006 storm event at the TSNR watershed.

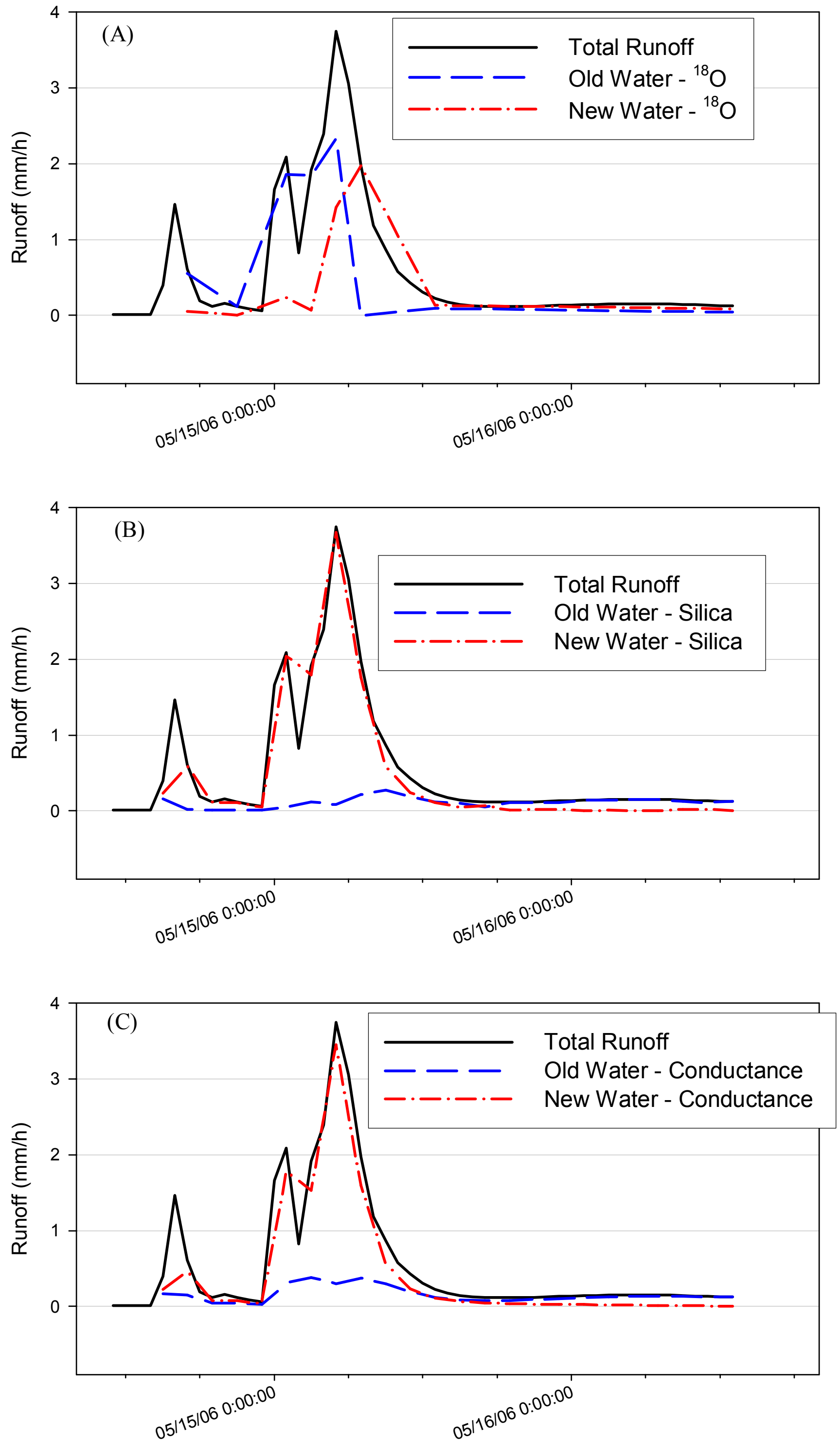


Figure 34. Runoff hydrograph and chemical and isotopic hydrograph separation using ^{18}O (A), silica (B) and specific conductance (C) as tracers for the May 14, 2006 storm event at the TSSR watershed.

TMAT New Water Runoff
September 17, 2004 Storm Event

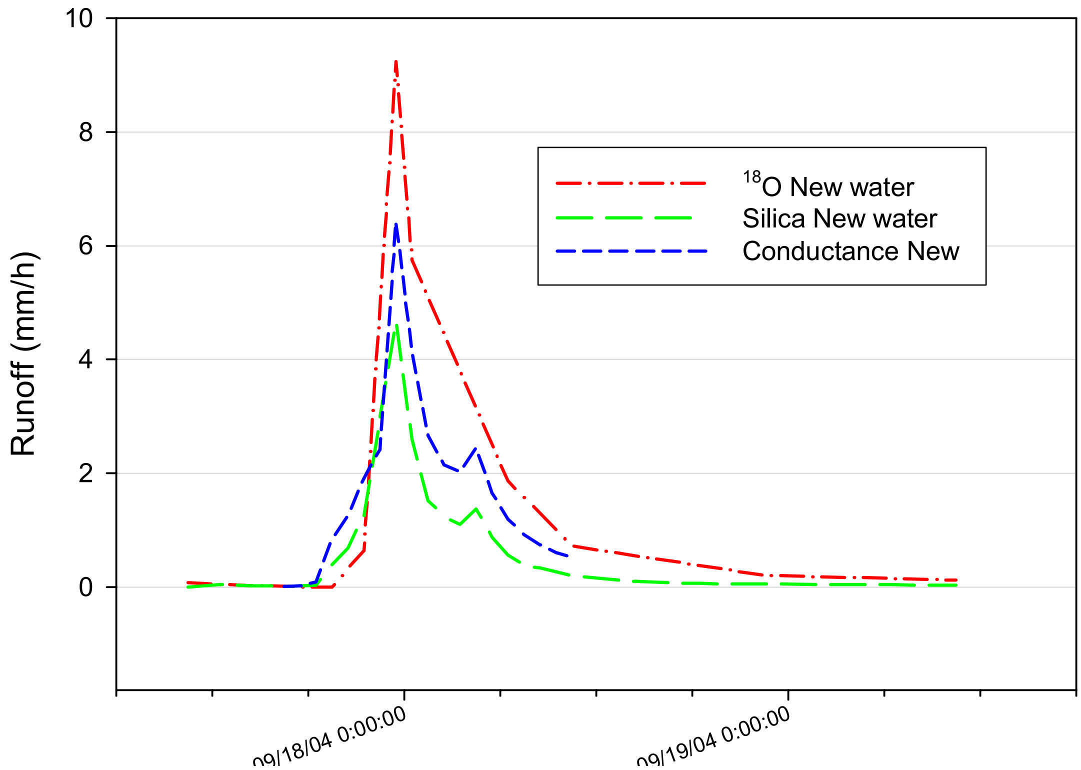


Figure 35. Differences in new water runoff volumes according to the natural tracers ^{18}O, silica and specific conductance at TMAT for the September 17, 2004 event.

TNEF New Water Runoff
April 22, 2006 Storm Event

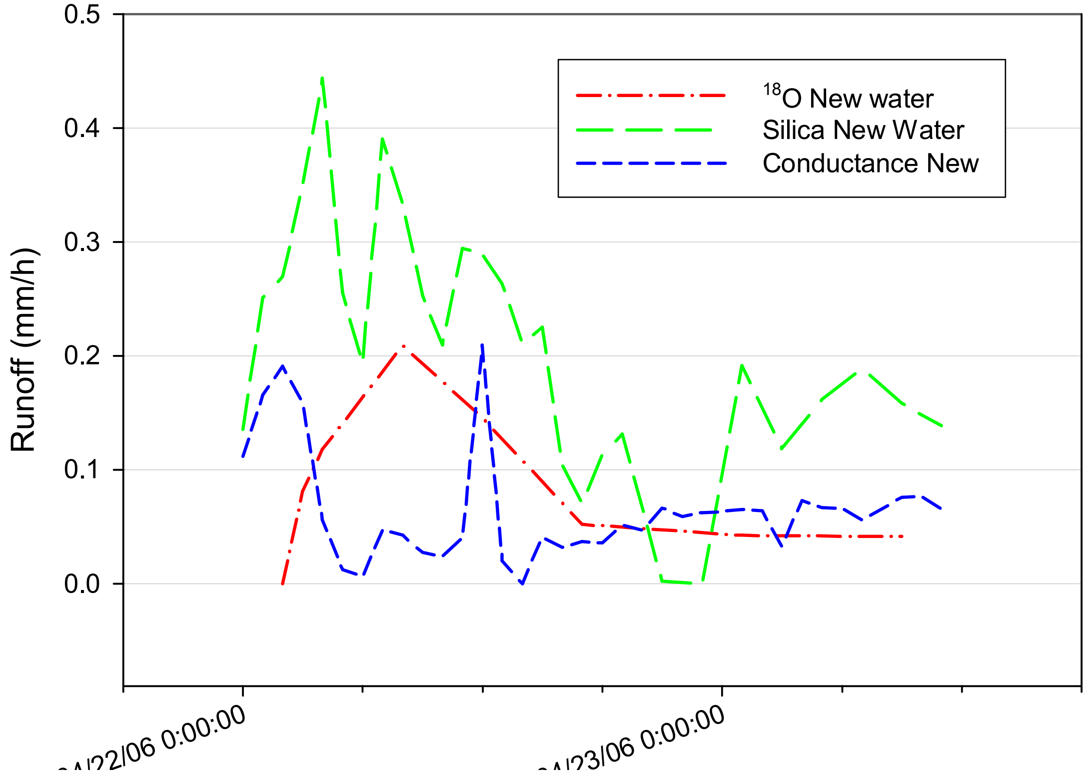


Figure 36. Differences in new water runoff volumes according to the natural tracers ^{18}O, silica and specific conductance at TNEF for the April 22, 2006 event.

TSSR New Water Runoff
May 14, 2006 Storm Event

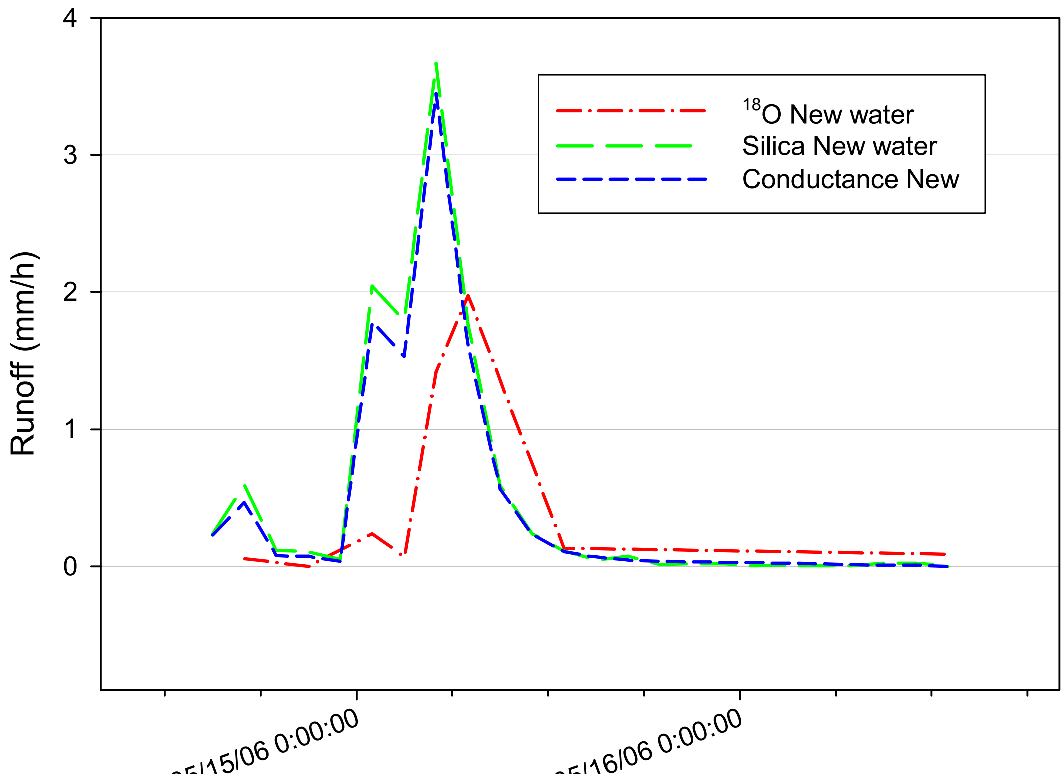


Figure 37. Differences in new water runoff volumes according to the natural tracers ^{18}O, silica and specific conductance at TSSR for the May 14, 2006 event.

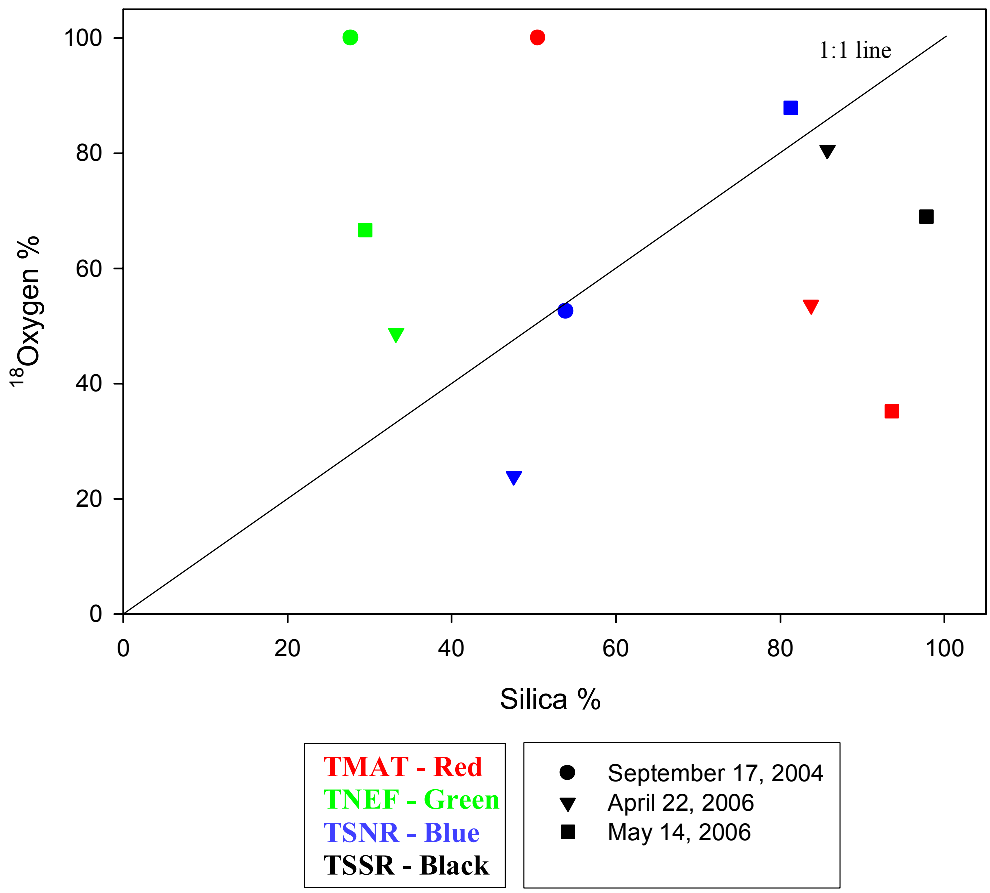


Figure 38. Correlation between new water percentages at peak runoff for the ^{18}O and silica time series data for three storms occurring between September 2004 and June 2006.

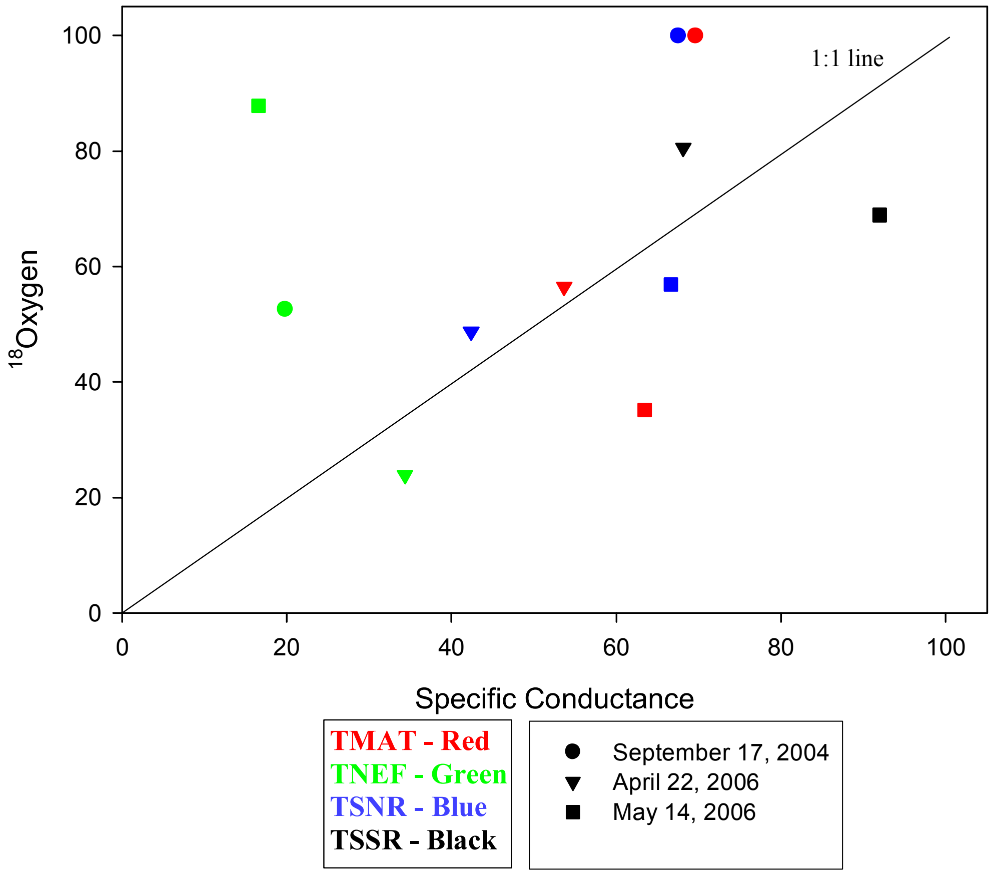


Figure 39. Correlation between new water percentages at peak runoff for the ^{18}O and specific conductance time series data for three storms occurring between September 2004 and June 2006.

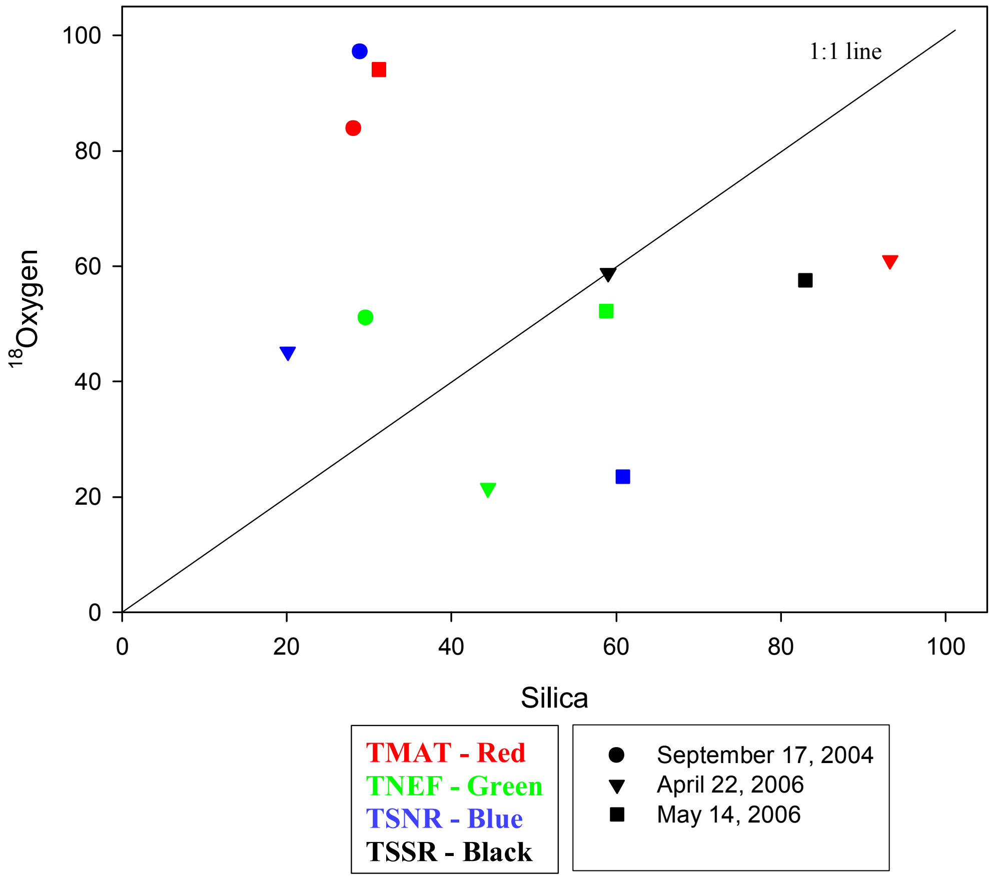


Figure 40. Correlation between new water percentages of total runoff for the ^{18}O and silica time series data for three storms occurring between September 2004 and June 2006.

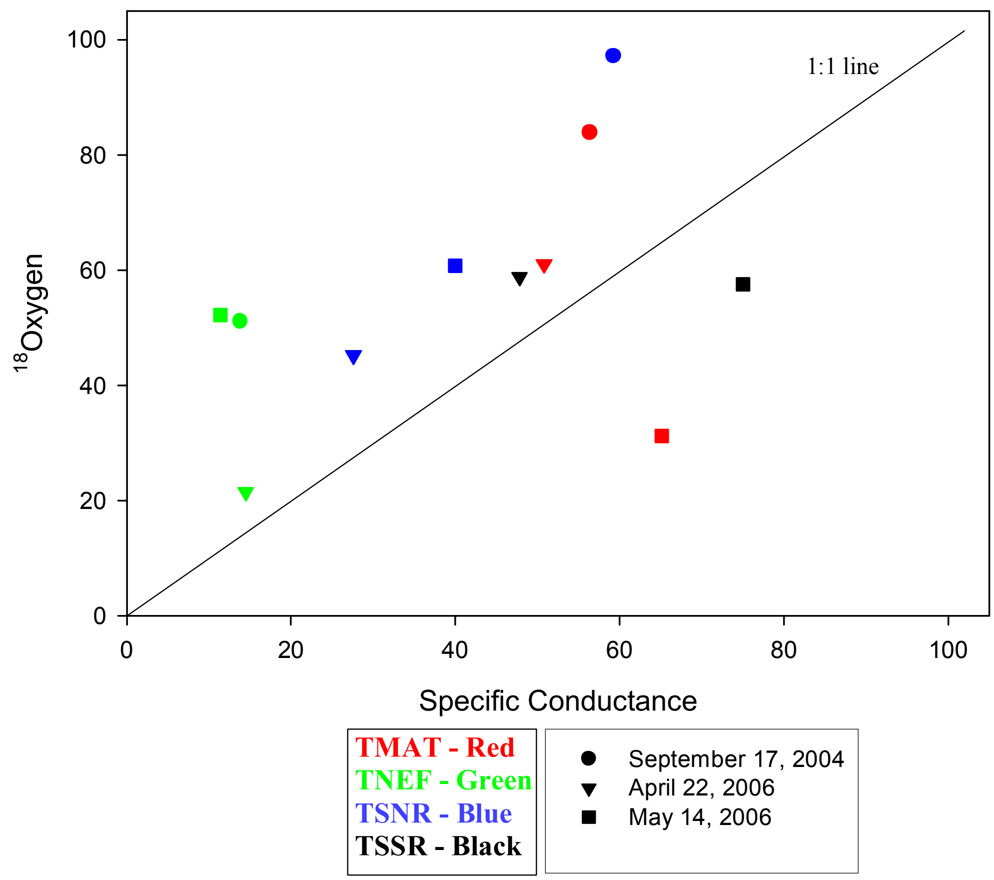


Figure 41. Correlation between new water percentages of total runoff for the ^{18}O and specific conductance time series data for three storms occurring between September 2004 and June 2006.

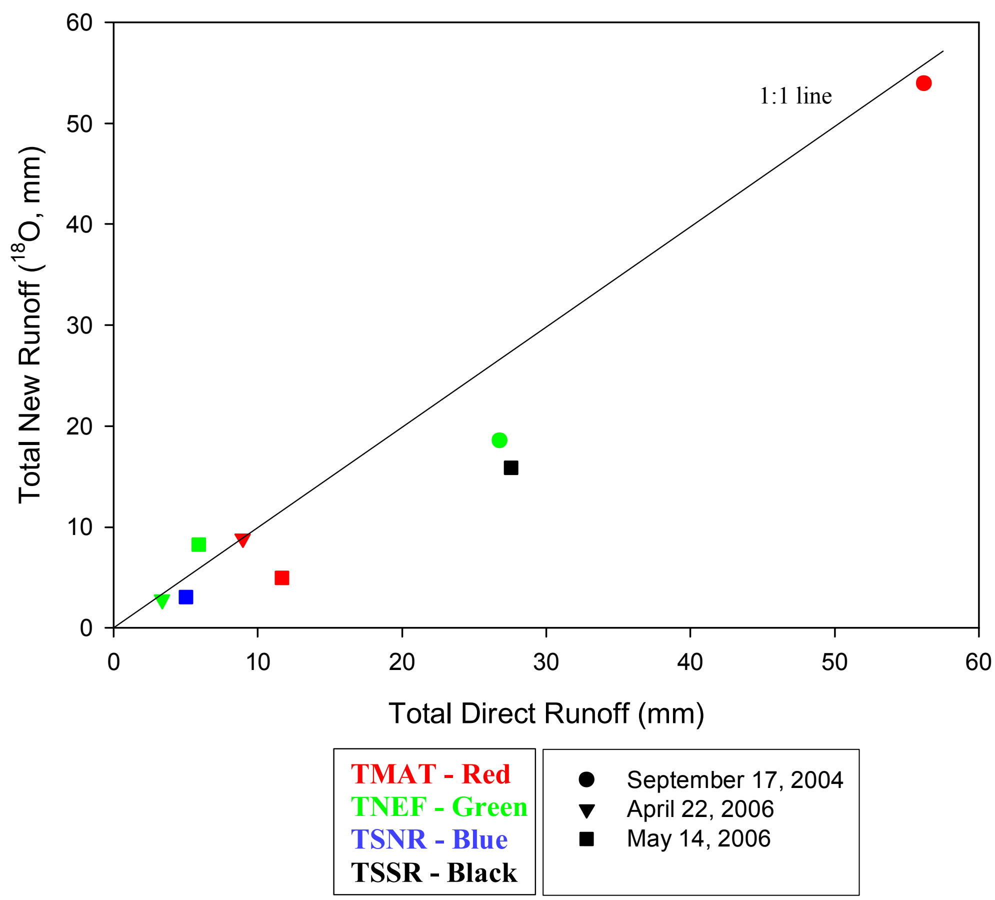


Figure 42. Correlation between total new water runoff depth (^{18}O) and total direct runoff depth for three storms occurring between September 2004 and June 2006.

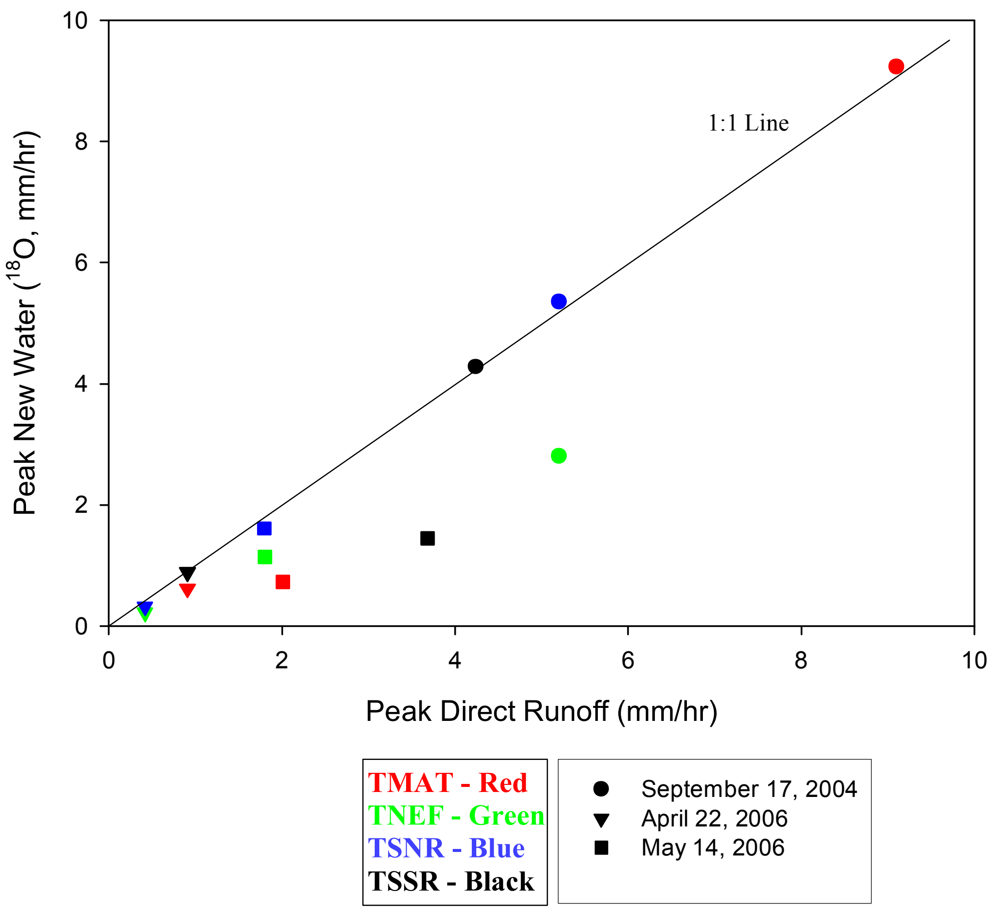


Figure 43. Correlation between peak new water runoff rate (^{18}O) and peak direct runoff rate for three storms occurring between September 2004 and June 2006.

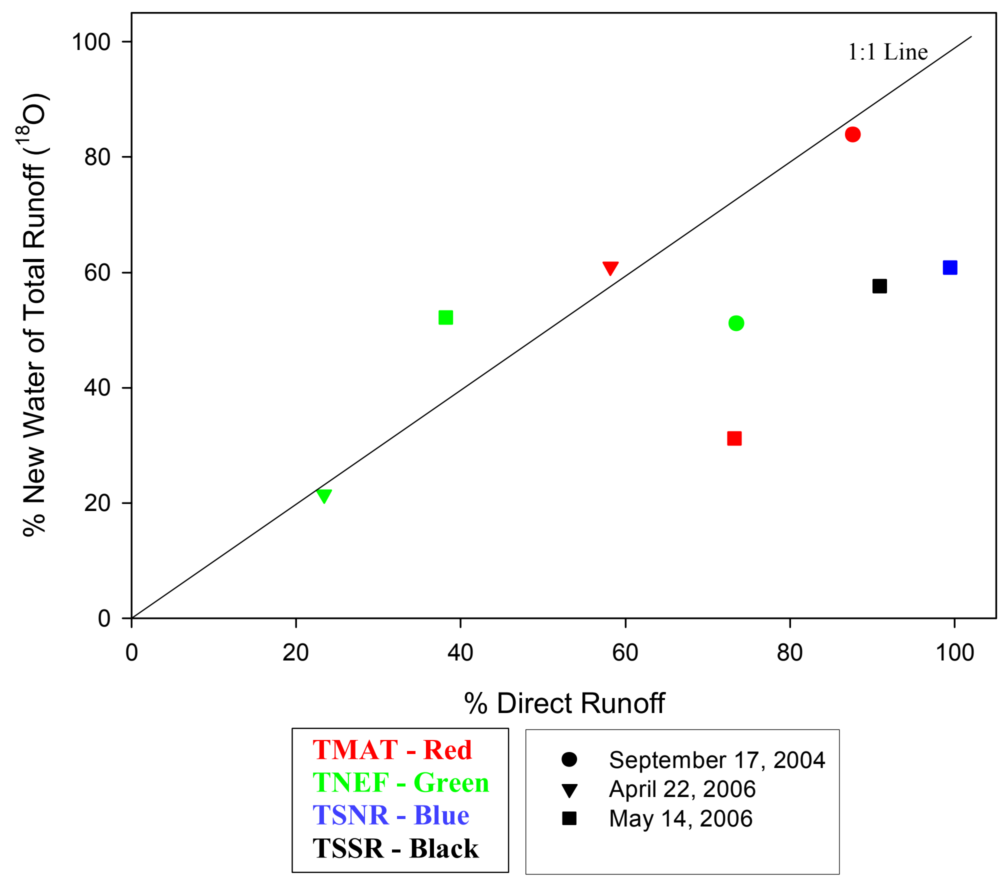


Figure 44. Correlation between total new water runoff percent (^{18}O) and direct runoff percent for three storms occurring between September 2004 and June 2006.

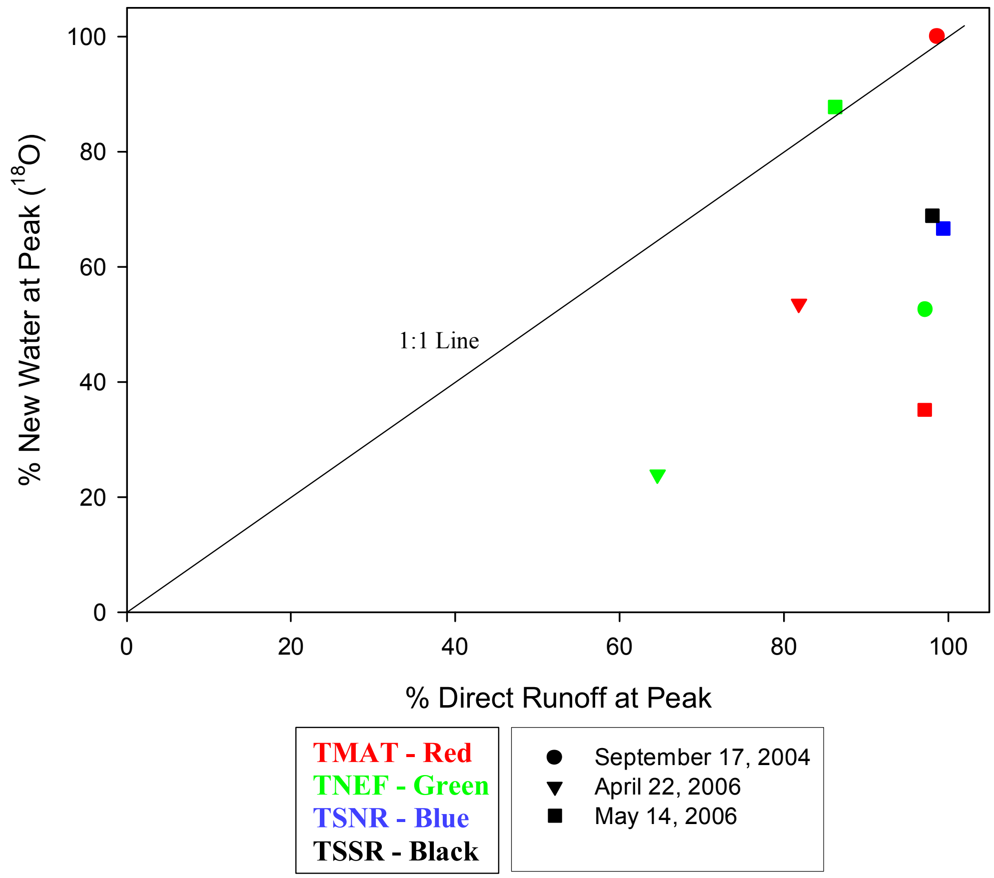


Figure 45. Correlation between peak new water runoff percent (^{18}O) and peak direct runoff percent for three storms occurring between September 2004 and June 2006.

Table 4. Stormflow summary for watersheds TMAT, TNEF, TSNR and TSSR from September 17, 2004 to June 1, 2006. " * " indicates that equipment was not functioning and no data were available. “nf” means no flow or the watershed did not respond to a particular rain event. Superscripts 1 and 2 refer to the different watershed areas for the TSSR watershed.

Event	Max. Rain	Tot. Rain	Total Surface Runoff (mm)				Direct Runoff (mm)				Runoff Ratio			
Date	(mm/hr)	(mm)	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR
9/17/2004	22.8	106.7	64.1	36.4	*	23.4^{1}	56.2	26.8	*	10.0^{1}	0.50	0.25	*	0.22^{1}
11/24/2004	5.0	35.0	20.9	9.2	*	17.7^{1}	13.3	2.6	*	8.5^{1}	0.40	0.08	*	0.51^{1}
1/5/2005	5.0	51.5	*	11.8	5.2	*	*	6.7	4.3	*	*	0.13	0.08	*
1/11/2005	5.5	27.0	*	5.4	3.6	22.8^{1}	*	2.0	2.9	13.1^{1}	*	0.07	0.11	0.84^{1}
5/20/2005	5.1	31.8	4.3	1.8	nf	5.5^{1}	3.8	1.3	nf	2.3^{1}	0.10	0.04	nf	0.17^{1}
7/8/2005	7.6	44.5	0.8	0.9	nf	9.7^{1}	0.8	0.4	nf	4.2^{1}	0.02	0.01	nf	0.22^{1}
7/16/2005	21.0	3.0	5.4	1.2	nf	2.1^{1}	4.7	0.8	nf	0.9^{1}	0.13	0.02	nf	0.06^{1}
10/7/2005	10.0	57.5	0.1	nf	nf	0.8^{1}	0.1	0	nf	0.4^{1}	0.00	0.00	nf	0.0^{1}
11/29/2005	7.62	41.9	26.4	17.3	11.5	18.8^{2}	23.1	11	11.1	17.5^{2}	0.55	0.26	0.27	0.42^{2}
1/2/2006	3.8	26.7	15.7	6.6	2.5	8.2^{2}	10.2	6.6	1.5	6.4^{2}	0.38	0.10	0.13	0.27^{2}
4/22/2006	5.1	39.4	15.4	14.3	*	*	8.9	3.4	*	*	0.23	0.09	*	*
5/11/2006	5.1	21.6	2.5	2.4	nf	2.0^{2}	1.01	1.0	nf	1.7^{2}	0.05	0.05	nf	0.07^{2}
5/14/2006	7.6	46.4	15.9	15.5	5.1	27.6^{2}	11.7	5.9	5.0	25.1^{2}	0.25	0.13	0.11	0.52^{2}
		Mean	15.6	10.2	5.6	12.6	12.2	5.3	5.0	8.2	0.24	0.09	0.14	0.30

Table 5. Stormflow summary for watersheds TMAT, TNEF, TSNR and TSSR from September 17, 2004 to June 1, 2006. " * " indicates that equipment was not functioning and no data were available. “ nf “ means no flow or the watershed did not respond to the rain event. Superscripts 1 and 2 refer to the different watershed areas for the TSSR watershed.

Event Date	Max. Rain (mm/hr)	Tot. Rain (mm)	Peak Stormflow (mm/hr)				Centriod Lag			
			TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR
9/17/2004	22.8	106.7	9.1	5.2	*	4.2^1	8	8	*	6^1
11/24/2004	5.0	35.0	1.1	0.3	*	3.4^1	4	5	*	1^1
1/5/2005	5.0	51.5	*	0.4	0.8	*	*	11	1	*
1/11/2005	5.5	27.0	*	0.4	1.2	4.8^1	*	16	16	15^1
5/20/2005	5.1	31.8	0.5	0.2	nf	1.5^1	3	2	nf	1^1
7/8/2005	7.6	44.5	0.1	0.1	nf	2.2^1	7	4	nf	3^1
7/16/2005	21.0	36.0	1.0	0.4	nf	0.8^1	7	3	nf	21^1
10/7/2005	10.0	57.5	0.1	0	nf	0.4^1	4	nf	nf	3^1
11/29/2005	7.6	41.9	3.0	1.6	2.6	3.4^2	8	8	6	6^2
1/2/2006	3.8	26.7	0.6	0.3	0.4	1.3^2	9	7	5	10^2
4/22/2006	5.1	39.4	0.9	0.4	*	*	6	4	*	*
5/11/2006	5.1	21.6	0.3	0.2	nf	0.3^2	4	3	nf	1^2
5/14/2006	7.6	46.4	2.0	1.8	1.8	3.7^2	5	5	2	1^2
		Mean	1.7	0.9	0.7	2.4	6	6	6	6

Table 6. Integrated new water runoff depth for three storms at TMAT, TNEF, TSNR and TSSR using ^{18}O silica and specific conductance as tracers. (" * " indicates missing data or equipment problems).

			Total New Water Runoff Depth(mm)											
	Total	Max. Rain	18-Oxygen Isotope				Silica				Specific Conductance			
Event Date	Rain (mm)	(mm/hr)	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR
10/17/2004	106.9	22.9	53.9	18.5	*	*	18.0	10.7	*	*	36.2	5.0	*	*
4/22/2006	39.4	5.1	8.8	2.8	*	*	13.5	6.3	*	*	7.4	2.1	*	*
5/14/2006	46.4	7.6	5.0	8.3	3.1	15.9	14.9	9.3	1.2	22.8	10.3	1.8	2.0	20.7

Table 7. New water percentages at peak flow for three storms at TMAT, TNEF, TSNR, and TSSR using O^{18}, silica and specific conductance as tracers. (“ * “ indicates missing data due to equipment problems).

			Total New Water %											
Event Date	Total Rain (mm)	Max. Rain (mm/hr)	18-Oxygen Isotope				Silica				Specific Conductance			
			TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR
10/17/2004	106.9	22.9	83.9	51.1	97.2	*	28.1	29.6	28.9	*	56.4	13.8	59.2	*
4/22/2006	39.4	5.1	61.0	21.5	45.2	58.8	93.2	44.4	20.1	59.0	50.8	14.5	27.6	47.8
5/14/2006	46.4	7.6	31.2	52.2	60.8	57.6	94.1	58.8	23.5	82.9	65.1	11.4	40.0	75.0

Table 8. Percentage of new water at peak flow as determined by O^{18}, silica and specific conductance for three storm events.

			% New Water at Peak Discharge											
	Total	Max. Rain	18-Oxygen Isotope				Silica				Specific Conductance			
Event Date	Rain (mm)	(mm/hr)	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR	TMAT	TNEF	TSNR	TSSR
10/17/2004	106.9	22.9	100.0	52.6	100.0	*	50.5	53.9	27.7	*	69.6	19.8	67.5	*
4/22/2006	39.4	5.1	53.6	23.9	48.8	80.5	83.7	47.6	33.2	85.8	56.5	34.4	42.4	68.1
5/14/2006	46.4	7.6	35.2	87.8	66.6	68.9	93.6	81.3	29.5	97.8	63.4	16.6	56.9	92.0

Chapter IV: DISCUSSION

Although the hydroisotopic separation technique is well documented at the river basin and even small watershed scale, this is the first known study to employ this method on zero order watersheds affected by surface mining. One major limitation of working at the zero order watershed scale is the lack of baseflow between storm events. This baseflow information is required for completing the mass balance equation. Because there is normally no antecedent baseflow to sample, one cannot obtain baseflow ("old" water) samples for determining isotopic (or chemical) concentrations of stream water. Other potential baseflow or old water sampling sources, such as natural springs, seeps and wells, were not present at any of the sites and, therefore, could not be sampled.

In zero order watersheds, soil water may comprise a large portion of old water released to a stream during storm events (Weiler et al. 2003). Therefore, during the first few months of the present study, soil lysimeters were installed and at each of the four watersheds to obtain samples for estimating old water concentrations. Analyses of these samples from the sites indicated that the variation in tracer concentration within each site was too great to allow this method to be used in estimating old water concentrations. This left only one alternative in estimating old water composition: use samples collected from either the rising or recession limb of the stormflow hydrograph. The assumption that such a sample is representative of baseflow and/or groundwater is one that is unique to this study and could not be avoided.

The assumption that a sample from either the rising or recession limb is representative of old water is recognized as a major limitation of this study. By making this assumption, it is implicit that each watershed must have a runoff generation mechanism that results in old water being a large portion (theoretically 100%) of streamflow during the rising or recession limb of the hydrograph. It is unlikely that runoff generation mechanisms (discussed later) at any of the sites are responsible for flushing such large volumes of old water into the stream at the beginning or the end of stormflow. Undoubtedly, both the rising and recession limbs are composed of some old water, but exactly how much is uncertain.

Few other studies of runoff generation in small headwater catchments and could be found that used an alternative methodology for estimating old water composition. Weiler et al. (2003) conducted a similar study on the 17.4 ha Maimai watershed (New Zealand), which is similar in size to the watersheds in this study. The Maimai site was, however, equipped with seven 90mm recording wells which were used to obtain isotopic and chemical information about pre-event (old) water (Weiler et al. 2003). Although TMAT and TNEF were part of the ongoing ROCA research study, neither site has been equipped with wells for obtaining old water chemical and isotopic data.

New water estimates, based on tracer data were analyzed by plotting data for all sites and all events on bivariate graphs. When $\delta^{18}O$ and silica were compared in this way, no consistent pattern in the data could be discerned. (Figures 38 and 40). Likewise, no consistent pattern could be detected by plotting new water $\delta^{18}O$ data against new water specific conductance data (Figures 39 and 41) with the exception of the results for TNEF. Specific conductance generated much lower new water percentages for both peak and total runoff at the TNEF site when compared to the other two tracers (Figures 39 and 41). In comparison to the mined sites, stream water specific conductance values were much lower at the TNEF site for all three storms. Unfortunately, the new water specific conductance data at the mined sites were highly variable and direct site to site comparisons could not be made for this data set. Inconsistencies in the specific conductance data among sites are discussed in a following section. The lack of a consistent pattern among storms, sites, or tracers, suggests that there may be a problem with the methodology used in this study, or a problem with using the hydroistopic technique in zero order watersheds.

One problem that occurred for all storms at several sites was that $\delta^{18}O$ values of stream samples at peak flow were more dilute than the rainfall $\delta^{18}O$ values. This problem occurred at all sites for the September 17, 2004 event, at TMAT for the April 22, 2006 event, and at TMAT, TSNR and TSSR for the May 14, 2006 event (Figures 6-10, 12 and 15). This problem also occurred in the Kendall et al. (2001) study when examining runoff generation at a small grassland catchment near Nanjing, China. In this study, $\delta^{18}O$ separations in the Kendall et al. (2001) estimated that between 98-112% of quickflow was new water. In the Kendall

(2001) study, estimates above 100% were a result of spatial variability of $\delta^{18}O$ in groundwater values throughout the watershed. This explanation could be, in part, responsible for variation in new water estimates in the present study, although the present study did not make use of groundwater samples for estimating old water.

Although the method by which the present study estimates old water composition may have violated a critical assumption of the hydroisotopic methodology, this violation did not render the data generated by the study useless. Obvious dilution (or concentration) trends were apparent in the data at all sites, storms and tracers examined. As expected, in most cases maximum dilution occurred near or at the hour of peak discharge. New water estimates by all three tracers at the forested TNEF site were similar to several other studies.

All three tracers used in this study showed that old water provided at least 50% of total runoff at TNEF for each of the three storm events (Table 7). This finding was supported by results from several other hydroisotopic (and chemical) studies that found groundwater to be the major (more than 50%) component of stormflow in humid, temperate, moderate rainfall environments (Sklash et al. 1976, Kennedy et al. 1986, McDonnell et al. 1990). One hydrograph separation study, performed in a forested watershed in north-central Maryland, found that groundwater (old water) was the major contributor to stormflow with old water accounting for up to 90% of total runoff (Rice and Hornberger 1998). These results were also similar to those found nearly 25 years earlier by Sklash and Farvolden (1979) in Ontario catchments and by Turner et al. (1987) in the Salmon River catchment in Western Australia.

The hydrograph separation study of Wels et al. (1991) study showed that silica yielded a well-defined separation of streamflow into surface flow (new water) and subsurface stormflow (old water) since silica is essentially absent in rain water and its concentration varies little throughout the soil profile. The success of using silica as a natural tracer in other hydrograph separation studies combined with the ability to conduct the analyses at the Appalachian Lab, made silica a suitable tracer for the present study. Upon examining the silica data for the three storm data set, it was obvious that a dilution of stream water silica concentrations occurred during all three storms and at all sites. The TNEF and TSNR sites, however, provided erratic silica concentrations during the rising and recession limbs that could not be explained by the mixing theory of the hydrochemical technique (Figures 7, 10, 11 and 14).

The silica time series data also produced very different new water estimates compared to the $\delta^{18}O$ and specific conductance (Figures 38 and 40). One disadvantage of using silica as a tracer is that stream water silica concentrations can be impacted by watershed processes. The presence (or lack thereof) of dissolved silica in stream water is a result of mineral weathering. The physical disturbance of soils in mined watersheds undoubtedly impacts the processes that result in the export of silica in a given watershed. Post mining conditions result in different soil layers near the surface as a result of mixing during the stockpiling and reapplication of overburden. The physical disturbance by heavy machinery and the breaking apart of rock during the blasting phase, results in weakly consolidated rock fragment throughout the stockpiled overburden. Several studies have shown mining and reclamation activities to significantly alter the contents of all soil horizons and the processes by which they are affected (Thomas et al. 2000, Roberts et al. 1988). As a result of soil mixing, it is likely that silicate rocks are weathered at different rates within a watershed resulting in heterogeneous silica concentrations in soils throughout the watershed. The Giffen (2004) study showed that the forested TNEF site exported significantly more silica than the mined TMAT site. Such results indicate that silica export at mined watersheds may not be a result of primary silicate or aluminosilicate weathering (Giffen 2004). The heterogeneity of silica in mined soils across a watershed could explain the erratic behavior in silica concentrations of samples from the recession limb at the mined sites. If this is in fact the case for mined watersheds, this violates the of the mixing theory assumption that tracer (silica) concentrations do not vary in the soil profile or spatially across a watershed. New water estimates for the silica time series were highly variable at all three mined sites and TMAT in particular. At TMAT, the new water percent of total runoff ranged from 28% for the September 17, 2004 event to 94% for the May 14, 2006 event (Table 7). Antecedent conditions may explain some of the variability for silica estimates for a particular site, but they do not account for the large variation in new water estimates observed at TMAT and the other mined sites (Figures 38 and 40). The results from this study suggest that silica may be a problematic tracer and should not be used when attempting to separate hydrographs in small mined watersheds.

Specific conductance analysis has been also used in many studies to separate stormflow into old water and new water portions (Matsuyabashi et al. 1993, Sklash et al. 1976, Pilgrim et al. 1979, Sklash and Farvolden 1979, and Freeze and Cherry 1979). Despite the variety and the numerous sources of ions within a watershed, specific conductance has served as an effective tracer in hydrograph separation studies. Perhaps the most favorable reason to use the measurement of specific conductance as a chemical tracer is that there are relatively few ions in rainfall compared to surface waters. Because rainfall has generally low specific conductance values, old water and new water will have unique and distinct specific conductance signatures, thus allowing hydrograph separation. Other reasons why this study used specific conductance as a tracer were that the analysis is cheap, relatively easy to perform, and could be done quickly at the Appalachian Laboratory. While the estimates of new water provided by the silica and ^{18}O time series were in some instances dramatically different from storm to storm; it is interesting that the specific conductance time series data for the three events produced the most consistent results (Figure 2 and 4).

Despite the apparent success of using specific conductance as a tracer to separate hydrographs it is known that watershed sources of ions are numerous; stream water conductance values can thus be influenced by a variety of ion sources and processes within a watershed. The large differences observed in specific conductance values among sites, suggest that specific conductance values are indeed being influenced by a variety of watershed processes. This influence was particularly apparent in the TNEF data series. Although dilutions were apparent near peak discharge at the TNEF site, the total ionic flux was not as pronounced when compared to the three mined watersheds. Like silica, because specific conductance can be impacted by a variety of processes, it is likely that the disturbance by mining and reclamation resulted in spatially heterogeneous specific conductance values across the mined watersheds. Likewise, the heterogeneity of specific conductance values in mined soils, either vertically or laterally, violates an assumption of hydrochemical mixing theory. For both peak and total new water, when specific conductance estimates were plotted against ^{18}O estimates, new water estimates at TNEF fell below the 1:1 line and were very similar for the three storms investigated (Figures 39 and 41). Conversely, no pattern could be detected for any of the three mined sites (Figures 39 and 41). These results suggest that the TNEF site may not be violating this important assumption of the mixing theory, while all of the mined sites may be violating this critical assumption. These results further support the claim that mining and reclamation activities do cause heterogeneity in specific conductance values in mined soils, leading to the conclusion that new water estimates based on specific conductance may be somewhat erroneous. Based on the trends observed in Figures 39 and 41, it appears that specific conductance data underestimates the new water contributions at all of the mined sites.

The third and final tracer used in this study was the stable isotope of Oxygen, ^{18}O. There are a plethora of studies that have used $\delta^{18}O$ as a natural tracer dating back to Sklash et al. study (1976). Since the first hydrograph separation study using ^{18}O as a tracer, many studies have used ^{18}O as a tracer and have made important contributions and insights into the isotopic hydrograph separation method as applied to watersheds in many different ecological settings (McGlynn et al. 2003, McDonnell et al. 1990, Kendall et al. 2001, Sklash and Farvolden 1979, and Freeze and Cherry 1979). A particular advantage of using $\delta^{18}O$ as a tracer is that it is non-reactive and is not impacted by watershed processes. The ^{18}O isotope in water has a conservative property, where the ^{18}O isotopic content ($\delta^{18}O$) of a mass of water can be altered only by mixing with water of a different isotopic concentration. The chemical reactions that affect ionic concentrations (specific conductance) do not affect $\delta^{18}O$ of water (Sklash et al. 1976). Also, unlike silica and specific conductance, $\delta^{18}O$ stream water is not influenced by watershed processes that may occur prior to or even during the course of a storm. Sklash et al. (1976) states that groundwater attains a uniform isotopic character where isotopic fractionation and mixing from precipitation are the only two likely factors to cause a change in groundwater $\delta^{18}O$. In theory, $\delta^{18}O$ should be a perfect tracer for hydrograph separation purposes. As discussed earlier, assumptions of the hydroisotopic technique can, however, be violated. Several studies have investigated how ^{18}O and other tracers are thought to violate the assumptions, which are critical to the mixing theory method of separating hydrographs.

McDonnell (1990) attempted to develop a methodology using a sequential rainfall collector to account for variations in temporal isotopic rainfall concentration. More recently, Weiler et al. (2003) have developed the TRANSEP model, which not only accounts for temporal variation in rainfall, but also the timing and mixing of pre-event (old) and event (new) water. In the present study, bulk precipitation was collected at the TSSR site at the end of sampling, approximately 48 hours later. This study, unfortunately, did not make use of the methodology described by Weiler et al. (2003) and McDonnell (1990) due to budget limitations, the unpredictable nature of precipitation events, and the difficulty of successfully collecting time series samples at four different watersheds. In future studies in the George's Creek Basin, a sequential rainfall sampler as described by McDonnell et al. (1990) is recommended so that some of the temporal variation is accounted and corrected for when calculating estimates of new water. It is also recommended that several rainfall collectors be installed at several other locations around the George's Creek basin to account for spatial variation.

The primary goal of this study was to determine if differences in watershed-scale stormflow responses and runoff mechanisms in zero order watersheds could be detected using conventional hydrologic methods. As discussed, the hydroisotopic results may be inaccurate and relying solely on these results may be erroneous in attempting to characterize the hydrologic response of each of the four watersheds.

The hydroisotopic data do, in most cases, support the results from the straight line separations and the infiltration experiments. In fact, new water data generated by three tracers used in this study offer many insights into how the watersheds in this study respond hydrologically. In the following discussion, results from each of the independent field measurements are used to develop a conceptual model of how each watershed generates runoff. The conceptual models that follow aim at answering the most important question of the study: Can conventional hydrologic techniques be used to determine reclamation success?

This study used the straight line hydrograph separation technique to the generate rainfall-runoff response for 13 storms occurring between September 2004 and June 2006 for each of the four watersheds. Total surface runoff, direct runoff, runoff ratios, peak stormflow and centroid lag were calculated using the straight line method in both the present study and the Negley (2000) study. Data from each of these parameters revealed that the mined watersheds, TMAT and TSSR, exhibited similar hydrologic responses. Interestingly, the mined TSNR site behaved much like the forested TNEF site in terms of rainfall-runoff response. The TMAT and TSSR sites tended to be flashier, whereas TNEF and TNSR tended to have a dampened hydrologic response.

This study suggests that the dramatic transformation of soil properties during mining and reclamation activities resulted in increased runoff generation, higher average new water percentages, and the overall flashy nature of storm hydrographs at TMAT and TSSR. The watershed characteristic that appears to best predict the dramatic responsiveness of TMAT and TSSR is soil infiltration capacity. The lack of topsoil at these sites, combined with the compaction of surface soils during reclamation activities, greatly decreased the infiltration capacities at TMAT and TSSR to less than 1 cm/hr compared to 3 cm/hr at TSNR and 50 cm/hr at TNEF (Figures 21 and 22). The low infiltration capacities observed at TMAT and TSSR are typical of minesoils investigated in other studies. Both the Chong and Cowsert (1997) study, as well as the Geubert and Gardner (2001) study, showed that the infiltration rates of post mining soils were near or less than 1 cm/hr. If the rainfall rate does, in fact, exceed the soil infiltration capacity during a storm event, water is routed to the stream by the process known as Hortonian (or infiltration excess) overland flow. Once rainfall intensity exceeds the infiltration capacity during a particular event, runoff rises rapidly to a sharp peak, followed by a rapid decline once rainfall intensity decreases (Horton 1933).

At both TMAT and TSSR, evidence of infiltration-excess overland flow was apparent. At both sites, rills have formed on the soil surface and water has been observed flowing through the rills during storm events. In theory, all surface mined sites have the potential to store large volumes of water in the soil. This theory is based on the idea that a surface mined area is essentially a large pit with homogenized soils. All natural impermeable layers such as clay and bedrock are destroyed when the initial overburden is removed and stockpiled. However, because of the extremely low infiltration rates at TMAT and TSSR, it is likely that very little of the potential storage volume is utilized as water cannot infiltrate the soil surface or percolate rapidly through soil profile. In fact, it appears that the increased proportion of clay in surface soils brought to the surface during reclamation activities create a relatively impervious layer that limits soil infiltration. One would expect that the primary runoff mechanism in a watershed that contains soils with such low infiltration capacities would be infiltration excess overland flow producing higher stormflow peaks, runoff ratios, total runoff and new water contributions to runoff.

For the 13 storms analyzed between September 1, 2004 and June 1, 2006, maximum rainfall intensities consistently exceeded the maximum rate at which precipitation could infiltrate surface soils at TMAT and TSSR (Figures 21 and 22, Table 4). The Negley (2000) study also found this result to be true for 15 storms investigated at the TMAT site between 1998 and 2000. The decrease in rainfall abstraction (water that never reaches the stream) at TMAT and TSSR resulted in increased total stormflow, runoff ratios, peak runoff rates and higher average new water estimates (for all three tracers) (Tables 4-8). For the four storms used to create the runoff hydrographs, runoff peaks at TMAT and TSSR were never exceeded by the runoff peaks at TNEF and TSNR (Figures 17-20). In fact, runoff ratios and peak runoff rates at TMAT and TSSR were more than double the values for those found at TNEF and TSNR. Such findings are supported by Schueler (1994) who found that increasing the imperviousness of a watershed by

35% to 50% can increase the runoff volume up to 20%. Negley and Eshleman (2006) found the peak runoff rates were on average two times greater at TMAT when compared to TNEF for fifteen storms occurring between 1998 and 2000. Likewise, for the 13 storms occurring between September 2004 and June 2006, peak runoff rates at TMAT were again, on average, two times greater than at TNEF. For the four watersheds investigated in this study, peak runoff rates were 1.70 mm/hr (s.e.= 1.61) at TMAT, 0.85 mm/hr (s.e.= 1.19) at TNEF, 0.67 mm/hr (s.e.= 0.96) at TSNR, and 2.35 mm/hr (s.e.= 1.27) at TSSR (Table 5). It is apparent from the rainfall-runoff response analysis that runoff generation at the TMAT and TSSR watersheds is dominated by Hortonian overland flow.

Not only should watersheds dominated by Hortonian overland flow exhibit increased peak and total runoff, but a large portion of the runoff should, hypothetically, be new water. Although the results from the hydroisotopic (and chemical) separations for the three storms may be problematic, they do support the theory that runoff generation at TMAT and TSSR is dominated by infiltration excess overland flow. Results from the September 17, 2004 storm event particularly indicate that Hortonian overland flow is the primary runoff generation mechanism at TMAT and TSSR. The $\delta^{18}O$ data estimated that stream water at the TMAT, TSNR and TSSR watersheds was 100% new water at peak discharge for this event (Table 8). Likewise, the new water percentages of total runoff were high as well at TMAT and TSNR at 83.9% and 97.2%, respectively (Table 7). Total new water runoff, unfortunately, could not be computed for the TSSR due to the sampling problems. The forested site responded more conservatively as expected, with new water at peak flow being 52.6% and the percentage of total runoff was 51.1% (Table 8). The three storm averages for percent new water at peak runoff and of total runoff were higher at TMAT and TSSR for all three tracers (Tables 7 and 8). Theoretically, when plotted against direct runoff, the new water depths (and percentages) of both total and peak runoff should fall near the 1:1 line in watersheds where the hydrograph is dominated by Hortonian overland flow suggesting that a large portion of direct runoff is new water. This 1:1 correspondence is the case for both TMAT and TSSR for peak runoff depth (Figure 43) as points fall near and sometimes above the 1:1 line. Likewise for total runoff at TMAT, points again fall near or on the 1:1 line indicating that, in fact, a large portion of runoff at TMAT is composed of new water. Total new water runoff could only be calculated for the May 14, 2006 storm at TSSR, thus preventing similar interpretations for the site. Based on the peak flow data, it is likely that both peak and total runoff are largely comprised of new water.

Although the primary runoff mechanism at TMAT and TSSR is theorized to be infiltration-excess overland flow, this flow is not the sole runoff mechanism in either watershed. If Hortonian overland flow was the only runoff mechanism at these watersheds, then stream flow would stop within minutes following the cessation of rainfall. Cessation of runoff, however, does not occur abruptly at either watershed. Depending on the storm characteristics, stream flow continued for several days after the precipitation had ceased. This result suggests that despite the low infiltration capacities at TMAT and TSSR, some water is effectively percolating through soil, following a subsurface flow path, and sustaining streamflow beyond the end of rainfall. The TMAT site is 47% mined and 53% forested. Likewise, although the TSSR[2] site is 100% mined, 59% of the 12.5 ha is covered with a forest, which was planted during reclamation activities in the late 1970's. To what degree the forested portions of each watershed are influencing the hydrologic response and streamflow is not entirely understood and continues to be investigated at both sites. Given that the forested portion of TMAT is very similar in geography, vegetation and physical soil characteristics, it is thought to behave hydrologically much like the TNEF site. That is, runoff generation is thought to be dominated by shallow subsurface stormflow and, to a lesser degree, by groundwater. The forested portion of the TSSR site is thought to behave hydrologically much like the TSNR site, in that they are of similar reclamation age and both have well established vegetation. Runoff generation at the TSNR site is thought to be dominated initially by shallow subsurface flow and then by saturation overland flow as the storm progresses. Runoff generation mechanisms at the TNEF and TSNR sites are discussed at length.

TNEF and TSNR exhibited similar hydrologic responses to 11 storms between January 1, 2005 and June 1, 2006, abstracting considerably more rainfall per event than the TMAT and TSSR watersheds (Table 4). The soils at the forested TNEF site are well established, well drained, and exhibit high infiltration capacities, thus they are capable of quickly abstracting rainfall amounts (Negley

2000). Likewise, the pre-mining soils of the TSNR watershed were similar to TNEF, being well drained. Given the vegetation success at TSNR, soils at this site appear to be of much high quality than those at TMAT or TSSR, consistent with the relatively high infiltration capacities of TNEF and TSNR (50 cm/hr and 3 cm/hr, respectively, Figures 21 and 22). The primary runoff mechanism in well drained soils with large infiltration capacities is shallow subsurface stormflow (Dunne and Leopold 1978). Despite the large difference in infiltration capacity between the two sites, at no point in any storm did rainfall intensity exceed the soil infiltration capacity at either site. Although post mining soil properties at TSNR indicate that mining and reclamation activities have altered soil hydrologic properties from pre-mining conditions, the ability of these soils to abstract rainfall is apparent.

Because rainfall intensity never exceeded soil infiltration capacity at TNEF and TSNR, it is likely that hydrographs of these sites are influenced, to some degree, by shallow subsurface stormflow. At the TNEF site, Negley (2000) suggested that after the initial wetting of the soil at the onset of an event, the wetted soil water is routed quickly to the stream via a subsurface stormflow mechanism. The subsurface runoff generation mechanism is well documented in the literature (Freeze 1974, Beven and German 1982, McDonnell et al. 1990). The particular subsurface stormflow path at TNEF is thought to be rather shallow. One physical characteristic of the TNEF site is that the soils are relatively shallow (for a forested site) and tend to be very rocky, which is typical of forests on the

Allegheny Plateau. Precipitation onto the shallow, loamy, well drained soils at TNEF infiltrates rapidly into the soil profile, but percolation is then impeded by the shallow bedrock layer. Dunne and Leopold (1978) suggest that water accumulates above this impermeable layer and then is routed downhill through the permeable topsoil to the stream channel quickly enough to dominate the hydrograph. This process displaces water stored in the soil, theoretically flushing old water into the streams and storing a large portion of the new water in the soil. Subsurface stormflow at TNEF may also be supported by rapid flow through the thick surface organic layer that is characteristic of forested soils. Watersheds dominated by this runoff mechanism should, in theory, produce lower runoff ratios, total and peak runoff and new water estimates, and a delayed centroid lag. The results from both this study, and the Negley and Eshleman (2006) study suggest that this flow path is a major influence on hydrographs at the TNEF site.

TNEF responded hydrologically as expected, in that, it exhibited reduced peaks, relatively low new water percentages, and generated much less runoff when compared to the mined sites. As discussed in earlier sections, peak runoff at TNEF was, on average, only half of what was observed at TMAT and TSSR (Table 5). Moreover, TNEF also exhibited the lowest runoff ratio at 0.09 (Table 4). Likewise, TNEF exhibited the lowest new water percentages of the four sites. The average new water percentages for both peak and total runoff were much lower than TMAT and TSSR (Tables 7 and 8). Average new water percentages for peak and total runoff at TNEF were below 50% for all tracers and were consistent with hydroisotopic results from other studies in humid regions that experience moderate rainfall (Sklash et al. 1976, Kennedy et al. 1986, McDonnell et al. 1990, and Rice and Hornberger 1998). Interestingly, Negley (2002) found the shapes and timing of unit hydrographs for TMAT and TNEF to be strikingly similar. Negley (2002) suggested that in order for the unit hydrographs to be so similar at TNEF and TMAT, the subsurface stormflow must be routed as quickly to the stream as it is by the Hortonian overland flow pathway at TMAT. The similarity in the timing of hydrograph peaks at TNEF and TMAT is thought to be, in part, due to the differences in the steepness of the watersheds. The TNEF watershed is much steeper than the TMAT watershed, thus channeling water to the stream at a quicker rate due to gravity. Because of the shallow bedrock layer (and shallow soils) and steeper slopes at TNEF, theoretically runoff would be generated much quicker than other forested watersheds, as rapid infiltration would quickly displace soil water. This scenario would also explain why TNEF does not sustain flow for extended periods between storms. The reduced storage capacity resulting from a shallow impermeable layer would also reduce the watersheds ability to sustain baseflow for long periods. These results indicate that runoff at TNEF is in fact generated by shallow subsurface stormflow as it is in most forested sites in humid regions. The TNEF site, however, differs from other forest watersheds as it has a reduced storage capacity due to shallow soils, which in turn, explains the timing of the hydrographs and the inability of the watershed to sustain baseflow.

One of the most interesting findings of this study was the hydrologic response of the mined TSNR site. Although the shallow subsurface runoff mechanism may be one component of runoff generation at TSNR, it is also likely that runoff is generated by the saturation overland flow mechanism. Recall that the infiltration rate at TSNR is 3 cm/hr, which is higher than the other two mined sites, but much lower than the 30 cm/hr at TNEF. The ability of soils to abstract rainfall is apparent, as it exhibited by a dampened hydrologic response that was similar to the forested TNEF. Musgrave and Holtan (1964) were the first to suggest the saturation overland flow runoff mechanism. Saturation overland flow has two components, return flow and direct precipitation onto saturated areas (Freeze 1972). Return flow, which occurs when a rainstorm is large enough to saturate the water table or an impeding soil horizon, is shallow enough to cause the water table to rise to the surface (Dunne and Leopold 1978). When soils do become saturated, subsurface water escapes from the soil and flows to the stream channel overland (Dunne and Leopold 1978). The second component of saturation overland flow is direct precipitation onto saturated areas. When a portion of the watershed becomes saturated, it does not allow infiltration into the soil. Therefore, the precipitation onto such areas must run off of such areas as saturation overland flow.

Because of the deep homogenized soils due to mining and reclamation, the TSNR site, hypothetically, has a voluminous water storage potential. Unlike the TMAT and TSSR sites, the TSNR site is thought to utilize this water storage potential.

The broad, gentle, well vegetated flanks of the watershed are thought to allow percolation, which then recharges or causes the displacement of water stored in the soils. Precipitation onto the upper watershed is thought to take a shallow subsurface pathway to the stream, eventually causing the water table to rise. As indicated (and discussed later) by the hydrograph characteristics, this process does not happen rapidly at TSNR. As discussed earlier, the soils at TSNR exhibit moderate infiltration capacities (3 cm/hr), the rate at which water moves laterally towards the stream is also thought to occur much slower compared to the same process at TNEF and other forested sites since the slope at TSNR is much less. Hence, the saturation overland flow process at TSNR is thought to be dominated by direct precipitation onto saturated areas and to a lesser degree by return flow. Saturation near the channel and footslopes was observed during and after several storms. If, indeed, most of the saturation overland flow is generated by direct precipitation onto saturated portions of the watershed, the stormflow response of TSNR should exhibit low runoff volumes, reduced peaks and should be largely composed of new water.

The ability of the TSNR site to store water is apparent as it did not respond (generate runoff) to six of the eleven storms (Table 4). Even the forested TNEF generated stormflow for 10 of the 11 storms. Likewise, the runoff ratio at TSNR was much lower than the other two mined sites and similar to the forested site at 0.14 (Table 4). For the four storms where rainfall-runoff response data were available, TSNR had similar peaks and hydrograph shapes to TNEF (Figures 17-

20). The saturation overland flow runoff generation mechanism described at TSNR is also supported by the high new water estimates from the three storm data set. According to the ^{18}O time series, for the September 17, 2004 event, approximately 97% of total runoff and 100% of peak runoff was determined to be new water (Table 7). Average new water percentages for both peak and total runoff were higher than the TNEF site, yet lower than the TMAT and TSSR site for both ^{18}O and specific conductance time series. Figure 43 makes it apparent that what little runoff that TSNR produces is largely composed of new water. When plotting new water peak runoff depth against peak direct runoff depth, all three storms fall near the 1:1 line indicating that a very large portion of runoff at peak flow is new water at TSNR (Figure 43). The results from both the straight line and hydroisotopic hydrograph separations support the idea that saturation overland flow at TSNR is dominated by direct precipitation onto saturated portions of the watershed.

Due to the geographic locations of the mined sites within the George's Creek Basin, the amounts of topsoil that existed at each of the three mined sites was certainly different. The position of TMAT and TSSR watersheds in the George's Creek watershed are much higher in elevation and tend to be more rocky and have little topsoil, whereas the TSNR site is lower in elevation and has more loamy soils (Figure 3). Pre-mining soils were mapped as Cookport silt loam (0-10% slopes) and Cookport very stony silt loam (10-30%) at TMAT and mapped as Cookport very stony silt loam, stony, rolling land, and Buchanan very stony loam at TSSR (USDA Soil Conservation Service 1977). That is, pre-mining soils (or lack thereof) at TMAT and TSSR were very rocky with little topsoil. At TSNR, pre-mining soils were mapped as a mixture of Gilpin silt loam (0-10%), Cavode silt loam, and Shelocta shaly silt loam (0-8%). Despite the similarities in reclamation plan, the differences in topsoil undoubtedly has impacted the quality of reclamation among these mined sites and other mined sites in the area. During mining activities, topsoil is stockpiled adjacent to the site and then is spread by a dozer over the site in the final stages of reclamation. Because of the differences in pre-mining soil types, the pre-mining volume of topsoil available at each of the sites differed substantially. As a result, the amounts of topsoil available for the final reapplication during the reclamation process were also much different between sites. The result end result at the TMAT and TSSR site was compacted surface soils that contained a large amount of clays, little topsoil and high bulk density, and low soil infiltration capacity. At TSNR, however, post-mining soils contain much more topsoil that currently supports a variety of grass and clover species.

Another factor that cannot be ignored when examining differences in rainfall abstraction among the mined sites is post reclamation vegetation success. Although the reclamation plans are similar at all sites (and are in accordance to PL 95-87) due to the differences in amount of topsoil at each site, the quality of reclamation was quite different among the mined and reclaimed lands. The difference in soil quality and quantity among the sites is apparent by the success of vegetation at each site. TSNR is presently covered with a variety of grass and clover species and revegetation of the site has been so successful that it is cut annually for the production of hay. The dense vegetation and loamy post mining soils at TSNR help this watershed retain water, contributing to lower runoff yields and new water ratios. At TMAT and TSSR, post reclamation vegetation has been much less successful compared to TSNR. At TMAT and TSSR, the poor post mining surface soil and the associated vegetation (or lack thereof) are likely to contribute to the higher runoff yields and new water contributions observed at these watersheds.

The conceptual models of runoff generation described above offer valuable insight into how these particular watersheds generate runoff. Furthermore, and more central to this study, the models also suggest that results from conventional hydrologic techniques can be synthesized and integrated to assess the effectiveness of reclamation. The straight line and hydroisotopic techniques both indicate that the reclamation success of TMAT and TSSR sites was poor, as they are generally more "flashy", exhibiting higher runoff peaks, runoff ratios and new water contribution, than the TMAT site. The TSNR site, however, appears to have recovered hydrologically as it produces stormflow hydrographs similar to the forested TNEF site. New water was found to be somewhat higher at TSNR than TNEF, indicating that although recovered, the runoff mechanism at TSNR remains altered as a result of mining.

Chapter V: CONCLUSIONS

The primary goal of the study was to determine whether results from the hydroisotopic and straight line hydrograph separations could be used to assess success of reclamation at three zero order mined watersheds of various reclamation ages. Similarly, a secondary goal was to determine if using such conventional methods could be employed with success at the zero order watershed scale comparable to their application at the small watershed and river basin scale. A final goal was to determine the effectiveness of the three tracers used in this study: ^{18}O, silica, and specific conductance. Data from 13 storms occurring between September 2004 and June 2006 were used to characterize the rainfall-runoff response of each of the four watersheds via the straightline hydrograph separation technique. Likewise, time series data were collected for three storms occurring on September 17, 2004, April 22, 2006, and May 14, 2006 to estimate new water contributions to the hydrograph at each of the four watersheds via the hydrisotopic hydrograph separation technique. Data generated by both the straightline and the hydroisotopic techniques were then combined with results from the infiltration experiments to develop a conceptual model of how each of these watersheds generates runoff.

A multitude of studies have used ^{18}O, silica and specific conductance as tracers and have found them to be effective natural tracers for hydrograph separation purposes. This study also found that ^{18}O, silica and specific conductance time series data to be valuable, as dilutions in stream water values of the tracers were obvious and timing of the dilutions generally corresponded to peak discharge. Likewise, all three tracers estimated that old water provided over 50% of total runoff at the forested TNEF. This finding was encouraging to this study, as these results were similar to those found in other hydrograph separation studies. Despite these encouraging results, all three tracers exhibited limitations. All three tracers were thought to violate assumptions concerning the chemical homogeneity of old water, which were critical to the mixing theory of hydrograph separation. Several studies have found ^{18}O to exhibit spatial and temporal variability, despite its success in a plethora of studies. Although it could not be avoided, assuming that a sample from either the rising or recession limb of the hydrograph is representative of old water was a problematic assumption and may have led to erroneous new water estimates. Specific conductance and silica were also thought to violate a mixing theory assumption, as values of each tracer were thought to vary spatially within a watershed and vertically through the soil profile as a result of mining and reclamation activities. The spatial heterogeneity of both silica and specific conductance at the mined sites made the interpretation of new water estimates difficult.

Surface mining and reclamation impacted the hydrologic response of the mined TMAT and TSSR watersheds more dramatically than the mined TSNR watershed. The infiltration, straight line, and hydroisotopic results each indicated that hydrologically, the reclamation success of TMAT and TSSR sites was poor. TMAT and TSSR are characterized as generally being more "flashy", exhibiting higher runoff peaks, higher runoff ratios and greater percentages of new water than TSNR. The results at both TMAT and TSSR suggested that the primary runoff mechanism is Hortonian overland flow at these sites. Evidence for infiltration excess overland flow is evident at both sites, as rills have formed on the surface of both watersheds. However, the forested portions of both watersheds are thought to influence hydrographs by producing runoff via a shallow subsurface stormflow mechanism. The inability of the TMAT and TSSR watersheds to abstract rainfall is thought to be largely due to soil compaction and the mixing of clays into surface soils, thus reducing the infiltration capacities of these sites.

Interestingly, the TSNR site, which was reclaimed at approximately the same time as TMAT, responded similarly to the forested TNEF site. A dampened hydrologic response was observed at both the TSNR and TNEF sites compared to TMAT and TSSR. Average peak discharge at both TSNR and TNEF was, in fact, less than half that observed at the TMAT and TSSR sites. Likewise, runoff ratios and total runoff were lower at these sites as well. Although TSNR exhibited a similar hydrologic response as the forested TNEF site, TSNR is not thought to have recovered completely from surface mining and reclamation activities. New water estimates were substantially higher at TSNR than at TNEF, while infiltration capacities were considerably lower. Results from the TSNR site suggest that a large portion of runoff in this watershed is generated by a saturation overland flow mechanism. The TSNR site produces relatively low runoff volumes and reduced runoff peaks compared to the other two mined sites. The moderate infiltration capacity and the large storage capacity of soils at the TSNR site are thought to be, in part, responsible for the dampened hydrologic response of the watershed. Interestingly, the hydroisotopic results suggest that a large portion of the runoff produced by the TSNR site is new water. Return flow is thought to occur very slowly at the TSNR site, and most of the runoff is thought to be produced by direct precipitation onto saturated areas. Precipitation falling onto saturated areas near the channel flows overland to the channel and quickly out of the watershed as new water runoff, thus explaining this phenomenon.

As hypothesized, the forested watershed, TNEF, exhibited the lowest runoff volumes and runoff ratios, as well as lowest estimates of peak and total new water for two of the three tracers. The primary runoff mechanism at the forested TNEF site appears to be shallow subsurface stormflow. Due to its steep slopes, relatively shallow, well drained soils, and a shallow bedrock layer, the TNEF site responds much quicker than expected for a forested site. Timing of hydrograph peaks at TNEF were similar to the mined TMAT site in both this study and the Negley (2002) study. This runoff mechanism also explains the short duration of baseflow between rainfall events at TNEF. The ability of the soils at TNEF to abstract rainfall is much greater than both the TMAT and TSSR sites.

Soil compaction and the mixing of clay with the topsoil during reclamation activities greatly reduced the infiltration capacities at all of the mined sites.

Compaction of the surface soil during reclamation has been recognized as a serious problem throughout the mid-Atlantic Region, as it not only impacts the hydrology of a mined watershed, but is also a concern for post-mining vegetation success. Interestingly, after this study began, the Federal Office of Surface Mining launched the Appalachian Regional Reforestation Initiative (ARRI). The primary goal of this initiative is to create a suitable rooting medium for good tree growth that is no less than 4 feet deep and comprised of topsoil, weathered sandstone and/or the best available material. I believe that there is a need to conduct watershed studies of runoff generation at ARRI sites. Finally, based on the results of this study, it is of the utmost importance that future land management and reclamation plans acknowledge the relationship between surface mining and hydrologic response and vegetation success of small watersheds within the George's Creek Basin.

Appendix I. TMAT tracer data for the September 17, 2004, April 22, 2006 and May 14, 2006 storm events.

Date	Sample	18-Oxygen	Conductance	Silica
9/17/2004 10:30	tMAT A1	-6.3	69.72	2.7949
9/17/2004 12:30	tMAT A3		66.75	2.3943
9/17/2004 14:30	tMAT A5	-5.93	65.04	2.5562
9/17/2004 16:30	tMAT A7		65.38	2.6497
9/17/2004 17:30	tMAT A8		63.78	2.5628
9/17/2004 18:30	tMAT A9		57.41	2.5767
9/17/2004 19:30	tMAT A10	-5.63	49.28	2.3982
9/17/2004 20:30	tMAT A11		36.67	2.0376
9/17/2004 21:30	tMAT A12	-6.17	37.87	1.9212
9/17/2004 22:30	tMAT A13		33.08	
9/17/2004 23:30	tMAT A14	-8.84	25.15	1.4452
9/18/2004 0:30	tMAT A15	-8.78	24.56	1.6093
9/18/2004 1:30	tMAT A16		28.19	1.8091
9/18/2004 2:30	tMAT A17		29.89	1.8324
9/18/2004 3:30	tMAT A18		30.1	1.8957
9/18/2004 4:30	tMAT A19		30.21	1.87
9/18/2004 5:30	tMAT A20		30.24	1.924
9/18/2004 6:30	tMAT A21	-8.69	30.5	2.0249
9/18/2004 7:30	tMAT A22		31.72	2.1078
9/18/2004 8:30	tMAT A23		32.64	2.1024
9/18/2004 9:30	tMAT A24		34.22	2.135
9/18/2004 10:30	tMAT B1	-8.11	33.76	2.2182
9/18/2004 14:30	tMAT B3		37.42	2.3496
9/18/2004 18:30	tMAT B5		39.78	2.3701
9/18/2004 22:30	tMAT B7	-7.71	44.23	2.3269
9/19/2004 2:30	tMAT B9		46.22	2.3337
9/19/2004 6:30	tMAT B11		46.58	2.295
9/19/2004 10:30	tMAT B13	-7.66	48.79	2.3314
9/17 to 9/19 2006	Precip	-8.09	5.64	0.1222
4/22/2006 2:00	tmat1		102.52	1.3849
4/22/2006 3:00	tmat2		78.19	0.7082
4/22/2006 4:00	tmat3		72.77	0.3169
4/22/2006 5:00	tmat4		76.02	0.1816
4/22/2006 6:00	tmat5	-5.88	75.59	0.2536
4/22/2006 7:00	tmat6	-5.72	68.36	0.2378
4/22/2006 8:00	tmat7	-5.87	61.96	0.2087
4/22/2006 9:00	tmat8		60.7	0.1852
4/22/2006 10:00	tmat9		60.62	0.2045
4/22/2006 11:00	tmat10		55.56	0.3121
4/22/2006 12:00	tmat2b	-5.54	52.33	0.2383
4/22/2006 13:00	tmat3b		52.49	0.1584
4/22/2006 14:00	tmat4b		55.23	0.1819
4/22/2006 15:00	tmat5b		55.61	0.116

Date	Sample	18-Oxygen	Conductance	Silica
4/22/2006 16:00	tmat6b	-6.13	56.23	0.2135
4/22/2006 17:00	tmat7b		55.9	0.2512
4/22/2006 18:00	tmat8b		56.09	0.1458
4/22/2006 19:00	tmat9b		56.09	0.294
4/22/2006 20:00	tmat10b	-6.3	57.12	0.0617
4/22/2006 21:00	tmat11b		57.05	0.0475
4/22/2006 22:00	tmat12b		56.84	0.2512
4/22/2006 23:00	tmat13b		57.58	0.1613
4/23/2006 0:00	tmat14b		57.78	0.294
4/23/2006 1:00	tmat15b		57.92	0.3249
4/23/2006 2:00	tmat16b		58.86	0.0475
4/23/2006 3:00	tmat17b		59.05	0.0635
4/23/2006 4:00	tmat18b		59.45	0.1613
4/23/2006 5:00	tmat19b		60.12	0.1559
4/23/2006 6:00	tmat20b	-6.7	60.92	0.3249
4/23/2006 7:00	tmat21b		61.18	

Appendix II. TNEF tracer data for the September 17, 2004, April 22, 2006 and May 14, 2006 storm events.

Date	Sample	18-Oxygen	Conductance	Silica
9/17/2004 10:00:00	tNEF A1	-8.06	40.62	6.65
9/17/2004 12:00:00	TNEFA3		41.78	6.77
9/17/2004 14:00:00	TNEFA5		43.17	6.79
9/17/2004 16:00:00	TNEFA7		44.37	6.84
9/17/2004 18:00:00	TNEFA9	-7.34	42.51	6.21
9/17/2004 19:00:00	TNEFA10		38.37	4.11
9/17/2004 20:00:00	TNEFA11	-6.51	38.47	4.36
9/17/2004 21:00:00	TNEFA12		37.01	
9/17/2004 22:00:00	TNEFA13	-6.68	34.35	3.50
9/18/2004 00:00:00	TNEFA15		36.72	3.19
9/18/2004 01:00:00	TNEFA16		36.61	3.60
9/18/2004 02:00:00	TNEFA17		35.90	3.97
9/18/2004 03:00:00	TNEFA18		35.27	4.17
9/18/2004 04:00:00	TNEFA19	-8.26	36.94	4.10
9/18/2004 05:00:00	TNEFA20		38.30	4.37
9/18/2004 06:00:00	TNEFA21		39.98	
9/18/2004 07:00:00	TNEFA22		41.29	4.95
9/18/2004 08:00:00	TNEFA23		40.25	5.14
9/18/2004 09:00:00	TNEFA24	-7.85	39.82	5.34
9/18/2004 10:00:00	tNEF B1		40.36	5.54
9/18/2004 15:00:00	tNEF B3		40.92	5.82
9/18/2004 17:00:00	tNEF B5	-7.98	41.36	6.01
9/19/2004 01:00:00	tNEF B8		41.93	6.16
9/19/2004 05:00:00	tNEF B10		42.28	6.18
9/19/2004 09:00:00	tNEF B12	-8.08	41.82	6.23
9/17 to 9/19 2006	Precip	-8.09	5.64	0.12
4/22/2006 00:00:00	tnef1		41.15	1.37
4/22/2006 01:00:00	tnef2		40.02	1.03
4/22/2006 02:00:00	tnef3	-8.52	40.06	1.12
4/22/2006 03:00:00	tnef4	-8.26	44.22	0.95
4/22/2006 04:00:00	tnef5	-8.18	51.98	0.76
4/22/2006 05:00:00	tnef6		54.47	1.09
4/22/2006 06:00:00	tnef7		54.92	1.20
4/22/2006 07:00:00	tnef8		52.38	0.88
4/22/2006 08:00:00	tnef9	-7.86	52.57	1.03
4/22/2006 09:00:00	tnef10		53.33	1.19
4/22/2006 10:00:00	tnef11		53.29	1.22
4/22/2006 11:00:00	tnef12		51.94	0.85
4/22/2006 12:00:00	tnef13	-8.07	41.17	1.24
4/22/2006 13:00:00	tnef2b		54.02	1.21
4/22/2006 14:00:00	tnef3b		55.56	1.28
4/22/2006 15:00:00	tnef4b		51.26	1.02
4/22/2006 16:00:00	tnef5b		51.9	1.67

4/22/2006 17:00:00	tnef6b	-8.23	50.95	1.85
4/22/2006 18:00:00	tnef7b		50.97	1.53
4/22/2006 19:00:00	tnef8b		49.17	1.44
4/22/2006 20:00:00	tnef9b		49.76	
4/22/2006 21:00:00	tnef10b		47.57	2.33
4/22/2006 22:00:00	tnef11b		48.48	
4/22/2006 23:00:00	tnef12b		48.3	2.34
4/22/2006 23:59:59	tnef13b		48.2	
4/23/2006 01:00:00	tnef14b	-8.3	47.99	1.10
4/23/2006 02:00:00	tnef15b		48.16	
4/23/2006 03:00:00	tnef16b		51.58	1.55
4/23/2006 04:00:00	tnef17b		46.8	
4/23/2006 05:00:00	tnef18b		47.27	1.22
4/23/2006 06:00:00	tnef19b		47.34	
4/23/2006 07:00:00	tnef20b		48.36	0.99
4/23/2006 08:00:00	tnef21b		47.13	
4/23/2006 09:00:00	tnef22b	-8.29	46.11	1.25
4/23/2006 10:00:00	tnef23b		48.2	
4/23/2006 11:00:00	tnef24b		48.41	1.50
4/23 to 4/24 2006	Precip	-6.64	13.67	0.02
5/14/2006 15:00	tnef1N		46.25	0.74
5/14/2006 17:00	tnef2N	-8.7	44.72	0.54
5/14/2006 19:00	tnef3N		48.06	0.61
5/14/2006 21:00	tnef4N		48.11	2.41
5/14/2006 23:00	tnef5N	-9.03	47.29	1.13
5/15/2006 1:00	tnef6N		47.12	2.34
5/15/2006 3:00	tnef7N		49.88	1.15
5/15/2006 5:00	tnef8N	-8.54	49.58	1.00
5/15/2006 7:00	tnef9N	-8.02	55.92	0.52
5/15/2006 9:00	tnef10N	-8.01	56.86	0.05
5/15/2006 11:00	tnef11N	-8.31	56.43	1.36
5/15/2006 13:00	tnef12N		53.71	0.90
5/15/2006 15:00	tnef13N		53.86	1.25
5/15/2006 17:00	tnef14N		51.53	1.08
5/15/2006 19:00	tnef15N	-8.59	51.54	1.30
5/15/2006 21:00	tnef16N		50.51	2.74
5/15/2006 23:00	tnef17N		49.13	2.08
5/16/2006 1:00	tnef18N		51.49	2.40
5/16/2006 3:00	tnef19N		50.19	1.52
5/16/2006 5:00	tnef20N		48.88	0.96
5/16/2006 7:00	tnef21N		48.75	0.96
5/16/2006 9:00	tnef22N		49.12	0.66
5/16/2006 11:00	tnef23N	-8.74	49.02	2.02
5/16/2006 13:00	tnef24N		47.94	2.09
5/14 to 5/16 2006	Precip	-7.44	12.9	0.01

Appendix III. TSNR tracer data for the September 17, 2004, April 22, 2006 and May 14, 2006 storm events.

Date	Sample	18-Oxygen	Conductance	Silica
9/17/2004 18:30:00	TSNR A1	-4.69	316.12	9.06
9/17/2004 19:30:00	TSNR A2		289.22	8.50
9/17/2004 20:30:00	TSNR A3		275.16	8.44
9/17/2004 21:30:00	TSNR A4	-5.5	248.37	7.31
9/17/2004 22:30:00	TSNR A5		197.97	7.38
9/17/2004 23:30:00	TSNR A6	-7.81	170.82	6.59
9/18/2004 00:30:00	TSNR A7	-8.11	182.28	6.36
9/18/2004 01:30:00	TSNR A8		210.4	6.89
9/18/2004 02:30:00	TSNR A9		226.21	
9/18/2004 03:30:00	TSNR A10		233.04	6.72
9/18/2004 04:30:00	TSNR A11	-8.59	224.06	6.80
9/18/2004 05:30:00	TSNR A12		237.07	7.20
9/18/2004 06:30:00	TSNR A13		257.13	6.55
9/18/2004 07:30:00	TSNR A14		273.75	6.83
9/18/2004 08:30:00	TSNR A15	-8.11	276.42	6.32
9/18/2004 09:30:00	TSNR A16		281.1	6.22
9/18/2004 10:30:00	TSNR A17		276.83	6.04
9/18/2004 11:30:00	TSNR B1		278.01	5.94
9/18/2004 13:30:00	TSNR B3		302.34	5.82
9/18/2004 15:30:00	TSNR B5	-7.56	338.53	5.44
9/18/2004 17:30:00	TSNR B7		392.17	5.19
9/18/2004 19:30:00	TSNR B9		435.71	4.88
9/18/2004 21:30:00	TSNR B11	-7.04	466.05	4.68
9/18/2004 23:30:00	TSNR B13		513.39	
9/19/2004 01:30:00	TSNR B15		472.72	4.62
9/19/2004 03:30:00	TSNR B17		500.48	4.80
9/19/2004 05:30:00	TSNR B19	-6.88	468.16	4.80
9/17 to 9/19 2006	Precip	-8.09	5.64	0.12
4/22/2006 05:00:00	tsnr1	-4.24	209.27	2.88
4/22/2006 06:00:00	tsnr2		200.05	3.15
4/22/2006 07:00:00	tsnr3	-4.39	205	3.21
4/22/2006 08:00:00	tsnr4		194.82	3.20
4/22/2006 09:00:00	tsnr5	-4.77	193.51	3.36
4/22/2006 10:00:00	tsnr6		199.64	3.36
4/22/2006 11:00:00	tsnr7		243.38	3.51
4/22/2006 12:00:00	tsnr8	-5.41	201.7	3.25
4/22/2006 13:00:00	tsnr9		205.24	3.53
4/22/2006 14:00:00	tsnr10		207.79	3.62
4/22/2006 15:00:00	tsnr2b	-5.66	211.52	3.76
4/22/2006 16:00:00	tsnr3b		228.26	3.87
4/22/2006 17:00:00	tsnr4b		225.99	4.03
4/22/2006 18:00:00	tsnr5b		281.74	3.98
4/22/2006 19:00:00	tsnr6b	-5.49	238.71	4.10
4/22/2006 20:00:00	tsnr7b		245.06	

4/22/2006 21:00:00	tsnr8b		255.82	4.08
4/22/2006 22:00:00	tsnr9b		255.03	
4/22/2006 23:00:00	tsnr10b		339.92	4.12
4/23/2006 00:00:00	tsnr11b		272.05	
4/23/2006 01:00:00	tsnr12b		275.72	4.21
4/23/2006 02:00:00	tsnr13b		273.99	
4/23/2006 03:00:00	tsnr14b	-5.84	276.79	4.14
4/23/2006 04:00:00	tsnr15b		315.12	
4/23/2006 05:00:00	tsnr16b		290.88	4.28
4/23/2006 06:00:00	tsnr17b		292.09	
4/23/2006 07:00:00	tsnr18b		298.05	4.20
4/23/2006 08:00:00	tsnr19b		296.22	
4/23/2006 09:00:00	tsnr20b		297.41	4.08
4/23/2006 10:00:00	tsnr21b		299.8	
4/23/2006 11:00:00	tsnr22b		284.16	4.85
4/23/2006 12:00:00	tsnr23b		284.89	
4/23/2006 13:00:00	tsnr24b	-5.52	286.31	4.51
4/23 to 4/24 2006	Precip	-6.57	13.67	0.02
5/14/2006 15:00	tsnr1Q		276.61	0.20
5/14/2006 17:00	tsnr2Q	-6.28	168.85	2.89
5/14/2006 19:00	tsnr3Q		200.5	3.54
5/14/2006 21:00	tsnr4Q	-6.46	207.61	3.70
5/14/2006 23:00	tsnr5Q		220.69	3.81
5/15/2006 1:00	tsnr6Q		226.23	3.75
5/15/2006 3:00	tsnr7Q	-6.57	214.06	3.25
5/15/2006 5:00	tsnr8Q	-6.24	243.81	3.36
5/15/2006 7:00	tsnr9Q	-7.6	147.22	3.01
5/15/2006 9:00	tsnr10Q		178.49	3.34
5/15/2006 11:00	tsnr11Q		183.12	3.34
5/15/2006 13:00	tsnr12Q		195.27	3.53
5/15/2006 15:00	tsnr13Q	-7.93	210.47	3.69
5/15/2006 17:00	tsnr14Q		226.12	4.26
5/15/2006 19:00	tsnr15Q		240.83	3.87
5/15/2006 21:00	tsnr16Q		261.49	4.02
5/15/2006 23:00	tsnr17Q		285.14	3.91
5/16/2006 1:00	tsnr18Q		305.05	3.91
5/16/2006 3:00	tsnr19Q		319.79	3.82
5/16/2006 5:00	tsnr20Q		316.96	3.67
5/16/2006 7:00	tsnr21Q		320.36	3.70
5/16/2006 9:00	tsnr22Q		323.19	3.70
5/16/2006 11:00	tsnr23Q	-7.47	324.32	3.83
5/16/2006 13:00	tsnr24Q		321.49	3.78
5/14 to 5/16 2006	Precip	-7.88	12.9	0.01

Appendix IV. TSSR tracer data for the September 17, 2004, April 22, 2006 and May 14, 2006 storm events.

Date	Sample	18-Oxygen	Conductance	Silica
9/17/2004 12:00	tssr A1		43.74	
9/17/2004 14:00	tssr A3	-4.56	46.04	4.32
9/17/2004 15:00	tssr A4	-4.05	35.19	3.41
9/17/2004 16:00	tssr A5		37.7	3.65
9/17/2004 17:00	tssr A6	-3.9	35.01	3.55
9/18/2004 12:00	tssr B1	-8.34	38.49	3.75
9/18/2004 14:00	tssr B3		40.85	4.21
9/18/2004 16:00	tssr B5		45.54	4.47
9/18/2004 18:00	tssr B7	-7.3	48.78	4.68
9/18/2004 20:00	tssr B9		48.89	4.70
9/18/2004 22:00	tssr B11		51.97	4.70
9/19/2004 0:00	tssr B13		54.4	4.63
9/19/2004 2:00	tssr B15		55.86	4.63
9/19/2004 4:00	tssr B17		57.14	4.52
9/19/2004 6:00	tssr B19		57.71	4.48
9/19/2004 8:00	tssr B21	-6.76	57.77	4.52
9/19/2004 10:00	tssr B23		54.45	4.47
9/17 to 9/19 2006	Precip	-8.09	5.64	0.12
4/22/2006 0:00	tssr1		49.91	0.14
4/22/2006 1:00	tssr2		52.05	0.14
4/22/2006 2:00	tssr3	-3.66	42.37	0.10
4/22/2006 3:00	tssr4	-3.97	32.22	0.11
4/22/2006 4:00	tssr5	-4.08	31.77	0.14
4/22/2006 5:00	tssr6		36.42	0.25
4/22/2006 6:00	tssr7		31.44	0.19
4/22/2006 7:00	tssr8		28.7	0.17
4/22/2006 8:00	tssr9	-4.86	34.03	0.61
4/22/2006 9:00	tssr10		39.12	0.80
4/22/2006 10:00	tssr11		44.19	1.00
4/22/2006 11:00	tssr12		31.13	0.48
4/22/2006 12:00	tssr13	-6.06	31.55	0.39
4/22/2006 13:00	tssr14		40.43	0.80
4/22/2006 14:00	tssr15		47.72	1.05
4/22/2006 15:00	tssr2b	-5.89	52.72	2.28
4/22/2006 16:00	tssr3b		53.52	1.44
4/22/2006 17:00	tssr4b		53.38	
4/22/2006 18:00	tssr5b		54.64	1.70
4/22/2006 19:00	tssr6b		54.63	
4/22/2006 20:00	tssr7b		53.47	2.57
4/22/2006 21:00	tssr8b		57.6	
4/22/2006 22:00	tssr9b		59.73	2.06
4/22/2006 23:00	tssr10b		52.28	
4/23/2006 0:00	tssr11b	-5.98	53.93	1.06
4/23/2006 1:00	tssr12b		56.92	

4/23/2006 2:00	tssr13b		60.53	2.06
4/23/2006 3:00	tssr14b		62.33	
4/23/2006 4:00	tssr15b		64.34	2.46
4/23/2006 5:00	tssr16b		65.56	
4/23/2006 6:00	tssr17b		65.73	2.07
4/23/2006 7:00	tssr18b		66.91	
4/23/2006 8:00	tssr19b	-5.64	44.21	0.70
4/23/2006 9:00	tssr20b		49.63	
4/23/2006 10:00	tssr21b		55.9	1.47
4/23/2006 11:00	tssr22b		61.99	
4/23/2006 12:00	tssr23b		67.85	2.65
4/23/2006 13:00	tssr24b		71.37	
4/23 to 4/24 2006	Precip	-6.57	13.67	0.02
5/14/2006 15:00	tssr1X		44.88	1.49
5/14/2006 17:00	tssr2X	-6.17	31.21	0.13
5/14/2006 19:00	tssr3X		39.35	0.22
5/14/2006 21:00	tssr4X	-5.94	41.65	0.31
5/14/2006 23:00	tssr5X		45.59	0.83
5/15/2006 1:00	tssr6X	-6.23	23.98	0.09
5/15/2006 3:00	tssr7X	-6.03	28.01	0.24
5/15/2006 5:00	tssr8X	-6.91	18.93	0.09
5/15/2006 7:00	tssr9X	-8.5	27.09	0.40
5/15/2006 11:00	tssr11X		46.85	1.61
5/15/2006 13:00	tssr12X	-7.45	52.88	1.89
5/15/2006 15:00	tssr13X		53.62	2.50
5/15/2006 17:00	tssr14X		61.16	1.49
5/15/2006 19:00	tssr15X		64.07	3.33
5/15/2006 21:00	tssr16X		68.83	3.16
5/15/2006 23:00	tssr17X		72.14	3.10
5/16/2006 1:00	tssr18X		74.53	3.61
5/16/2006 3:00	tssr19X		76.27	3.46
5/16/2006 5:00	tssr20X		78.91	3.63
5/16/2006 7:00	tssr21X		81.72	3.61
5/16/2006 9:00	tssr22X		83.06	3.12
5/16/2006 11:00	tssr23X		83.67	3.00
5/16/2006 13:00	tssr24X	-7.67	87.78	3.66
5/14 to 5/16 2006	Precip	-7.88	12.9	0.01

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