COMPARISON OF PARTICULATE AND DISSOLVED ORGANIC CARBON EXPORTS FROM FORESTED PIEDMONT CATCHMENTS

by

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ABSTRACT

While much is known about dissolved organic carbon (DOC), considerable uncertainty exists regarding the relative contributions of particulate organic carbon (POC) to the total organic carbon (C) flux, especially from small, headwater catchments. This study investigated the temporal patterns and relative contributions of POC and DOC to storm runoff from two (12 and 79 ha) nested, forested catchments in the mid-Atlantic, Piedmont region of USA. A total of 14 storm events were sampled over a 16-month period extending from September 2010 to December 2011. The POC and DOC in runoff samples were separated using a 0.45 μm filter. While the concentrations of both DOC and POC increased with storm-event discharge, the increase in POC concentrations was greater and occurred earlier on the rising limb of the hydrograph. DOC concentrations peaked at or after the discharge peak. End-member mixing analyses suggested that POC transport occurred with surface runoff delivering carbon-rich forest floor material to the stream, whereas DOC export was facilitated by surface runoff and rising groundwater that leached accumulated DOC from surface soil horizons.

Peak POC concentrations decreased with closely spaced, successive storm events whereas no such decrease in concentrations was observed for DOC. On the other hand, very large events with peak discharges exceeding 3mm/hr (storms

associated with remnants of hurricanes) produced a dilution in DOC concentrations at peak flow whereas POC concentrations continued to increase. These results suggest that there are important differences in the storage pools and leaching rates and kinetics for POC and DOC. Concentrations of both POC and DOC decreased with increasing catchment scale (12 to 79 ha) but there was a sharper drop in POC concentrations. POC: DOC ratio dropped from 4.3 at the 12 ha catchment to 2.5 at the 79 ha catchment.

Export of POC and DOC from the study catchment was estimated to be 34 kg C ha^{-1} yr^{-1} and 17.5 kg C ha^{-1} yr^{-1} respectively. Thus, POC was the dominant form of organic carbon export. During stormflow conditions, POC accounted for 84% of the total organic carbon flux from the watershed during storm events. The three largest events in terms of sampled event precipitation (48% of total precipitation) contributed to 84 % and 63 % of the storm-event exports of POC and DOC, respectively. Flow-duration analysis revealed that 90 % of POC and 75 % of DOC was exported during storm flows that were exceeded less than 10 % of the time. These results underscore the importance of POC for the total carbon flux during storm events, as well as the dominant role of large, high-intensity storm events for C flux from catchments. Large, high-intensity storm events that are predicted to increase under future climate-change scenarios will likely enhance the storm-induced carbon flux from catchments with substantial contributions from POC. This study also suggests that POC in headwater catchments could be an important component of fluvial C cycling and its interactions with the atmospheric carbon stores.

Chapter 1

INTRODUCTION

Organic carbon in aquatic systems is operationally classified into dissolved (less than 0.45 µm) and particulate forms (greater than 0.45 µm) (Gimbert *et al.*, 2007, Hope *et al.*, 1994, Thurman, 1985). The transport of organic carbon through streams and rivers plays an important role in global carbon cycling and the regional budgets of organic carbon entering the oceans (Meybeck, 1982, 1993, Robertson *et al.*, 1996, Sarin *et al.*, 2002). Cole *et al.* (2007) estimated that around 0.9 Pg y^{-1} of carbon is delivered from the inland waters to the oceans. However the magnitude and drivers of the carbon flux in the inland water systems such as streams, rivers and wetlands remain poorly understood (Cole *et al*., 2007). Since these systems represent a major pathway in the global carbon cycle, it is important to investigate the concentration and flux of the forms of carbon being transported out of these systems. Understanding dissolved (DOC) and particulate organic carbon (POC) losses and their impact on carbon budgets is also essential to meet the carbon sequestration targets in light of potential future climate changes (Pawson *et al.*, 2008).

Various studies such as McCarthy & Zachara (1989) have reported DOC enhanced transport of pesticides and hydrophobic organic chemicals in soils. POC also acts as a carrier for the transport of organic chemicals (Ni *et al.*, 2008) and is believed to be responsible for the export of hydrophobic contaminants (Luo *et al.*, 2009). Hence

for mitigation and control of contaminants in aquatic systems, an important prerequisite is to understand the transport and fate of POC and DOC in terrestrial and aquatic ecosystems.

Even though the differences in the sources and transport mechanisms of POC and DOC have been recognized (Battin *et al.*, 2008), few attempts have been made to compare and study the hydrological processes governing POC and DOC dynamics and export. There is also a great degree of uncertainty about the relative contributions of DOC and POC to the total carbon export. Although POC has traditionally been regarded as the minor component of organic carbon export (Meybeck, 1982), especially in large watersheds, some recent studies in small, headwater watersheds have reported elevated concentrations of POC and storm-event exports exceeding those of DOC (Jeong *et al.*, 2012, Jung *et al.*, 2012, Kim *et al.*, 2010, R. R. Pawson *et al.*, 2008). In his review, Hope *et al.* (1994) reports varying DOC/POC ratios in different watershed systems ranging from 0.1 to 70. It is therefore important to investigate and compare the concentrations and exports of DOC and POC for different hydrological and watershed conditions.

The key goal of this study was to investigate the export patterns and amounts of POC during storm events and compare and contrast them to the total (TOC) and dissolved (DOC) forms of organic carbon in runoff. This study was conducted in two, nested, headwater (12 and 79 ha), forested catchments located in the Piedmont region of Maryland (MD), USA. Sampling was performed for 14 storm events over

the period of September 2010 to December 2011. Specific questions that were addressed were:

1) What are the within-event temporal patterns of POC and DOC? What are the hydrologic flow paths and sources of POC and DOC?
2) How do exports of POC and DOC vary across individual storm events and what is the influence of event hydrologic conditions and seasonal timing on the amounts of POC and DOC?
3) What proportion of the total carbon export from the watershed during the storm events is constituted by dissolved and particulate forms of carbon?

Chapter 2

LITERATURE REVIEW

This review provides an overview of important findings on POC and DOC with the special focus on POC and DOC dynamics during storm events, effect of hydrologic conditions on carbon export and the relative contribution of POC and DOC to the total carbon export. End member mixing analysis (EMMA) as an investigative tool to characterize sources and flow paths of runoff within the watershed is also discussed.

2.1 Definition and importance of POC and DOC

Dissolved organic carbon (DOC) is operationally defined as the fraction that can pass through the 0.45 μm filter. It is a reliable measure of many simple and complex organic compounds dissolved in a water sample (Thurman, 1985). Particulate organic carbon (POC) is the fraction of organic carbon retained on the 0.45 μm filter. Particulate organic matter consists of plant litter, algal debris, eroded soil organic matter and soil detritus (Hope *et al*., 1994). POC can be further divided into fine particulate organic carbon (FPOC) and coarse particulate organic carbon (CPOC). FPOC is from 0.45 μm to 1 mm while CPOC is larger than 1 mm (Bilby & Likens, 1979). DOC is considered chemically more reactive because it is a measure of

individual organic compounds in the dissolved state while POC is the discrete plant and organic matter and organic coatings on silt and clay (Thurman, 1985). The size of POC and DOC relative to various aquatic entities is illustrated in Figure 1.1.

Organic carbon is an important constituent for water quality (Ouyang, 2003). Both dissolved organic carbon (DOC) and particulate organic carbon (POC) can act as complexing agents for toxic metals such as iron, aluminum, zinc and mercury, thus affecting their solubility and transport (Buffle, 1984, Driscoll *et al.*, 1988, Hope *et al.*, 1994). DOC can form compounds such as carcinogenic trihalomethanes in chlorinated drinking water (Nokes *et al.*, 1999). Decomposition of POC plays an important role in river water quality such as decreasing dissolved oxygen concentration and increasing biochemical oxygen demand (Ouyang, 2003). Total organic carbon (TOC), comprising dissolved organic carbon (DOC) and particulate organic carbon (POC), is also an indicator of organic contamination of aquatic systems (Ni *et al*., 2008). Studies have reported a positive correlation between the TOC concentration and the content and degradation rates of organic contaminants such as PAH's (Chen *et al.*, 2005, Hinga, 2003). Dissolved organic carbon (DOC) is considered as a sorbent and carrier for organic contaminants (Knabner *et al.*, 1996) and can also increase the solubility and mobility of organic contaminants (Ouyang, 2003).

Organic carbon forms also play important ecological roles. Organic carbon is the primary source of energy for the aquatic organisms and macro invertebrates in the stream systems (Cummins, 1975, Cummins *et al.*, 1983). Coarse particulate organic matter, such as leaf litter is believed to be the major source of energy in small

headwater streams in forests (Fisher & Likens, 1973, Sedell *et al.*, 1974). Thus, the understanding of dynamics of dissolved and particulate forms of carbon has ecological and environmental significance.

2.2 Comparison of POC and DOC concentrations and export

The transport of POC and DOC via streams and rivers to the oceans is an important part of global carbon cycling (Battin *et al.*, 2009, Hope *et al.*, 1994). Previous studies have estimated the global flux of organic carbon in rivers to be 370-400 x 10^{12} g C/year (Schlesinger & Melack, 1981) of which 180-195 x 10^{12} g C/year is contributed by the particulate form (Meybeck & Vörösmarty, 1999, Meybeck, 1982) and 200–215 x 10^{12} g C/year is in the dissolved form (Meybeck & Vörösmarty, 1999). The annual DOC and POC export from various selected streams and rivers around the world is reported in Table 2.1

POC typically comprises 5-50% of the total organic carbon load (TOC) (Dawson *et al.*, 2002). Meybeck (1993) estimated that around 33 % of the total carbon exported by rivers is in the particulate form. In a recent review by Alvarez-Cobelas *et al.*(2010) on 550 catchments worldwide, POC comprised on an average 27% of the total carbon export. However some recent studies such as Jung *et al*. (2012), Jeong *et al*. (2012), Pawson *et al.* (2008), and Kim *et al.* (2010) have demonstrated that POC can play a dominating role in the export of carbon from the watersheds. In a study on an eroding peatland catchment, Pawson *et al.* (2008) reported that POC accounted for 80 % of the total annual carbon flux from the catchment. Kim *et al.* (2010) estimated

an annual flux of 0.04 t C ha^{-1} yr^{-1} for DOC and 0.05 t C ha^{-1} yr^{-1} for POC from a forested headwater catchment. Table 2.2 lists the annual export of POC and DOC from various temperate and boreal watersheds.

Storm events play a very important role in the export of organic carbon from catchments. Previous studies such as Crisp & Robson (1979), Wiegner *et al.* (2009), Bass *et al.* (2011) and Oeurng *et al*. (2011) have reported that storm events that constituted only 10-20% of the total study period contributed to > 80% of POC and >70% of DOC exports.. In another study (Eimers *et al.,* 2008), a single rainfall event was responsible for up to 66% of total annual DOC export. Pawson *et al*. (2008) reported that 95% of the POC was exported in the storm events which accounted for only 8% of the time. Jeong *et al.* (2012) reported 84% of total POC export in storm events, with 62% of the POC export in one extreme event.

Meybeck (1982) reported riverine DOC concentration range of 1-20 mg/l and POC concentrations in the range of 1-30mg/l. Ittekkot & Lanne (1992) report the POC concentrations to be in the range of 0.6 - 14.2 mg C/l. However, these concentrations are based on measurements in large rivers and on the basis of weekly to monthly sampling regimes. Studies conducted on smaller catchments draining lower-order streams and with an increased sampling frequency tend to show higher C concentrations. In a study by Pawson *et al*. (2008) in a small headwater peatland catchment, POC ranged from 0-250 mg/l under various discharge conditions while DOC ranged from 6.20 – 22.4 mg/l. Similarly, Oeurng *et al*. (2011) reported the POC concentrations of 0.1-173.2 mg/l and DOC concentrations of 1.5-7.9 mg/l under

different hydrological conditions in an agricultural catchment in France. Thus, DOC concentrations tend to show a lower range of variability with changes in discharge compared to POC concentration**.**

DOC/POC ratio for small temperate forested watersheds is reported to be to be around 10:1 (Wetzel & Rich, 1974, Wetzel, 1975) This ratio is based on lowland rivers with low erosion rates and low POC levels (Meybeck, 1982). For rivers draining the grasslands, DOC/POC ratios may be closer to 1:1 (Malcolm & Durum, 1976, Schlesinger & Melack, 1981). The DOC/POC ratio is also reported to decrease with the increase in suspended sediment concentration (Ittekkot and Lanne, 1992). Ittekkot and Lanne (1992) reported the DOC/POC ratio of 10.8 for suspended sediment concentrations of less than 15 mg/l, while DOC/POC ratio of less than one is reported for suspended sediment concentrations greater than 500 mg/l (Ittekkot and Lanne, 1992). Meybeck (1982) reported that DOC/TOC ratios are highly variable and may range from 0.1 to 0.9 with an average of 0.6.

POC content as a percentage of the suspended sediment amount has been reported to be between 0.5 to 40%, with most rivers carrying suspended material with POC between 1.6 to 6% (Meybeck, 1982). POC % is inversely related to the concentration of suspended sediments (Meybeck, 1982, Ittekkot, 1988, Ittekkot and Lanne, 1992, Coynel *et al*., 2005, Oeurng *et al*., 2011) and follows a hyperbolic relationship (Figure 2.2) (Coynel *et al.*, 2005, Oeurng *et al.*, 2011). This is because of the increase in silt and clay fractions in the suspended sediments at high discharge, which are characterized by low organic carbon content (Ittekkot and Lanne, 1992,

Coynel *et al*., 2005). Another reason is the reduction of primary production during high turbidity that subsequently reduces the fraction of carbon-rich autochthonous material (Meybeck, 1982, Ittekkot and Lanne, 1992). Ittekkot and Lanne (1992) reported a POC content of 8.4 % for the suspended sediment concentration of 5-15 mg/l, which drops to 1.6 % for suspended sediment concentrations of 500-1500 mg/l. Oeurng *et al*. (2011) reported a POC % range of 0.9- 8% with a mean value of 2.5%

2.3 Temporal patterns in the concentration of POC and DOC during storm events

The concentrations of both DOC and POC increase with storm-event discharge (Buffam *et al.*, 2001, Hope *et al.*, 1994, Inamdar & Mitchell, 2007a, Pawson *et al.*, 2008). Hope *et al.* (1994) reports an increase of 1.4 to 5.5 times in DOC concentration for an increase in stream discharge from 0.1 to 10 liter/sec. However the increase in discharge appears to have lesser effect on the concentration of DOC compared to the POC (Pawson *et al.*, 2008). Wiegner *et al.* (2009) reported a two-fold increase in concentration of dissolved organic matter (DOM) and an eleven-fold increase in the concentration of particulate organic matter (POM) during storms. POC concentration tends to peak before peak discharge on the rising limb of discharge hydrograph (Bilby & Likens, 1979, Naiman, 1982). Bilby and Likens (1979) attribute the early peak in POC to the suspension of fine sediments in the areas adjacent to stream bank as the stream becomes wider with increase in discharge as well as to the washout of particulate matter from the canopy into the stream.DOC peaks have been observed to

be concurrent with discharge or on the falling limb of discharge hydrograph (Hagedorn *et al.*, 2000, Inamdar & Mitchell, 2007a). However, studies such as Buffam *et al.* (2001) and Boyer *et al.* (1997) reported DOC peaks on the rising limb of the discharge hydrograph. The peak in DOC concentration corresponds to the flushing of DOC from the upper soil into the stream by a rising water table (Hinton *et al.*, 1997, Hornberger *et al.*, 1994, Inamdar *et al.*, 2004). POC concentrations also tend to decrease rapidly following the discharge peaks and returns to the pre-peak value within a short span of time (Pawson *et al*., 2008). Unlike POC, DOC concentrations decrease much slowly on the hydrograph recession limb and in many cases (storm events) do not fall back to the pre-event values (Inamdar *et al.*, 2004; Inamdar and Mitchell, 2007).

Organic carbon concentrations also tend to show hysteresis effect during a stormflow event(Asselman, 1999, Coynel *et al.*, 2005, Oeurng *et al.*, 2011, R. R. Pawson *et al.*, 2008). Hysteresis is commonly classified by the direction of hysteresis loop - clockwise or counterclockwise (Asselman, 1999, Coynel *et al.*, 2005, Williams, 1989) and the patterns of these loops have been used to identify the sources and transport mechanisms of sediment or nutrients to the streams (Bowes *et al.*, 2005, Coynel *et al.*, 2005, House & Warwick, 1998, Stutter *et al.*, 2008). Williams (1989) classified the hysteresis loops patterns into five classes – single valued, clockwise loop, counterclockwise loop, single-valued plus a loop and figure eight. When the concentration of nutrients on the rising limb is greater than those on the falling limb for the same value of discharge, clockwise loop is formed and when the concentrations

on falling limb are greater than on rising limb for the same discharge value, anticlockwise loop is formed (Williams, 1989). Clockwise loops are generally associated with close proximity of nutrient or sediment source to the drainage channel (or sampling location) and/or easily erodible, nutrient rich sources. In contrast, counterclockwise loops are associated with sources that are further away from the drainage or the stream channel and which are typically mobilized during large magnitude flood events (Coynel *et al.*, 2005, Oeurng *et al.*, 2010, 2011, Williams, 1989). While clockwise hysteresis loops are more common in case of POC(Coynel *et al.*, 2005, Jeong *et al.*, 2012) anticlockwise loops have also been observed in some studies (Nagorski, 2003, Whitfield & Schreier, 1981). In case of DOC, all the three hysteresis patterns – clockwise (Buffam *et al.*, 2001, Hood *et al.*, 2006, Jeong *et al.*, 2012), anticlockwise (Butturini *et al*., 2006; Inamdar and Mitchell, 2007) and mixed (Andrea *et al.*, 2006, Oeurng *et al.*, 2011) – have been observed. POC hysteresis loops are also observed to be open and wide due to the large variability in POC concentration on the rising and falling limbs of discharge hydrograph (Jeong *et al*., 2012, Coynel *et al*., 2005).

2.4 Relationship of POC and DOC concentrations with the hydrologic attributes

Various studies have reported a positive correlations between discharge and concentrations of dissolved (DOC) and particulate (POC) forms of carbon (Bilby & Likens, 1979, Edwards & Cresser, 1987, Hope *et al.*, 1994, Meybeck, 1982,

Mulholland, 1981, Naiman, 1982, Oeurng *et al.*, 2011, R. R. Pawson *et al.*, 2008). POC shows a stronger positive correlation with discharge compared to DOC (Pawson *et al.,* 2008, Oeurng *et al.,* 2011)**.** Oeurng *et al.* (2011) reported a strong positive correlation between maximum POC concentration and peak discharge (R = 0.71) compared to a weak correlation (R = 0.31) between maximum DOC concentration and peak discharge. Similarly, Pawson *et al.* (2008) reported a stronger POC-discharge relationship (R = 0.45) compared to a weaker DOC-discharge relationship (R = 0.15). Many studies have reported a power function relationship between the discharge and carbon concentration (Oeurng *et al.*, 2011, Walling & Webb, 1985). However, there is a lot of scatter in these relationships and they are not considered to be appropriate to describe the solute response to changing streamflow discharge (Biron *et al.*, 1999, O'Connor, 1976). Hope *et al.* (1994) in his review, reports that the relationship between POC and discharge tends to more complex than the relationship between DOC and discharge, and exhibits characteristics typical of a supply limited system.

While stormflow discharge is a very important factor, it cannot alone explain the complete variation in DOC and POC concentrations (Hope *et al.,* 1994, Oeurng *et al*., 2011). Factors such as storm magnitude and intensity, antecedent storm conditions such as moisture, temperature and antecedent precipitation as well as the catchment soil type, land use and the availability of organic carbon sources affect the DOC and POC concentrations (Coynel *et al.*, 2005, Oeurng *et al.*, 2011, Robertson *et al.*, 1996). Oeurng *et al.* (2011) found a strong statistical relationship between total precipitation, storm duration, total water yield and suspended sediment and organic carbon fluxes

and attributed them as the major factors controlling the POC and DOC loads along with the mean discharge. Rainfall intensity determines the soil erosion potential within the catchment which impacts the concentration of soil sediments and particulate organic carbon in runoff (Bormann *et al.*, 1969, Oeurng *et al.*, 2011). Some studies have suggested that certain threshold energy in the runoff is required before POC can be exported from the catchment (Dawson & Smith, 2007, Thurman, 1985).

Antecedent storm conditions are recognized as the major factor responsible for the differential solute response in case of similar storm events (Biron *et al.*, 1999, Jenkins *et al.*, 2007). Soulsby (1995) found that both the magnitude of storm events and antecedent conditions strongly influence the magnitude and nature of solute response. Antecedent moisture conditions of the catchment regulate the hydrological connectivity of portions of the watersheds, which affects the chemical distinction and expression of watershed sources in streamflow runoff (Inamdar and Mitchell, 2006, 2007, Inamdar *et al.*, 2012). Time since antecedent precipitation and the wet/dry cycles also play a very important role in the determination of solute response. Various studies such as Alexandrov & Laronne (2003), Coynel *et al.* (2005), Pawson *et al.* (2008), Rovira & Batalla (2006), Walling (1978) have reported a gradual reduction in SS and POC concentrations for successive storm events occurring over short time intervals. Coynel *et al.* (2005) attributes the reduction in %POC to the depletion of litter fraction from the catchment resulting in more mineral matter being transported in the later events. Similarly, studies such as Bilby and Likens (1979), Boyer *et al.* (1997), Bass *et al.* (2011) reported a flushing effect in which significantly high DOC

and POC concentrations were observed in storms following an extended dry period. Bass *et al.* (2011) attributed this flushing effect to the increased solubility and mobilization of DOC and POC due to the drying up of soil. Due to the influence of individual storm event characteristics and antecedent moisture conditions, each event usually has unique response features (Soulsby, 1995).

2.5 Sediment sources and hydrologic flow paths

End member mixing analysis (EMMA) is a major tool to identify runoff sources and flow paths within the watershed (Inamdar, 2011). Many previous studies (Hangen *et al.*, 2001, Inamdar and Mitchell, 2006, Inamdar and Mitchell, 2007b, Inamdar *et al.*, 2011, 2012, Morel *et al.*, 2009, van Verseveld *et al.*, 2008) have used EMMA to investigate the runoff sources within the catchments. Inamdar and Mitchell (2007b) showed a systematic evolution in the contribution of groundwater seeps, throughfall and riparian groundwater to the streamflow runoff throughout the storm event. Similarly, Hangen *et al.* (2001) observed the saturation overland flow, soil and groundwater from the riparian reservoir, and hillslope interflow to be the major contributors to the streamflow runoff. Studies such as Inamdar and Mitchell (2007b), Morel *et al.* (2009) and Inamdar *et al*. (2012) have also shown that the contributions from the observed end members may vary with event size and antecedent conditions. Inamdar *et al.* (2012) also investigated the variations in end-member chemistry with the change in hydrologic conditions and how these variations affect the EMMA mixing space and mixing patterns of storm events. In this way EMMA has been

successfully used in understanding the catchment response to different hydrological conditions by characterizing the sources and flow paths of runoff under different conditions. EMMA results have also been used in association with the hydrometric data such as groundwater depth to make additional observations about the catchment response (Inamdar and Mitchell, 2007b, Buttle, 2005).

EMMA has also been used to identify the sources and flow paths for DOC in the watershed (Hagedorn *et al.*, 2000, Inamdar and Mitchell, 2007b, Versevald *et al*., 2008). The watershed sources that have been identified by these studies to be contributing to the flux of DOC include throughfall, forest floor leachate, surficial soils, riparian zones and wetlands. Morel *et al.* (2009) found that 64 to 86% of the DOC flux was contributed by riparian wetland soils.

In comparison, the potential sources of sediments in the watershed have not been well documented, primarily due to the high spatiotemporal variability of the sediment sources(Collins & Walling, 2004). Sediment fingerprinting is the most frequently used technique to determine the potential sediment sources within the watershed (Walling, 2005) and has included the use of fallout radionuclides (Mukundan *et al.*, 2010) or stable isotopes of C and N (Fox & Papanicolaou, 2007). While many potential sediment sources such as stream banks, stream beds, forests, and pastures, areas under cultivation, and unpaved roads and construction sites have been identified, contrasting results on their relative importance exist in literature (Collins & Walling, 2004). Mukundan *et al.* (2010) showed that 60% of the stream suspended sediment originated from eroding stream banks, 23-30% from upland subsoil sources

and 10-15% from pastures in a piedmont stream catchment. In another study, Russell *et al.* (2001) working in lowland agricultural catchment found that surface sources contributed to 34-65% of the sediment yield while the contribution from stream banks was less than 10%. Walling (2005) suggested that while the bank erosion has a higher contribution in the upland catchments, surface erosion is dominant in lowland catchments.

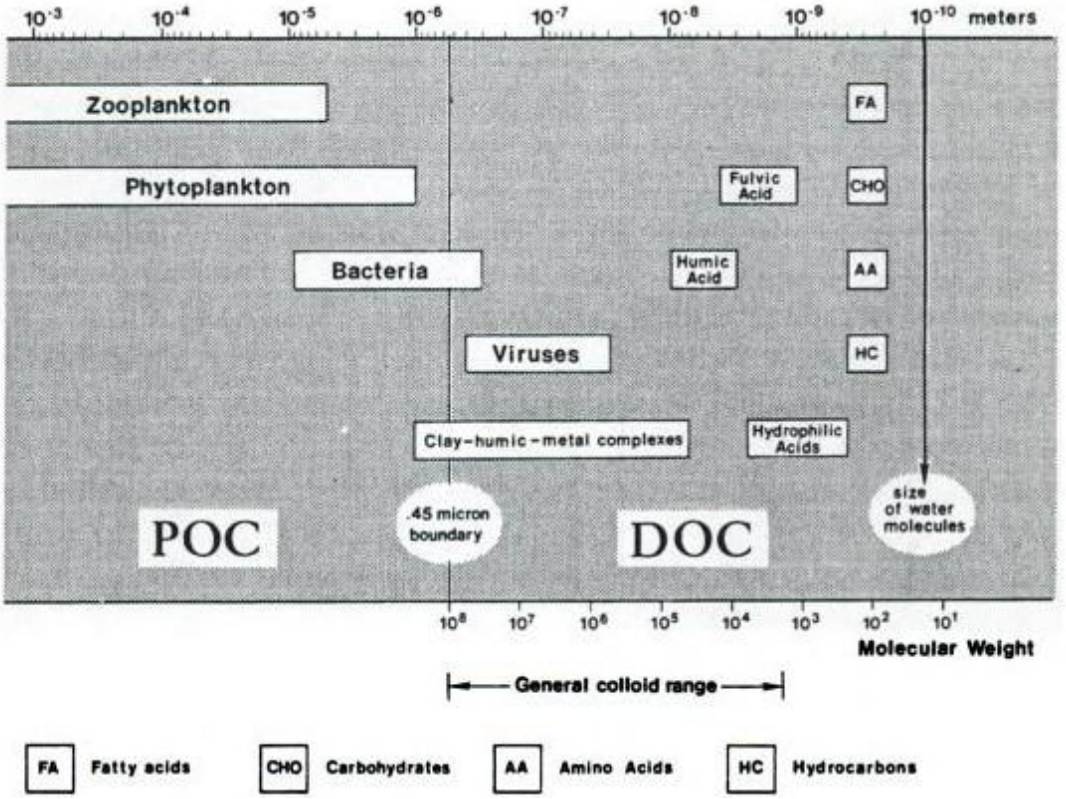


Figure 2.1 Size of particulate organic carbon and dissolved organic carbon relative to the size of various aquatic entities (adapted from Thurman, 1985)

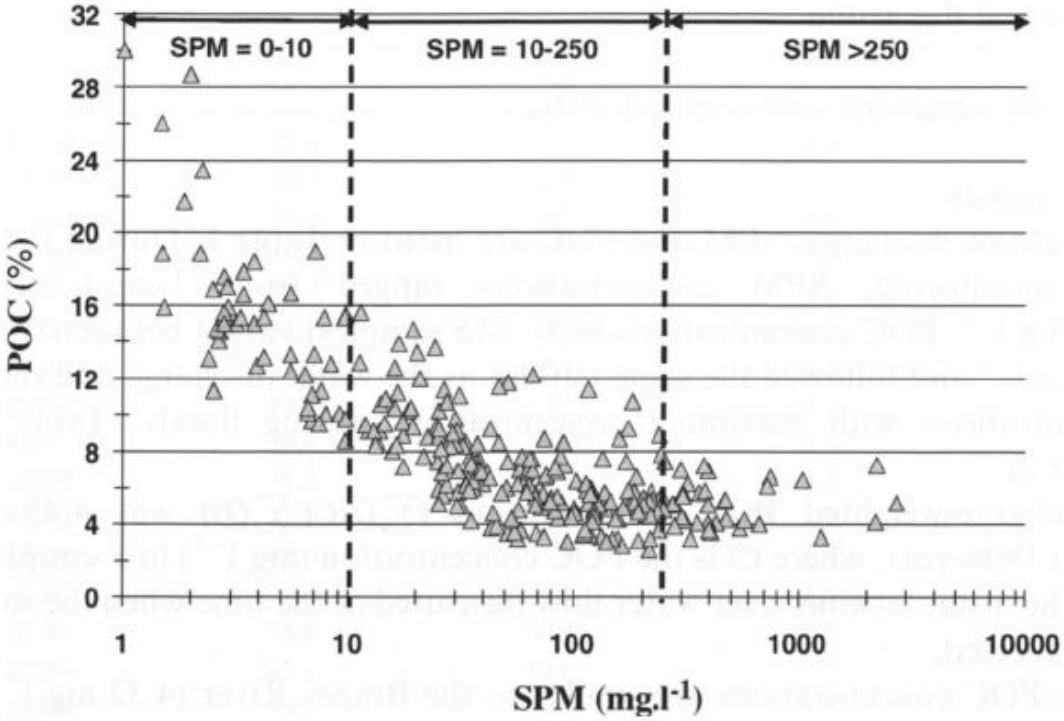


Figure 2.2 Relationship between % POC content and suspended particulate matter (SPM) showing hyperbolic relationship (adapted from Coynel et al., 2005)

Table 2.1 Annual Export of DOC and POC from selected streams and rivers (modified from Wiegner *et al.*, 2009)

Rivers and Streams	**Location**	**DOC (kg km^{-2} y^{-1})**	**POC (kg km^{-2} y^{-1})**
Niger River	Africa	400[a], 672[b]	500[a], 600[c]
Orange River	Africa	54[b]	600[c]
Zaire River	Africa	3300[a], 1646[b]	400[a], 1400[c]
Chang Jiang	Asia	4200[a]	1600[c]
Ganges	Asia	2000[a], 2664[b]	6400[c]
Huang He	Asia	600[a]	300[c]
Lena	Asia	987[b]	300[c]
Quebrada Sonadora	Caribbean	6900–7910[d]	640–910[d]
Quebrada Toronjag	Caribbean	2610–4280[d]	413–900[d]
Rio Icacosg	Caribbean	8330–10,900[d]	2000–5200[d]
Danube	Europe	1152[b]	1000[c]
Po	Europe	3046[b]	4600[c]
Rhine	Europe	1700[a], 1388[b]	1000[a], 900[c]
Seine	Europe	917[b]	500[c]
Columbia	North America	700[a], 1646[b]	200[a], 500[c]
Mackenzie	North America	800[a], 1127[b]	300[c]
Mississippi	North America	1100[a], 898[b]	300[a], 400[c]
St. Lawrence	North America	1100[a], 1734[b]	100[a], 700[c]
Yukon	North America	2800[a], 2201[b]	400[a], 400[c]
Amazon River	South America	5235[b]	2900[c]
Orinoco River	South America	5241[e]	1492[e]
Wailuku River	Oceania	829[f], 1282[f]	819[f], 1778[f]

a. Esser & Kohlmaier, (1991).
b. Harrison *et al.*, (2005)
c. Beusen *et al.*, (2005)
d. McDowell & Asbury, (1994)
e. Lewis & Saunders, (1989)
f. Wiegner *et al.*, (2009)

Table 2.2 Export of organic carbon from temperate and boreal watersheds (modified from Schlesinger and Melack, 1981 and Hope et al., 1994)

Location & Reference	**Watershed size (km^2)**	**Ecosystem type**	**DOC export (kg C ha^{-1} yr^{-1})**	**POC export (kg C ha^{-1} yr^{-1})**	**DOC/ POC**
Hubbard Brook,N.H. (Hobbie & Likens, 1973)	0.1	Temperate forest	11.8	3.4	3.5
Bear Brook, N.H. (Fisher & Likens, 1973)	1.0	Temperate forest	17.8	1.7	10.2
Moisie River, Quebec (Naiman, 1982)	19871	Boreal forest	42.6	4.8	8.9
Mississippi River (Malcolm & Durum, 1976)	3220716	Temperate grasslands	5.0	5.6	0.9
Haean Basin, S. Korea (Jeong et al., 2012)	0.38	Mountainous, deciduous forest	6.7	4.34	1.6
MacKenzie River, Oregon (Naiman & Sedell, 1979)	1287	Temperate forest	11.4	6.4	1.8
Beaver Creek, Quebec (Naiman, 1982)	0.83	Boreal forest	483.8	33.7	14.4
North Pennies, UK (Worrall et al., 2003)	11.4	Peatland	94	199	0.5
South Pennies, UK (Pawson et al., 2008)	0.38	Peatland	153.9	739.7	0.2
NE Scotland (Hope et al., 1997a)	1320-2100	Range of catchments	13.4-115	1-85.3	
Britain (Hope et al., 1997a)	159	Range of catchments	7.7-103.5	57	
Humber river (Tipping et al., 1997)	381-8231	Range of catchments	23-54	7-32	
Gwangneung catchment (Kim et al., 2010)	0.22	Deciduous forest	40	50	0.8
Jyozankei, Japan (Sakamoto et al., 1998)	N/A	Temperate forest	33	21	1.6

Chapter 3

SITE DESCRIPTION AND METHODS

3.1 Site description

3.1.1 Location

The study catchments (12 and 79 ha) are located within the Fair Hill Natural Resources Management Area (39°42' N, 75°50' W) in Cecil County in northeastern Maryland (Figure 3.1). They are a part of the Big Elk Creek watershed and lie within the Piedmont physiographic region. The Big Elk Creek watershed eventually drains into the Chesapeake Bay.

3.1.2 Climate

Cecil County has a humid, continental climate with well-defined seasons. The Chesapeake Bay and its tributaries and, to a lesser degree, the Atlantic Ocean have a modifying effect on the climate by modifying extreme temperatures (Andersen & Matthews, 1973). The maximum daily mean temperature is 24.6°C (July) and the daily minimum is -0.6°C (January), with a mean annual temperature of 12.2°C (Maryland State Climatologist Office Data Page). Prevailing winds are from west-northwest to north-west. During May through September they become more southerly (Andersen & Matthews, 1973). Mean total annual precipitation in this region is 1231 mm with about 350 mm occurring as snowfall in winter (Maryland State

Climatologist Office Data Page). Late summer (August-September) tends to be the driest period of the year.

3.1.3 Geology

The study catchments fall within the Piedmont Plateau region and are underlain by the Mt. Cuba Wissahickon formation. It includes pelitic gneiss and pelitic schist with subordinate amphibolite and pegmatite. The predominant lithology is quartz-plagioclase-biotite-muscovite gneiss, with or without sillimanite and small garnets. Pegmatite bodies of various sizes and ages are ubiquitous (Blackmer, 2005). The compact bedrock is overlain by a zone of weathering which is between 4 and 14.5 m thick in the Fairhill area, and a soil layer of varying thickness (Water Resources of Cecil County, 1958).

3.1.4 Soils

The soils in the study area belong to the Glenelg series, which consists of deep, well-drained, nearly level to moderately steep soils. On the hill slopes, soils are coarse loamy, mixed, mesic Lithic Dystrudepts. In the valley bottoms seasonal water saturation leads to the formation of Oxyaquic Dystrudepts. The backslope soil profile has an 8 cm thick organic A horizon which shows a granular to small subangular structure. The boundary to the first B horizon is diffusive. At 22 to 45 cm below the surface the higher clay content indicates translocation of clay minerals into lower portions of the soil profile. The boundary to the C horizon at 68 cm depth is gradual.

The C horizon is rich in muscovite and biotite and with increasing depth the orange color gradually disappears. Fragments of the weathered parental saprolite are present.

The wetland soil profile which is located at the toeslope position shows a shallow water table at about 30cm below surface. The dark A horizon is extremely rich in highly decomposed organic matter. Beneath the A horizon is a grey E horizon (eluvial horizon) which displays specks of orange color, indicative of variable groundwater table depths. It gradually merges into a Bw horizon at about 20 cm depth. The high abundance of muscovite in the Bw horizon (water influenced horizon) may indicate that this is already the parental sediment.

3.1.5 Vegetation

The catchment is covered predominantly with deciduous forest with pasture along the catchment edges. Around 75-80% of the 12 ha (ST3) catchment is forested, while in 79 ha (ST12) catchment, the area under forested vegetation decreases to 60-70% and the rest of the area is under pastures (Figure 3.1). Dominant tree species are *Fagus grandifolia* (American beech), *Liriodendron tulipifera* (yellow poplar), and *Acer rubrum* (red maple). Based on a survey of canopy trees (> 10 cm diameter at breast height) (Levia *et al.*, 2010), there is a stand density of 225 trees ha^{-1}, a stand basal area of 36.8 m^2ha^{-1}, a mean dbh of 40.8 cm, and a mean tree height of 27.8 m. The stand leaf area index (LAI) is 5.3 m^2 m^{-2}. The percentages of stand basal area for the species are: poplar (40%), beech (35%), maple (5%), oak (14%), and others (6%) (Levia *et al.*, 2010).

3.1.6 Stream Description

The 12 ha catchment is drained by a second order stream while the 79 ha catchment is drained by a third order stream. The stream has variable morphology. Some of the parts of the stream are rocky while others are dominated by high sediment deposition (Figure 3.2). Within the 12 ha catchment, the width of the stream varies from 60-120 cm while the depth varies from 15-60 cm.

3.2 Instrumentation, monitoring and sample analysis

3.2.1 Hydrologic monitoring

Stream flow discharge was monitored at the outlet of the 12 ha catchment (ST3 in Figure 3.1) using a 6-inch Parshall flume and water flow depths were recorded every 15 minutes using a Global Water (Inc.) logger and pressure transducer. While stream water levels were measured infrequently at the 79 ha outlet (ST12 in Figure 3.1) discharge data was not available. Depth to groundwater (from the soil surface) was recorded at three locations - LW2, LW4 and LW5, in the 12 ha catchment at 30-minute intervals using Global Water loggers (Inc.). Groundwater logging wells consisted of PVC pipes (5 cm diameter) extending ~2 m below the ground surface that were continuously slotted from a depth of 0.3 m below the soil surface. These three wells were distributed spatially across the catchment and their combined observations provided an overall estimate of the wetness conditions in the catchment. Well LW4 was located in valley bottom riparian wetlands; well LW2 was located at the foot of a hillslope in close vicinity to a seep but not within a wetland and well LW5 was located

in a former river bend adjacent to the stream (Figure 3.3). Precipitation and air temperature data was available at 5-minute frequency from a Delaware Earth Observation System (DEOS) weather station located in the Fairhill NRMA, about 1000 m from the outlet of the 12 ha catchment. All data was collected over the study period of September 2010- December 2011.

3.2.2 Stream water sampling during events

Storm event sampling for stream water was performed using automated ISCO samplers which were installed at the outlets of the 12 ha catchment (ST3) as well as the 79 ha catchment (ST12). The ISCO samplers were triggered to sample when the rainfall amount exceeded 2.54 mm in a one hour period or in some cases were triggered manually based on the expected arrival of the storm event. The ISCO samples were collected in the "non-uniform time" program mode with a sampling frequency that ranged from as low as 15 minutes on the hydrograph rising limb to 3 hours on the recession limb. Storm event sampling for stream water was performed from September 2010 to December 2011.

3.2.3 Soil sampling to characterize runoff sediment sources

Soil and sediment samples were collected from multiple locations in the 12 ha watershed to identify the sources of sediment during storm runoff. Soil and sediment samples were collected one time in July 2010 from eleven sites (Figure 3.4) that accounted for four kinds of potential sediment sources - riparian wetlands (eight

samples from two sites), upland soils (sixteen samples from four upland sites at varying elevations and distance from stream), stream bed (six samples from three sites in the stream bed) and stream bank (eight samples from two sites). At each sampling location, samples were collected from the A and B soil horizons and each sample had one replicate. Prior to the analysis, the samples were homogenized using pestle and mortar and sieved through a 2 mm sieve to remove gravel and other coarse particles like wood.

3.2.4 Sample processing and chemical analyses

All stream water samples were collected in HDPE bottles and filtered through a 0.45 μm filter paper (Millipore, Inc.) within 24 hours of collection. The filtered water samples were stored at 4°C. The filter papers with the retained material was dried to a constant weight by heating in an oven for 103-105^{O}C for one hour. After drying, the filter paper along with retained material was weighed again and the weight of filter paper was subtracted to obtain the dry weight of sediment. The weight of sediment was divided with the sample volume to obtain the concentration of suspended sediments (SS) in mg l^{-1}. The SS in this study represented a size range of 0.45 μm to 1mm.

The sediment collected on the filters as well as the soil samples collected from various watershed locations (described in section 3.2.3) were analyzed in the University of Delaware (UD) soil testing laboratory. Total carbon (TC) and total nitrogen (TN) in the samples was determined using the Elemental TC and TN analyzer

- Elementar VarioMax CN by following Dumas method and reported as % C and % N content of the sediments respectively. The % C and % N contents were multiplied with the concentration of suspended sediments (in mg l^{-1}) to determine the concentration of particulate organic carbon (POC) and particulate nitrogen (PN) in the streamflow (in mg l^{-1}). Major cations (Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cu^{2+}, Zn^{2+}) in the sediment were determined by microwave digestion of samples followed by analysis through inductively coupled plasma mass spectrometry (ICP-MS).

The dissolved phase analysis was performed by the Biogeochemistry Laboratory at SUNY-ESF, NY, which is a participant in the USGS QA/QC program (Inamdar and Mitchell, 2007). The water samples were analyzed for : pH using a pH meter; major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and silica (Si) using a Perkin-Elmer ICP-AEC Div 3300 instrument; anions (Cl^{-}, NO_3^{-},SO_4^{2-}) using a Dionex IC; NH_4^{+} with an auto analyzer using the Berthelot Reaction followed by colorimetric analysis; total dissolved nitrogen (TDN) using the persulfate oxidation procedure (Ameel et al., 1993) followed by colorimetric analysis on an auto analyzer; and dissolved organic carbon (DOC) using the Tekmar-Dohrmann Phoenix 8000 TOC analyzer.

3.2.5 Data analysis

3.2.5.1 Characterization of events and hydrologic conditions

The start of a storm event was defined when a perceptible rise in discharge was observed after precipitation or the occurrence of first ISCO sample, whichever occurred earlier. The end of the event was defined when the streamflow discharge

returned to within 10% of the pre-event values or when no perceptible decrease in discharge was observed over a period of 2 hours, whichever occurred earlier. Catchment hydrologic conditions during and prior to the storm events were characterized using a number of metrics (Table 4.1). The metrics used to characterize precipitation included total amount of precipitation for the storm event (mm), maximum 5-min rainfall intensity (mm), sum of 7-day antecedent precipitation (API7, mm). Streamflow discharge was characterized using total specific discharge for the event (mm per unit catchment area), peak specific discharge (mm/hr), average of streamflow discharge 24 h prior to event (AR24, mm/hr), and the ratio of total specific discharge to total precipitation for the event (runoff ratio). Antecedent moisture conditions in the catchment were characterized by a 7-day running average of groundwater (GW) depths (meters below soil surface) for wells LW2, LW4 and LW5 (Figure 3.3). Using these metrics, storm events were characterized based on duration and intensity (long duration/low intensity and short duration/high intensity storms), antecedent moisture conditions (dry/wet), pre-storm groundwater table (low groundwater/high groundwater table) and seasonal timing of the events. Events were compared to see how storm event characteristics and antecedent moisture conditions affected the concentrations and temporal patterns of POC and DOC. Correlations between concentrations, fluxes and ratios of POC and DOC with these hydrologic matrices were also investigated using the Pearson correlation coefficient.

3.2.5.2 Stream chemistry data analysis

Streamflow discharge (mm/hr) and concentrations of SS (mg/L), POC (mg/L) and DOC (mg/L) from ST3 and ST12 were plotted against time to evaluate the temporal patterns during storm events (streamflow discharge for ST12 was not available). The POC and DOC concentrations were also plotted against discharge values on an x-y plot to investigate the changes in concentration-discharge (CQ) relationship during the course of an event.

The storm events were compared on the basis of peak POC and DOC concentration as well as the flow-weighted mean concentration of POC and DOC for individual storm events. The flow-weighted mean concentration (Cm) was calculated using the formula –

$$Cm = \sum_{i=1}^{i=n} Ci.Qi \Big/ \sum_{i=1}^{i=n} Qi$$

where Ci was the measured concentration of constituents (POC or DOC) and Qi was the corresponding discharge value at time i during the storm event. Since the streamflow discharge data for ST12 was not available the flow-weighted mean concentrations of POC and DOC could not be calculated for ST12. Thus, comparisons for catchment scale, ST3 versus ST12, were performed by comparing the arithmetic mean and median values of SS, DOC, and POC.

To compute the mass flux of SS, POC and DOC during storm events, the concentrations of SS, POC and DOC were linearly interpolated between sampling

intervals for discharge values measured at 15-minute intervals during the storm events. These concentrations were then multiplied by the discharge values to arrive at the mass flux for that time step. The total mass flux for the storm event was ten determined by summation of the mass fluxes for individual time steps. A frequency analysis on streamflow discharge and SS, POC, and DOC was also performed. Individual (15-minute) streamflow discharge values for all storm events were collated and the exceedence probability of the discharge values was determined using the formula (Risley *et al.*, 2008)–

$$P = 100 * [M / (n + 1)]$$

where P is the exceedence probability, M is the ranking, from highest to lowest, of all the stormflow discharge values within the study period, and n is total number of recorded discharge values. The SS, POC and DOC flux was computed for the flows with exceedence probability in the ranges of highest 10%, highest 10 to50% and the lower 50% to investigate the impact of various flow ranges on carbon export.

3.2.5.3 End member mixing analysis (EMMA)

A brief description of mixing models and end member mixing analysis (EMMA) technique is provided in this section, followed by its application in this study.

3.2.5.3.1 Mixing models

Mixing models have been successfully used in the identification and characterization of runoff sources by a number of studies (Buttle, 1994, Inamdar, 2011, Inamdar and Mitchell, 2006, James & Roulet, 2006, Sklash *et al.*, 1976). Mixing models use tracers that behave conservatively to determine the contribution of various sources to stream runoff (Hooper, 2003).

Mixing models rely on the solution of simple mass balance equations for water and the chosen tracers:

$$Q_t = \sum_{i=1}^{n} Q_i$$

$$Q_t\, C_t^j = \sum_{i=1}^{n} Q_i\, C_i^j \qquad where\ \ j = 1,.....,(n-1)$$

where Q_t is the catchment outflow or streamflow, Q_i is the contribution from the end-member or runoff component i, and C_i^j is the concentration of tracer j for end-member i. In the absence of hydrometric data, the solution of these equations for n end-members requires a minimum of n-1 tracers. The key assumptions for geochemical mixing models are:

1. the tracers behave conservatively, i.e., the tracer concentrations do not change due to biogeochemical processes over the time scale considered by the mixing model;

Hooper (2003) suggested that assumptions of linearity of mixing and conservative behavior of tracers can be evaluated using bivariate scatter plots and residuals derived from the selected model.

2. the mixing process is linear;
3. the chemical composition of end-members (tracer concentrations) does not change over the time scale considered by the mixing model (time invariance)
4. the chemical composition of end-members (tracer concentrations) does not change with space (space invariance)

3.2.5.3.2 EMMA

While the early applications of mixing models involved the use of 2-3 tracers (Bazemore *et al.*, 1994, Dewalle *et al.*, 1988), Christopherson & Hooper (1992) and Hooper *et al.* (1990) introduced the analysis of maximum number of tracers by using multivariate statistical methods. This technique is known as End member mixing analysis (EMMA) and the key runoff sources are referred to as end members (Hooper, 2003, Inamdar, 2011). For the detailed description of EMMA technique the readers are referred Hooper (2003) and Inamdar (2011); however a brief description of the steps involved is provided in the following paragraphs.

Tracers that behave conservatively are vital for a successful application of EMMA. Bivariate scatter plots should be developed for all potential combination of available solutes. While Hooper (2003) suggested that a collinear structure in the

bivariate plots could be used to infer conservative behavior, it does not necessarily confirm or prove conservative behavior of the solutes. A more objective method to evaluate the linearity of solute mixing, however, is still lacking. Stream water concentrations of the selected tracers for the sampled storm events are standardized by the mean and standard deviation for each tracer in the data set. This prevents solutes with greater variation from exerting a greater influence on the model. A correlation matrix is then developed from this standardized matrix. Principal component analyses (PCA) is performed on the correlation matrix to determine the Eigen vectors and values (Hooper, 2003).

To determine the runoff end-members, the chemistry of potential runoff sources is required. Runoff sources could include – precipitation, soil water, ground water, etc. In a three-component mixing model, the potential end members (i.e. the runoff sources) are projected in the EMMA U-space by using first two principal components (U1 and U2 of the eigenvector matrix).

To project the potential end-members in the EMMA U-space, the tracer concentrations for all potential end-members should be normalized to the stream water by using the mean and standard deviation of the stream solutes. The standardized end-member values can then be projected into the EMMA U-space by multiplying with the two principal components or eigenvectors (Hooper, 2003). Finally, three key end-members are selected based on their ability to enclose the stream water concentrations in the EMMA U-space. The chosen EMMA model is used to back-calculate the standardized stream water values. The standardized values are de-standardized by

multiplying by the standard deviation of each solute and adding the corresponding mean concentration to yield the predicted value of solute concentration. However, instead of determining the individual contribution of three end members, the stream chemistry for storm events can also be compared against the continuum of watershed source chemistry in the EMMA U-space to assess the influence of all the potential runoff sources on the stream runoff during the storm events.

3.2.5.3.3 Application of EMMA in this study

End member mixing analysis (EMMA) was performed individually for the dissolved and particulate phases to determine the hydrologic flow paths for DOC and the sediment sources for POC, respectively. Tracers were chosen by plotting the bivariate scatter plots of all the potential combinations of available solutes. For the dissolved phase EMMA analysis, sodium (Na), calcium (Ca), total aluminum (Al), silica (Si), and dissolved organic carbon (DOC) were selected as tracers since they displayed linear patterns in bivariate plots (Figure 3.5). Runoff source chemistry was not measured in this study. However, source chemistry data was available for 2008-2010 for the ST3 catchment from previous work (Inamdar *et al.*, 2011, 2012). These runoff sources included - groundwater sources such as shallow, riparian and deep groundwater as well as seep, hyporheic and wetland soil water and surficial sources such as precipitation, throughfall and litter leachate. Mean concentrations of selected tracers for these sources were used. Similarly, in EMMA analysis on particulate phase, aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium

(Mg), manganese (Mn) and zinc (Zn) were selected as suitable particulate tracers using bivariate plot analysis (Figure 3.6). The potential sediment sources that were projected into the EMMA U-space included wetland soils, upland soils, stream bed sediment, stream bank soil. The EMMA procedures, as described in the above paragraphs, were used to determine hydrologic flow paths and the sediment sources.

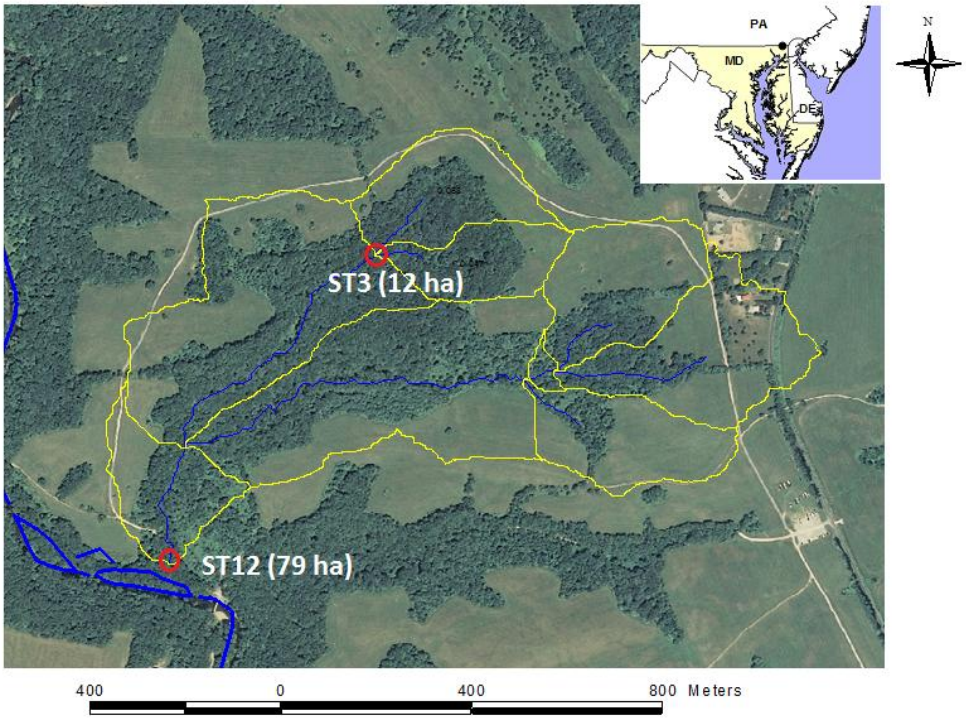


Figure 3.1 Location of study site in Maryland (MD) (inset) and the study catchments (ST3 and ST12) within the Big Elk Creek drainage basin

Figure 3.2 Stream morphology at different places and under various hydrologic conditions – streamflow runoff in 12 ha catchment during stormflow conditions (above, left); stream tributary at 79 ha catchment during low-flow condition (above, right); dried up stream in 12 ha catchment during summer season (below, right); stream flow at the outlet of the 12 ha catchment (below, left)

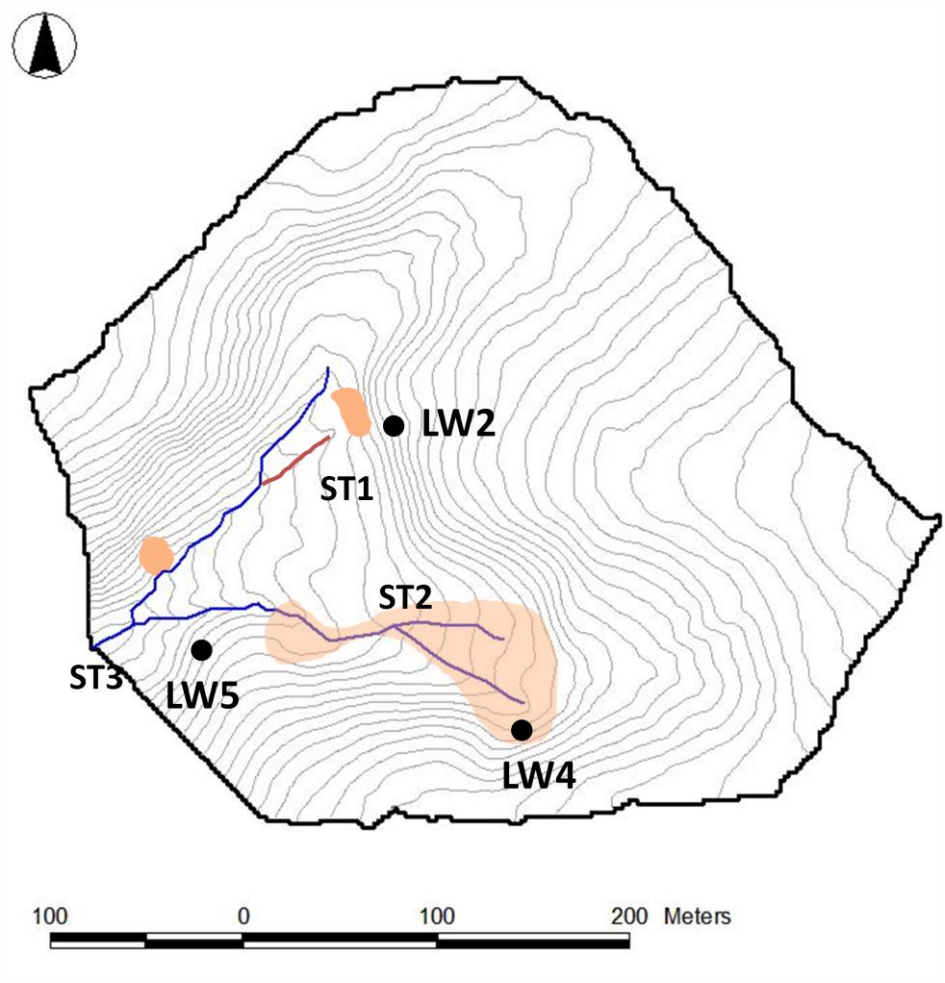


Figure 3.3 Location of groundwater wells LW2, LW4 and LW5 in the ST3 catchment

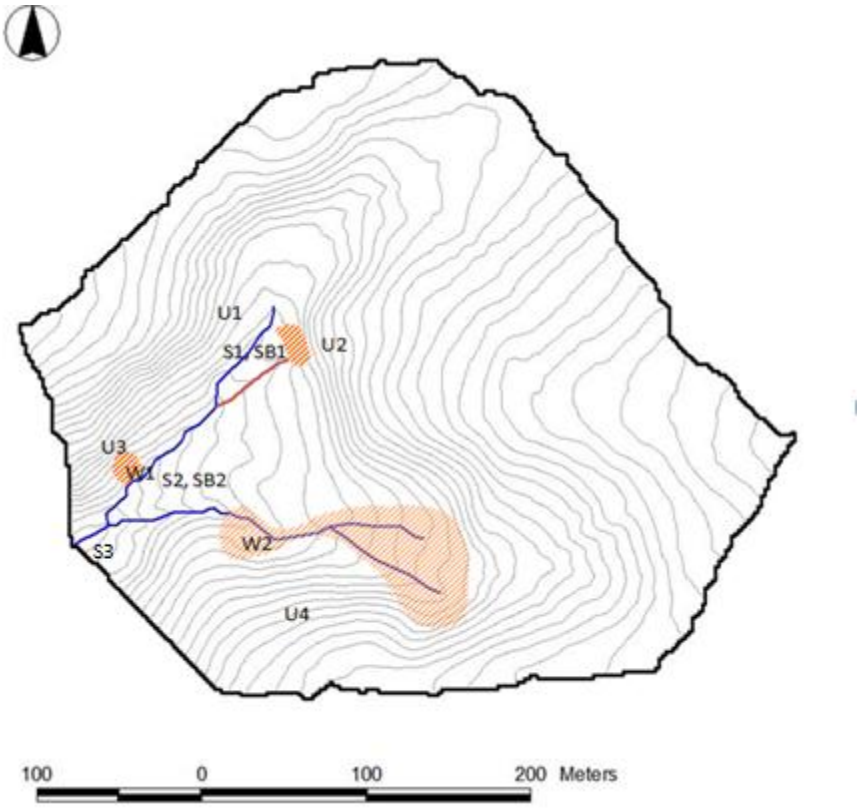


Figure 3.4 Sampling locations for soil and sediment samples from potential sediment sources in the ST3 catchment

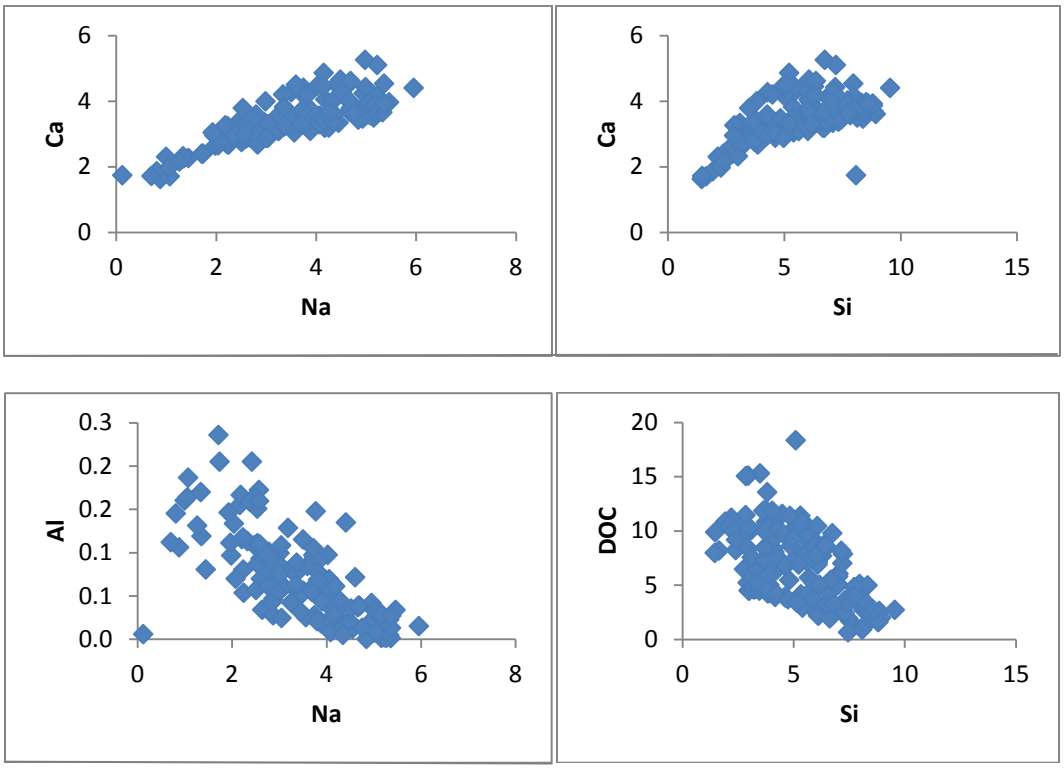


Figure 3.5 Selected bivariate plots used to identify the tracers in EMMA on dissolved phase constituents. Linear patterns suggest conservative solute mixing – one of the key assumptions of EMMA. All concentrations are in mg/l.

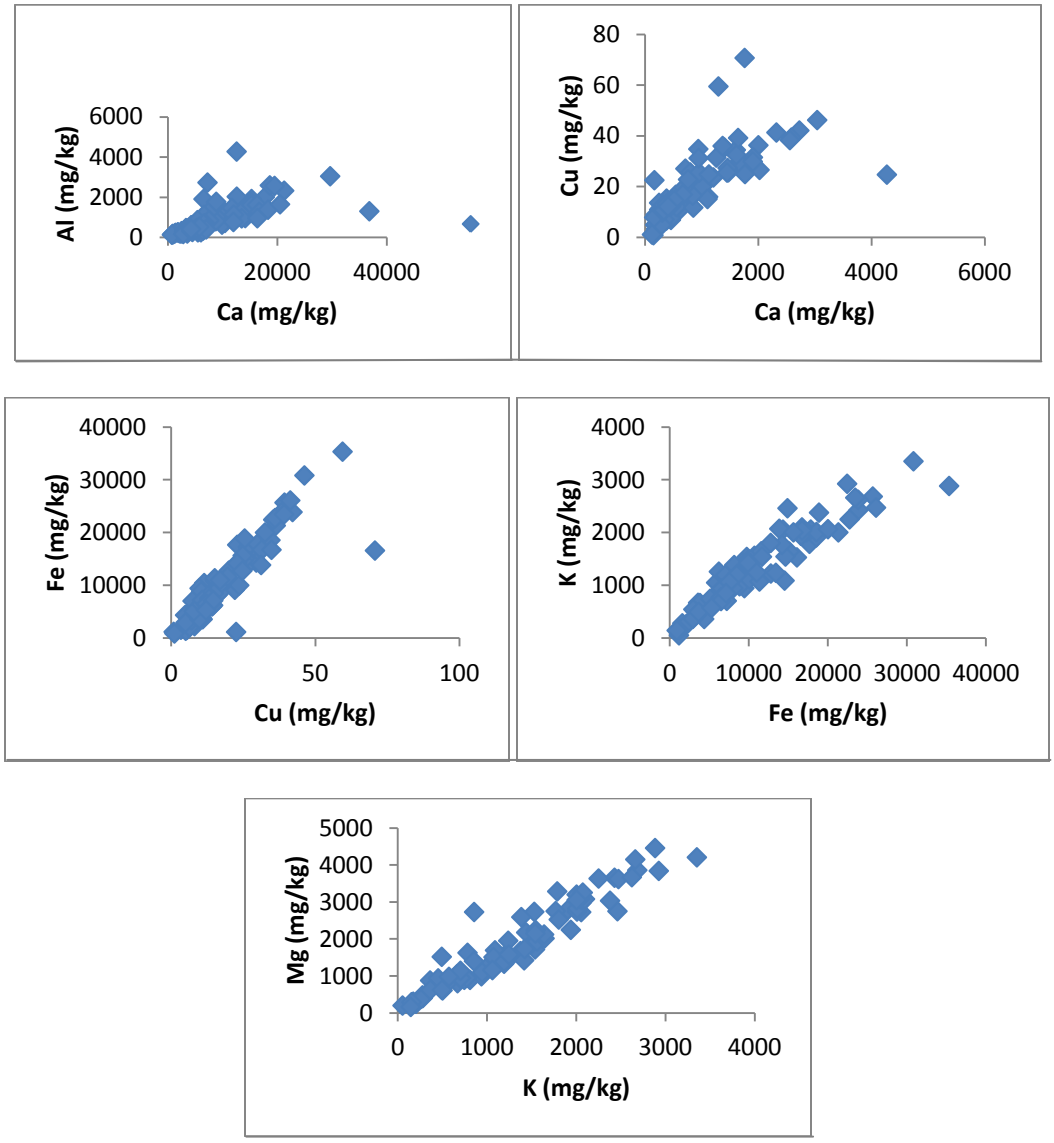


Figure 3.6 Selected bivariate plots used to identify the tracers in EMMA on particulate phase constituents. All concentrations are in mg/kg. Linear patterns indicate conservative mixing of solutes.

Chapter 4

RESULTS

The results presented here describe the – the within-event patterns of POC and DOC concentrations, the among event differences, the relationships of POC and DOC with catchment hydrologic conditions, differences in POC and DOC with catchment scale, and the mass exports of POC and DOC with storm events. For most of these comparisons, except those for catchment scale, POC and DOC concentrations measured at ST3 (12 ha catchment outlet) are used. For the catchment scale comparisons, POC and DOC values for ST3 are compared against those recorded for ST12 (79 ha catchment outlet).

4.1 Hydrologic conditions for sampled storm events

A total of 14 storm events were sampled over the study period of 16 months from September 2010 to December 2011 (Figure 4.1 and Table 4.1). The total precipitation for the 16-month study period was 1842 mm. Of this, 1462 mm of precipitation was observed in year 2011 (January through December). The annual precipitation for 2011 was higher than the previous years – 2008 (1052 mm), 2009 (1238 mm) and 2010 (972 mm). Total stream discharge measured at ST3 for the 16 month study period was 497 mm, resulting in a runoff ratio of 0.27.

Of the 14 storm events, seven events were sampled in summer (June-September), two in fall (October-November), three in winter (December-February)

and two in spring (March-May). The maximum 5-minute rainfall intensity for the events varied from 0.8 mm to 6.5 mm. Peak streamflow discharge during storm events varied from 0.07mm/hr to 5.0 mm/hr. Mean streamflow discharge during the whole study period was 0.05 mm/hr. Duration of storm events varied from 7h to 84 h. Largest amount of rainfall (155 mm) was recorded in the event of August 27, 2011 (event 9, Table 4.1), which was associated with hurricane Irene and had a return period of 25 years (Appendix C, Ward and Trimble, 2004). This event also produced the highest peak discharge (5.0 mm/hr) and highest total amount of streamflow discharge (33 mm). Similarly the event of September 30, 2010 (event 1) which was associated with hurricane Nicole yielded a rainfall amount of 151 mm and had a return period of 25 years (Appendix C, Ward and Trimble, 2004). The storm events of July 28, 2011 (event 7) and November 16, 2011 (event 12) produced the lowest discharge peaks. Event 7 (July 28, 2011) had a duration of only seven hours and produced the lowest amount of streamflow runoff (0.1 mm). Among all events, the summer events of September 30, 2010, August 9, 2011, August 14, 2011 and August 27, 2011 had the highest rainfall intensity (Table 4.1) while the events of February 25, 2011 and November 16, 2011 had the lowest rainfall intensity. The events of February 25, 2011, November 22, 2011 and December 23, 2011 had the highest runoff ratios while the summer events of July 8, 2011, July 28, 2011 and August 9, 2011 had the lowest runoff ratios.

Overall catchment antecedent moisture conditions are characterized using groundwater depth below the soil surface (Figure 4.1) and by the 7-day antecedent

groundwater index for wells LW2, LW4 and LW5 (Table 4.1). High values of GW index indicate drier conditions. Based on a combination of these indices, the catchment was at its driest preceding the event of September 30, 2010. Catchment conditions were also very dry during the summer events of July 28, 2011, August 9, 2011 and August 14, 2011. The catchment was at its wettest prior to the event of December 23, 2011 when water levels for wells LW2 and LW4 were above the groundwater surface (negative values in Table 4.1). Similarly, the catchment was also very wet during the events of November 16, 2011 and November 22, 2011. The events of February 25, 2011, March 10, 2011 and April 16, 2011 occurred under the conditions of moderate wetness. In general, catchment moisture conditions were driest during later summer (August-September) and wettest during late fall and early winter (November-December). The groundwater depth was observed to rise during storm events and peak near the discharge peak and remained elevated through the hydrograph recession (Figure 4.2).

4.2 Within-event temporal patterns of POC and DOC

The within-event patterns of POC and DOC concentrations are described in this section with comparisons among storm events and the relationships with hydrologic conditions being explored in the following sections. Large and rapid changes in the concentration of POC and DOC were observed during the storm events. POC and DOC concentrations increased rapidly with the increase in stream flow discharge and peaked around maximum discharge (Figures 4.3-4.16). POC and DOC concentrations

at the start of the storm event were similar in magnitude; however, the increase in POC concentration with discharge outpaced the increase in DOC concentration such that the peak concentration of POC was 2-20 times higher than that of DOC for individual storm events. DOC concentrations for storm events ranged from 0.7-18.3 mg/l while the POC concentrations ranged from 0.05 – 252.2 mg/l.

There were important differences in the within-event temporal patterns of POC and DOC for the 14 storm events (Figures 4.3-4.16). The POC concentrations peaked before the streamflow discharge peak, on the rising limb of the hydrograph. In contrast, the peak in DOC concentrations occurred always after the peak in POC concentrations and was either concurrent with the discharge peak or occurred on the recession limb of the hydrograph. Following a steep rise in concentrations immediately before peak discharge, POC concentrations dropped rapidly back to the pre-event values. Again, in contrast to POC, DOC concentrations revealed a steady increase on the rising limb and then decreased gradually through hydrograph recession. DOC concentrations on the recession limb did not drop back to the pre-event values for most of the events. Temporal patterns of suspended (SS) sediments followed those for POC for the sampled storm events (Figures 4.3-4.16). The ratio of POC to DOC concentrations varied from 0.06 to 40 for the storm events. This ratio was higher on the rising limb (0.2 to 40) versus the recession limb (0.06 to 11).

The within-event temporal pattern of POC and DOC can also be characterized using concentration-discharge (CQ) hysteresis loops (Figure 4.3-4.16). Clockwise hysteretic loops are associated with higher concentration of the constituent on the

rising limb compared to the falling limb while for the anticlockwise loops the concentration on the falling limb for a given discharge is higher than for the same discharge on the rising limb. The shape of POC hysteresis loops was generally consistent for the storm events even under different hydrologic conditions and followed the clockwise direction. DOC hysteresis loops, however, varied with storm events and displayed all three hysteresis patterns - clockwise, anticlockwise and mixed. POC hysteresis loops were also wider compared to the DOC loops indicating greater change POC concentrations per unit change in discharge compared to DOC.

For storm events with multiple discharge peaks (generated because of discrete rainfall inputs), there were differences in how the peak concentrations of POC and DOC varied with discharge peaks. Two scenarios (or cases) were observed for both POC and DOC (Table 4.2). In the first scenario/case, the peak POC concentration was higher for the second discharge peak. This was observed for only two storm events - event 1 (September 30, 2010) and event 5 (April 16, 2011). In the second scenario/case, observed for majority of the storm events, the peak POC concentration decreased with subsequent discharge peaks irrespective of the peak discharge values (Table 4.2). This is seen for event 2 (December 1, 2010), 4 (March 10, 2011), 8 (August 9, 2011), 9 (August 14, 2011), 12 (November 16, 2011), 13 (November 22, 2011) and 14 (December 23, 2011). It needs to be reiterated here that the POC concentrations (plotted in Figures 4.3-4.16) were computed as a product of the suspended sediment concentrations (mg/L) and the % POC (percent of POC in the suspended sediment). Thus, POC concentrations were a function of two variables –

suspended sediment amounts and % POC in runoff. Low POC concentrations for subsequent sub-events were due to lower POC content of the soil sediments (%POC) (Figure 4.17). For e.g., in event 9 (August 14, 2011), the % POC dropped from 8.7 % during the first sub-event to 2.7 % during the second sub-event. Similarly for DOC, two different scenarios were observed in how the peak values occurred for sequential events (Table 4.2). Although, compared to POC, there was a more equitable distribution of events for the two categories (Table 4.2). Peak DOC concentrations increased with discharge peak in the first category while a decrease in the peak DOC values occurred for the second case/category.

While most storms revealed an increase in DOC with discharge and a peak concentration in the vicinity of the discharge peak, an interesting difference was observed for the largest storm events – September 30, 2010 (event 1), August 14, 2011 (event 9), and August 27, 2011 (event 10). All three events had rainfall amounts in excess of 100 mm, with events 1 and 10 exceeding 150 mm of rainfall. All of these events also exceeded a streamflow discharge value of 3 mm/hr. Although all three events displayed increases in POC concentrations with a peak in the vicinity of the discharge peak, the DOC pattern did not follow the same trajectory. For events 1 and 9, DOC concentrations did indeed peak with discharge for the first subevent, for the second subevent with larger discharge a slight dilution is seen in the vicinity of the peak discharge. Similarly, for the event of August 27, 2011, DOC concentrations increased quickly on the rising limb of the hydrograph but then dropped slightly when discharge was at its maximum. Taken together, these observations suggest that,

occasionally, for large events (in excess of 100 mm of rainfall or when streamflow discharge exceeds 3mm/hr), DOC pools in the catchment may be exhausted (and thus the dilution pattern) but the same may not happen for POC. This suggests that the size of POC pools or storage in catchments is likely greater than that for DOC.

4.3 Among-event comparison of POC and DOC concentrations for stream ST3

POC and DOC concentrations for events when pooled by seasons revealed important differences with seasons (Figure 4.18). ANOVA test revealed significant differences among the seasonal categories (Figure 4.19 – 4.20). Specific t tests between individual seasons indicated that summer POC and DOC values were significantly greater than the other seasons but there was no significant difference between spring, fall, and winter events.

Flow-weighted mean POC concentrations for the storm events ranged between 5 mg/l (November 16, 2011; event 12) and 112 mg/l (August 9, 2011; event 8). In comparison, the range for flow-weighted DOC concentrations was smaller with values from 3.3 mg/l (November 16, 2011; event 12) to 10 mg/l (August 27, 2011; event 12). Hydrologic attributes for events grouped according to their flow-weighted mean POC concentration are provided in Table 4.1. It can be seen from Table 4.1 that high-discharge summer events such as September 30, 2010 (event 1), August 14, 2011 (event 9) and August 27, 2011 (event 10) had the highest flow-weighted mean POC concentration while low-discharge events such as February 25, 2011 (event 3), March 10, 2011 (event 4), April 16, 2011 (event 5), July 8, 2011 (event 6), July 28, 2011

(event 7) and November 16, 2011 (event 12) had medium to low flow-weighted mean POC concentrations. Highest flow-weighted mean DOC concentrations were also observed in the high-discharge summer events (Table 4.3). However, the highest peak POC concentration of 252mg/l was observed in the event of August 9, 2011 (event 8), which had low discharge (Qmax = 0.4 mm/hr) but the highest peak precipitation-intensity (PImax = 6.5 mm) among all the events. Highest peak DOC concentration of 18.3 mg/l was observed in the event of August 14, 2011, which was a high-intensity and high-discharge event (event 9; Qmax = 3.6 mm/hr, PImax = 4.9 mm).

The POC concentrations for storm events were also influenced by the exhaustion of POC storage pools during successive storm events. This was seen for four successive storm events at ST3 (Events 8 to 11) which occurred within a period of one month (August 9, 2011 – September 8, 2011). Flow-weighted POC concentrations displayed a gradual decline despite the elevated streamflow discharge for events 10 and 11 (Figure 4.21). Event 8 (August 9, 2011) recorded a flow-weighted mean POC concentration (POCm) of 112 mg/l and peak POC concentration (POCmax) of 252 mg/l for a corresponding maximum discharge of 0.36 mm/hr. POC concentration (POCm; POCmax) decreased, despite the increase in discharge for the events that followed – August 14, 2011 (event 9; Qmax = 3.6mm/hr ; POCm = 70 mg/l; POCmax = 224 mg/l), August 27,2011 (event 10; Qmax = 5 mm/hr ; POCm = 66 mg/l; POCmax = 112 mg/l) and September 6, 2011 (event 11; Qmax = 4.2 mm/hr ; POCm = 7.1 mg/l; POCmax = 11 mg/l). These storm events also revealed a gradual impoverishment in the % POC. Event 8 had a % POC value of 8.9% which decreased

to 5.4% in event 9, 3.1% in event 10 and 0.26 % in event 11. The same decreasing pattern was however not replicated for DOC. While DOC was not measured for event 11, flow-weighted DOC values for ST3 increased slightly from event 8 to 10 (Figure 4.21 and Table 4.3).

4.4 Relationships between POC and DOC concentrations and hydrologic attributes

Concentrations of POC and DOC for all events were evaluated against the corresponding discharge values (Figure 4.22). While there was considerable scatter for POC ($R = 0.07$), DOC values revealed a weak relationship ($R = 0.20$). Flow weighted mean POC concentrations for ST3 storm runoff were strongly correlated to the peak precipitation intensity ($R = 0.76$; $p < 0.01$; Table 4.4), however the correlation with peak discharge was weak and insignificant ($R = 0.18$; $p > 0.1$). In comparison to POC, flow weighted mean DOC concentrations were significantly correlated with both the peak discharge ($R = 0.56$; $p < 0.05$) and peak precipitation intensity ($R = 0.82$; $p < 0.01$).Antecedent catchment wetness, measured as depth of groundwater at LW2, LW4 and LW5 wells, was strongly correlated to the flow-weighted mean POC and DOC concentration (Table 4.3). However, antecedent discharge (AR24) and antecedent precipitation (AP24; AP7d) did not show any significant correlation with the flow-weighted mean POC and DOC concentration ($p > 0.1$; Table 4.3).

The % POC content of suspended sediments showed a decreasing trend with increasing runoff ratio (Figure 4.23a). This may be due to the higher proportion of

mineral-rich heavy sediments suspended in the increased amount of runoff produced per unit of rainfall. Thus the winter events with higher runoff ratios had lower content of % POC while the suspended sediments in the summer events were rich in % POC content (Figure 4.17). % POC content also showed a decreasing trend with increasing SS concentration (Figure 4.23b).

4.5 Comparison of POC and DOC concentration at different catchment scales

The pooled storm event concentrations of POC and DOC (Figure 4.24 - 4.25) for the catchments ST3 (12 ha) and ST12 (79 ha) indicated that they were significantly different. The median POC concentration for catchment ST3 was 9.7 mg/l whereas that for catchment ST12 was 3 mg/l. Similarly, the median DOC concentration for catchment ST3 was 6 mg/l whereas that for catchment ST12 was 5 mg/l.

To compare the concentrations for individual events, box plots for SS, POC and DOC concentrations for catchments ST3 and ST12 are presented in Figure 4.26. The comparison of flow-weighted mean concentrations could not be performed since the discharge data at the ST12 catchment was not available. Across all events, the median concentrations of POC for ST3 exceeded the ST12 values. There was also greater variability in POC concentrations at ST3 than ST12.The highest concentration of POC observed at ST12 during the whole study period was 113 mg/l compared to 252 mg/l at ST3 catchment. Similarly, the highest DOC concentration at ST12 was 13.2 mg/l compared to 18.3 mg/l at ST3 catchment. Hence, the difference in concentration between the ST3 and ST12 catchments was more pronounced for POC compared to

DOC. The highest SS concentration at ST12 was 6891 mg/l compared to 7589 mg/l at ST3 catchment. The POC: DOC ratio was observed to decrease with the increase in catchment scale from ST3 to ST12. POC: DOC ratios for ST3 ranged from 0.06 to 40 while the corresponding values for ST12 were 0.004 to 29.

4.6 Hydrologic flow paths and sediment sources for the events

End member mixing analysis (EMMA) was carried out separately on the dissolved and particulate phase constituents of streamflow runoff to investigate the sources and flowpaths of runoff and sediments. Watershed sources and stream water chemistry for ST3 during storm events are displayed in EMMA space in figures 4.27 and 4.28, respectively. The surficial and groundwater runoff sources aligned separately in the U-space with the surficial sources on the right-hand side of the U-space in the quadrants 1 and 2 and the groundwater sources on the left-hand side in the quadrants 3 and 4 (Figure 4.27). While the groundwater sources were clustered tightly indicating their chemical similarity, the surficial sources aligned along a straight, vertical line in quadrant 1 and 2, indicating their similar characters but increasing concentration of constituents from throughfall and rainfall sources to the litter leachate source. These watershed sources enclosed the storm event stream runoff chemistry from all sides indicating their contribution to stream runoff during the storm events.

While the summer events were dispersed throughout the U-space and revealed large open loops (Inamdar *et al.,* 2012), the winter events were tightly clustered towards the middle of the EMMA plot (Figure 4.28). The open loops of the summer

events indicate a greater diversity of runoff sources compared to the winter events. Summer events with high precipitation amounts and streamflow discharges such as September 30, 2010 (event 1), August 14, 2011 (event 9) and August 27, 2011 (event 10) displayed the largest shifts towards the surficial sources (throughfall and rainfall) in quadrants 1 and 2 (Figure 4.28). In contrast, the summer events with low streamflow discharges such as July 28, 2011 (event 7) and August 9, 2011 (event 8) did not display large shifts. The winter and spring events such as February 25, 2011 (event 2), March 10, 2011 (event 3) and April 16, 2011 (event 4) were furthest away from surficial sources especially litter leachate source and were clustered between the groundwater sources and the throughfall, rainfall sources (Figure 4.28).

Overall, while there were differences among events, the storm events displayed a counterclockwise evolution in EMMA space with contributions of groundwater seeps at the start of event to surficial sources such as throughfall and rainwater on the rising limb of the hydrograph, followed by litter leachate, and soil and shallow groundwater sources on the recession limb of the hydrograph (Figure 4.29). This temporal pattern of runoff source contributions has recently been reported by Inamdar *et al.* (2012) who investigated the sources and hydrologic flow paths for runoff in this same catchment using data from 2008-2010.

EMMA analysis plots for sediment sources in the catchment and runoff sediment chemistry for ST3 are presented in Figures 4.30 and 4.31 respectively. Nearly all of the sediment sources were located in quadrant 3 of the EMMA plot (Figure 4.30). The wetland and stream bed sources were closer to the origins of the

axis while the upland and stream bank sources were located further away from the origin and in the lower portion of the quadrant 3 (Figure 4.30). These sources, however, did not enclose the stream sediment chemistry for ST3 indicating that there were likely additional sources of sediments which were not sampled. The storm sediment plots especially displayed large shifts towards an unknown source located in quadrant 4 which was not identified in this study. Despite the inability to capture all sediment sources the storm sediment patterns in Figure 4.31 reveal some interesting trends. High-intensity summer events such as September 30, 2010 (event 1), July 28, 2011 (event 7), August 9, 2011 (event 8), August 14, 2011 (event 9) and August 27, 2011 (event 10) were spread out in the third and fourth quadrants of the EMMA space indicating a greater diversity of sediment sources. On the other hand, the low intensity winter and spring storm events such as events of December 1, 2010 (event 2), February 25, 2011 (event 3) and March 10, 2011 (event 4) were clustered on the right-hand side of the EMMA space suggesting a different set of sediment sources from the summer events.

4.7 Mass contributions of POC and DOC to total carbon export at ST3

Mass exports of POC and DOC varied considerably across the 14 storm events. The mass exports of POC varied from 0.5 to 255 kg while the exports of DOC ranged from 0.1 to 39.2 kg (Figure 4.32). The relative contribution of POC to the total carbon export ranged from 51 to 91 % for the sampled storm events (Figure 4.32; Table 4.5). The total amount of carbon exported for 13 storm events was 603 kg (Event 11,

September 6, 2011, was not included since DOC data on this event was not available) of which, POC contributed 503 kg. Hence, POC contributed to 83.5 % of the total carbon export during storms for the study period.

Maximum export of POC and DOC was observed for event 10 (August 27, 2011), which was also the event with highest total precipitation and streamflow discharge. The three largest events in terms of total precipitation – event 1 (September 30, 2010), event 9 (August 14, 2011) and event 10 (August 27, 2011) accounted for 84% of the total POC export and 63 % of the total DOC export during the whole study period (Figure 4.33). This indicates the importance of large storm events in export of total carbon and especially particulate organic carbon. The importance of high-discharge events is also underscored by flow duration analysis (Figure 4.34) that indicates that more than 90% of POC and 75% of DOC was exported when the flow rate was between 0.7 – 5.0 mm/hr which occurred less than 10% of the time. Hence high flow periods that occur for a short duration play a dominating role in the export of POC and DOC from catchments.

While total mass exports of POC and DOC were obviously influenced by streamflow discharge, the relative % contributions of POC and DOC to total C flux were not dictated by discharge alone. POC contribution during summer events ranged from 81-91 % of the total C export whereas it ranged from 51-75 % for events during the rest of the year (Table 4.5). This was attributed to the elevated concentrations of POC that were associated with summer events. Thus seasonal factors could influence POC concentrations and therefore the relative contribution of POC to total C export.

The total C export during events also varied with the stages of storm events and was observed to be higher on the rising limb of the discharge hydrograph compared to the falling limb. The rising limb accounted for only 18 % of the total event time and 31 % of total discharge, but it was responsible for 56 % of the export of POC and 39 % of the export of DOC (Table 4.6). Hence major portion of POC export during an event occurred prior to peak discharge.

Large storm events play a very dominating role in the total POC export and the POC export during small storm events and baseflow conditions can be neglected in comparison to the POC export during large storm events. Since most of the moderate to large storm events during the study period were sampled, it can be safely assumed that the POC export during the rest of the non-sampled period (small storm events + baseflow conditions) was not significant compared to the sampled storm events. So we can assume the total POC export from the ST3 catchment during 2011 to be approximately equal to the total POC export during the sampled storm events in 2011 (events 3 to 14), which is 405 kg. This is equivalent to the annual POC export of 33.75 kg ha^{-1} yr^{-1} from the ST3 catchment. However, similar assumptions cannot be made about the DOC export, since a significant amount of DOC is exported during small storm events and baseflow conditions. Total DOC export during 2011 was estimated to be 210 kg, which is equivalent to 17.5 kg $ha^{-1}yr^{-1}$.Out of this, DOC exported during the baseflow conditions was 4.24 kg $ha^{-1}yr^{-1}$ (24%) and during stormflow conditions was 13.26 kg $ha^{-1}yr^{-1}$ (76%). The total C export during 2011 was 51.25 kg $ha^{-1}yr^{-1}$.

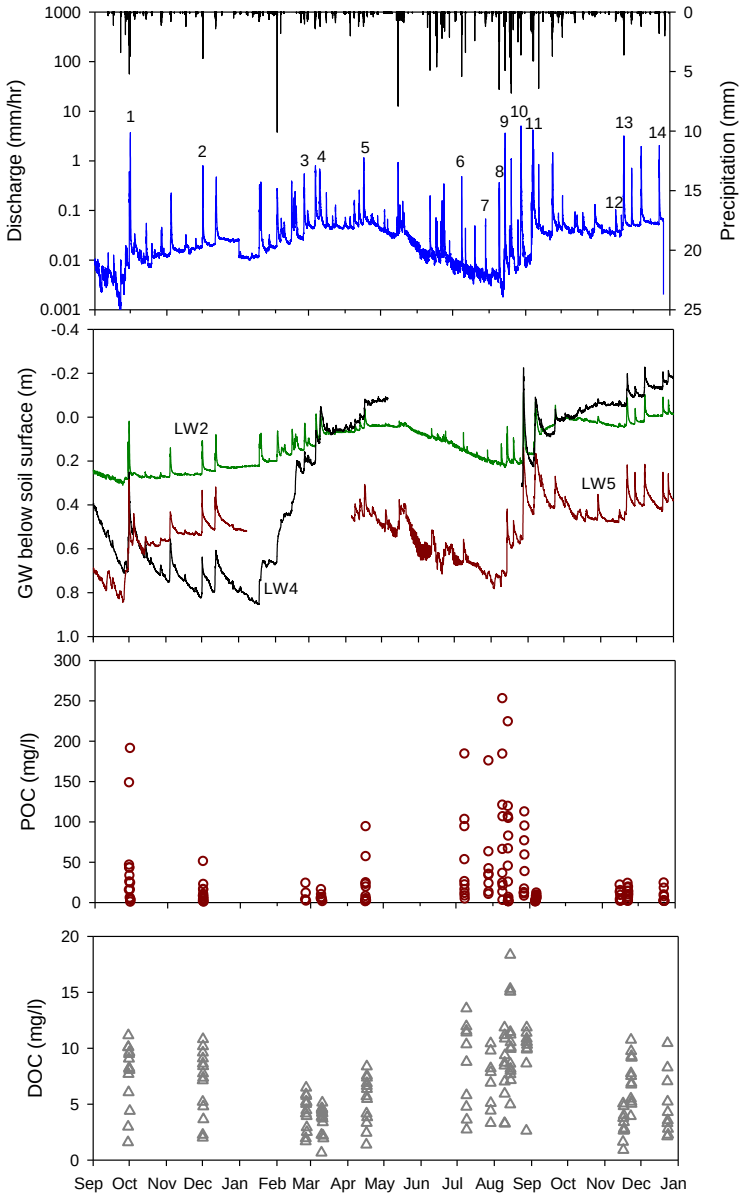


Figure 4.1 Time-series plot for the study period (Sept. 2010 – Dec. 2011) for precipitation and discharge; Groundwater depth at wells LW2, LW4 and LW5; POC concentration for sampled events; DOC concentration for sampled events

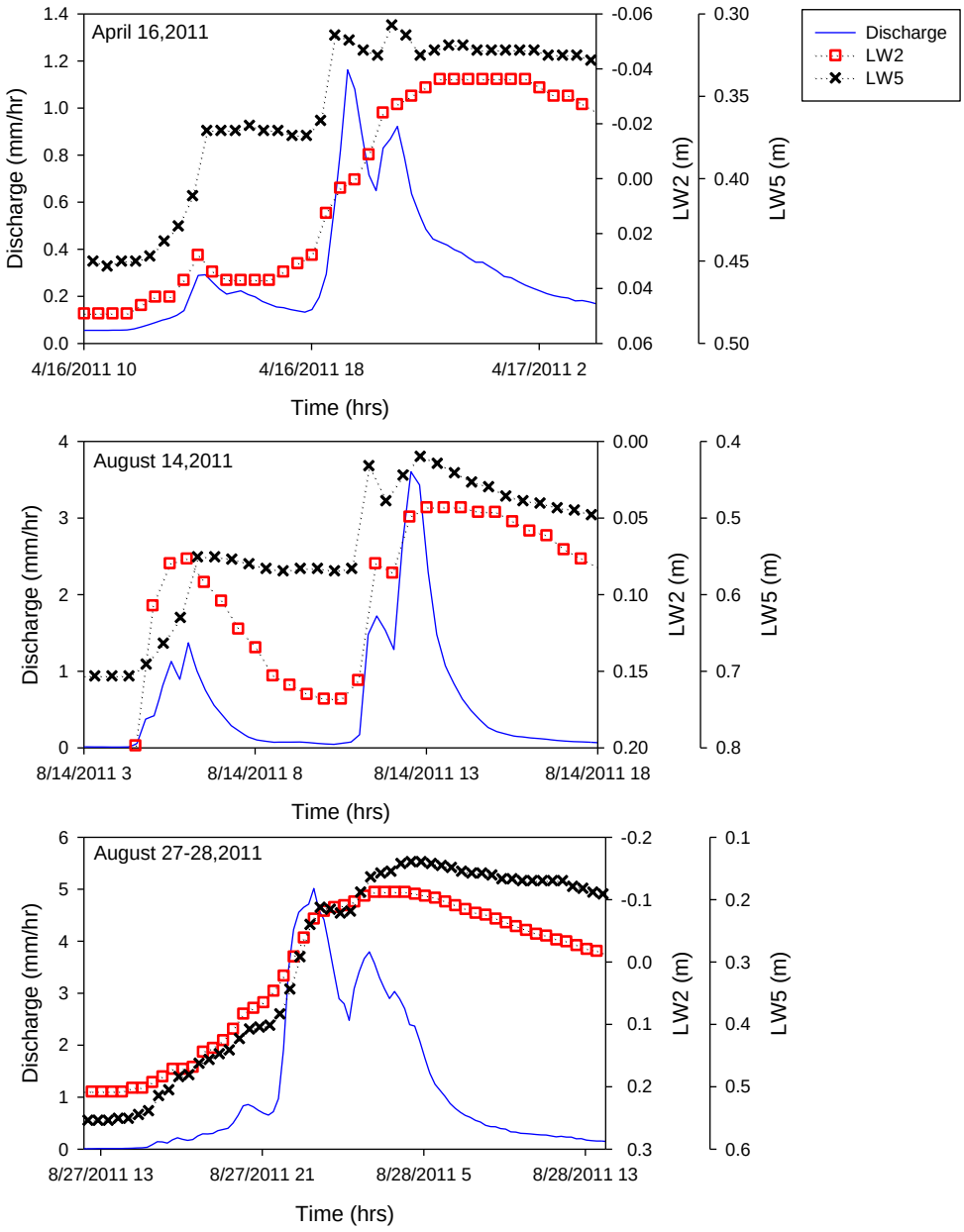


Figure 4.2 Streamflow discharge and groundwater depth below the soil surface for LW2 and LW5 for the events of April 16, 2011, August 14, 2011 and August 27-28, 2011 at ST3

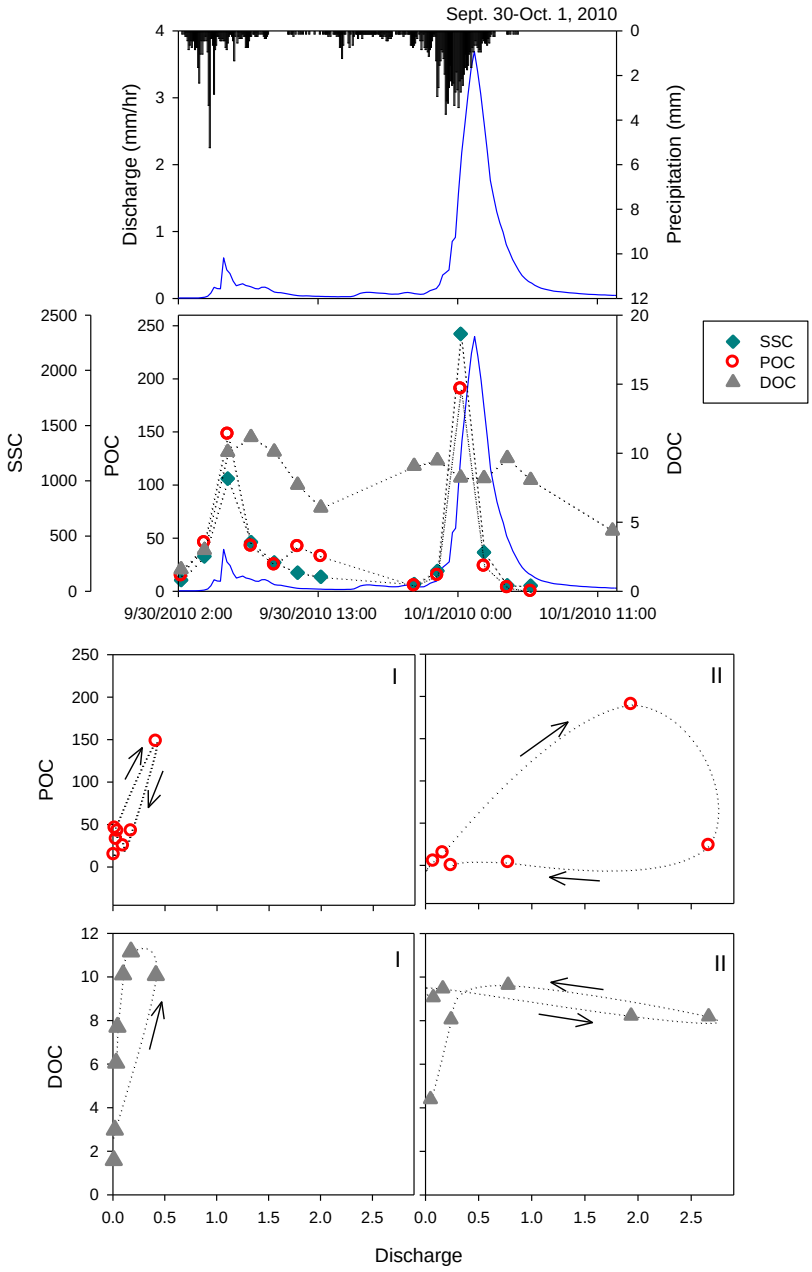


Figure 4.3 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of September 30 – October 1, 2010

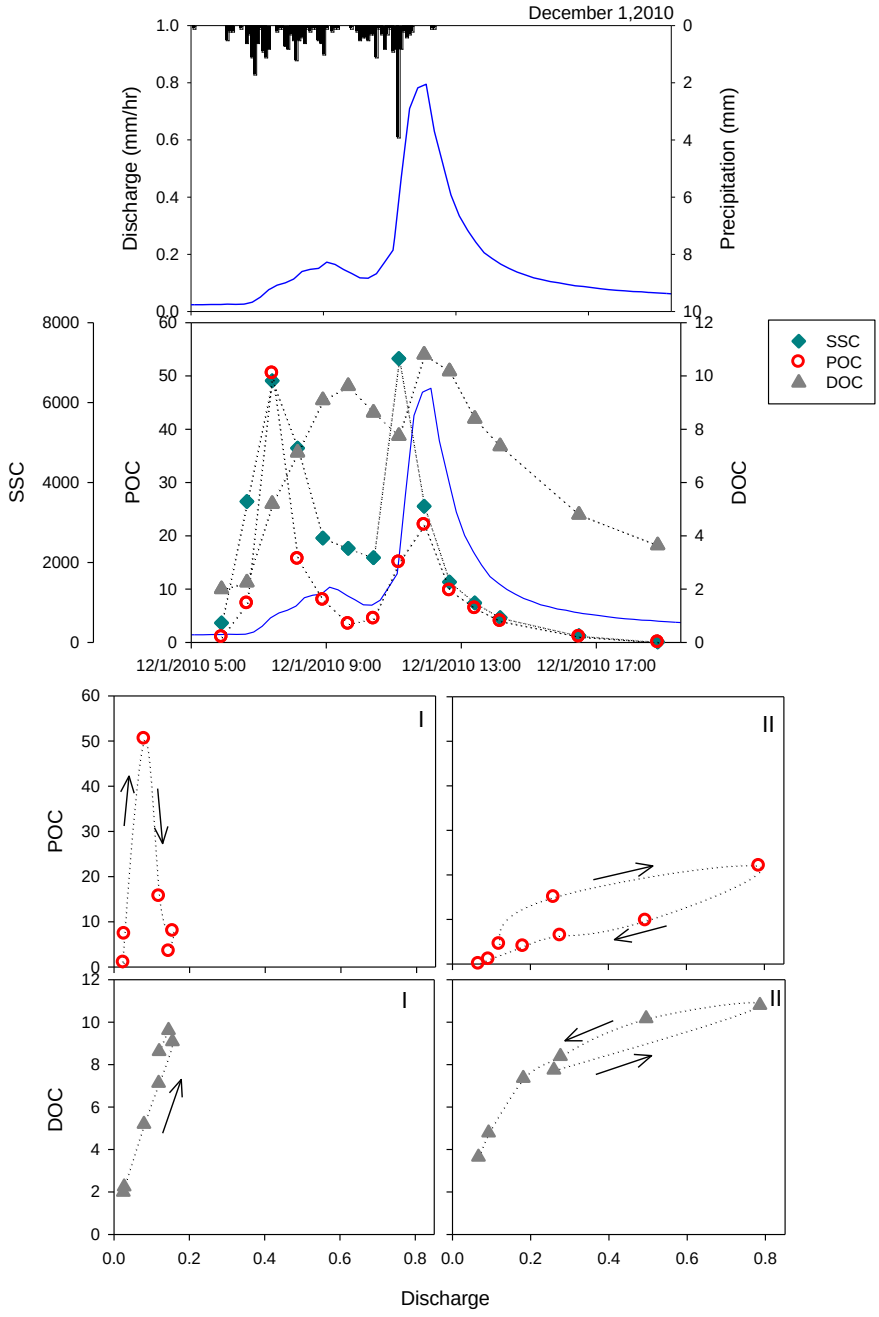


Figure 4.4 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of December 1, 2010

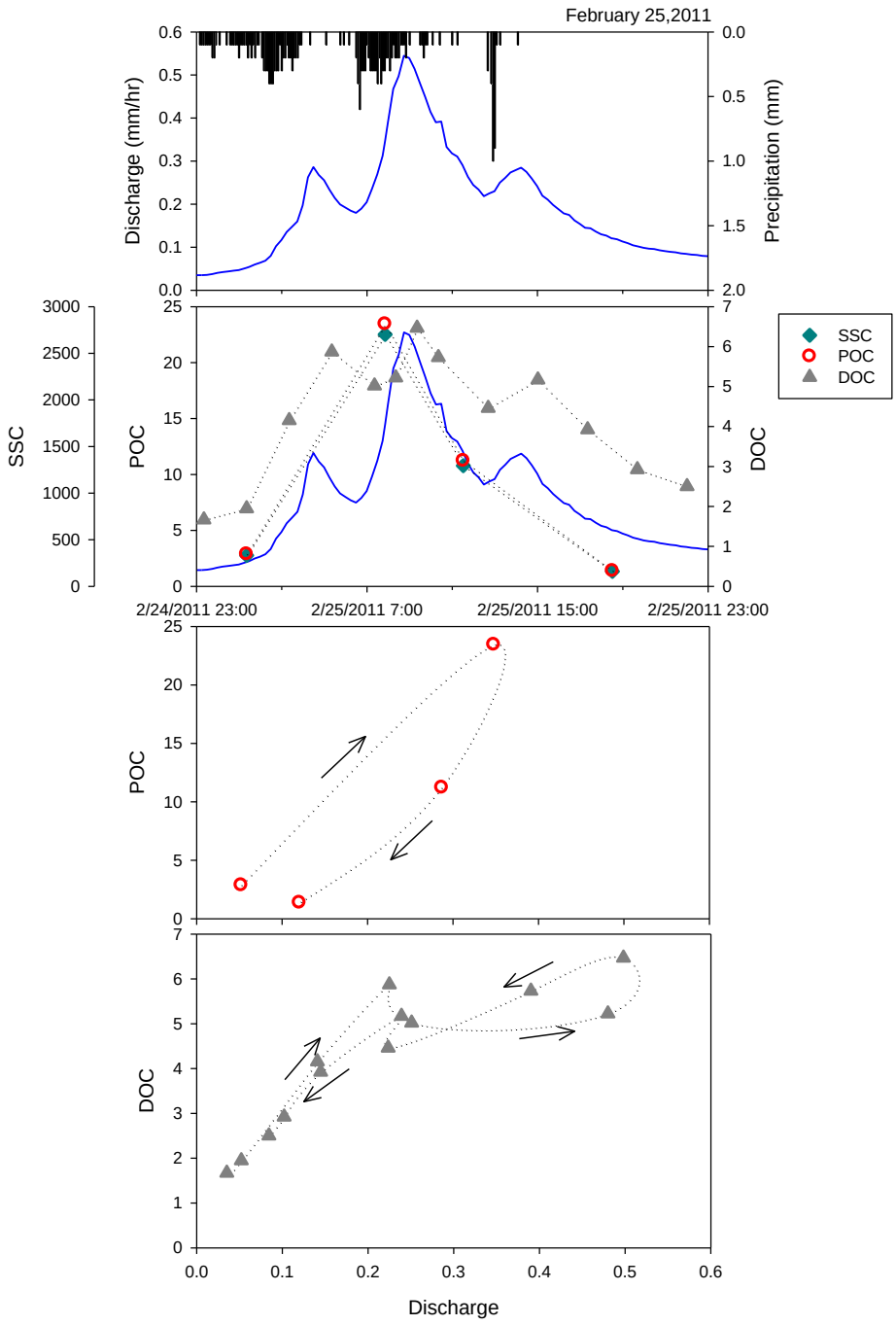


Figure 4.5 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of February 25, 2011

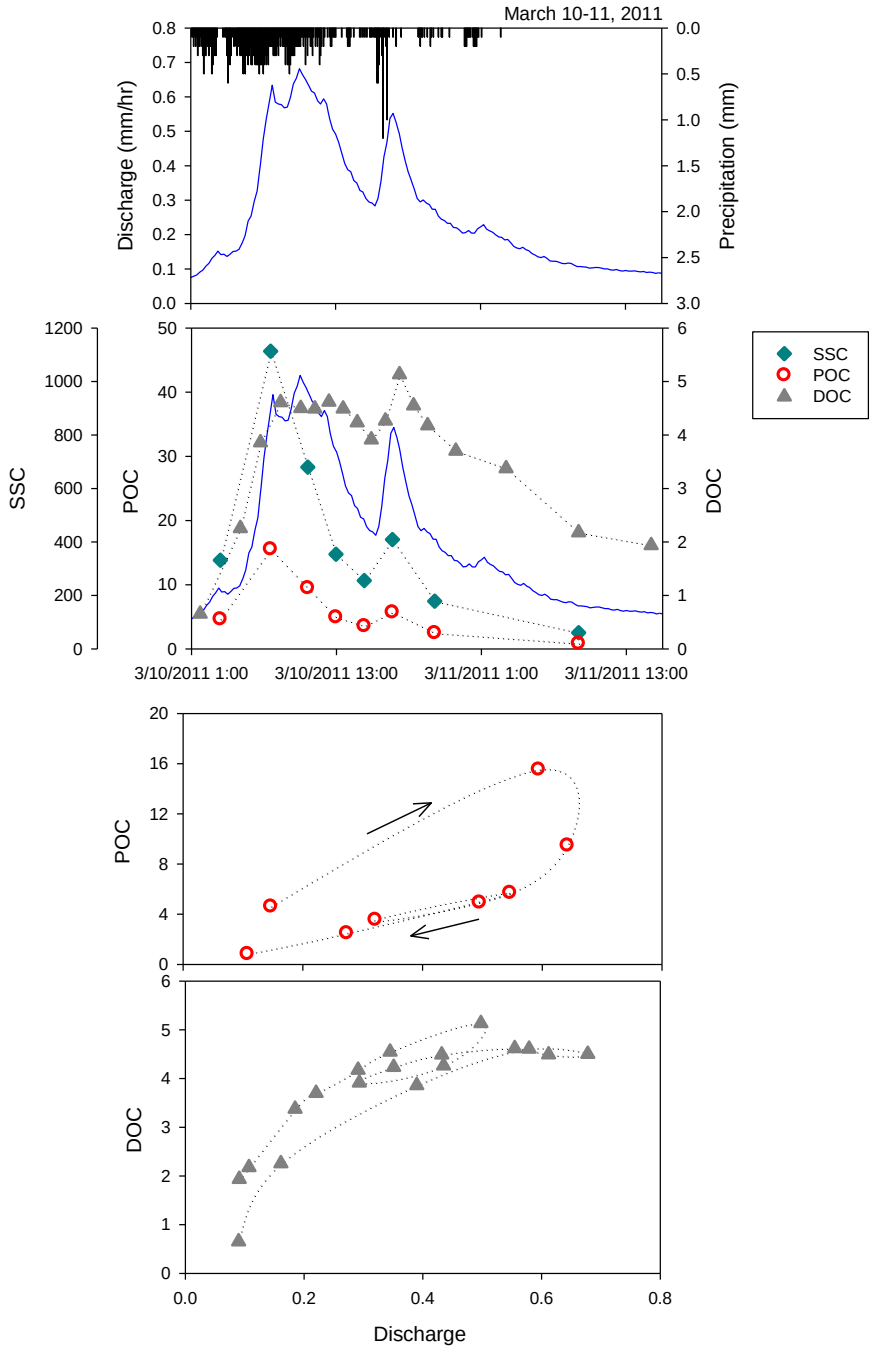


Figure 4.6 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of March 10-11, 2011

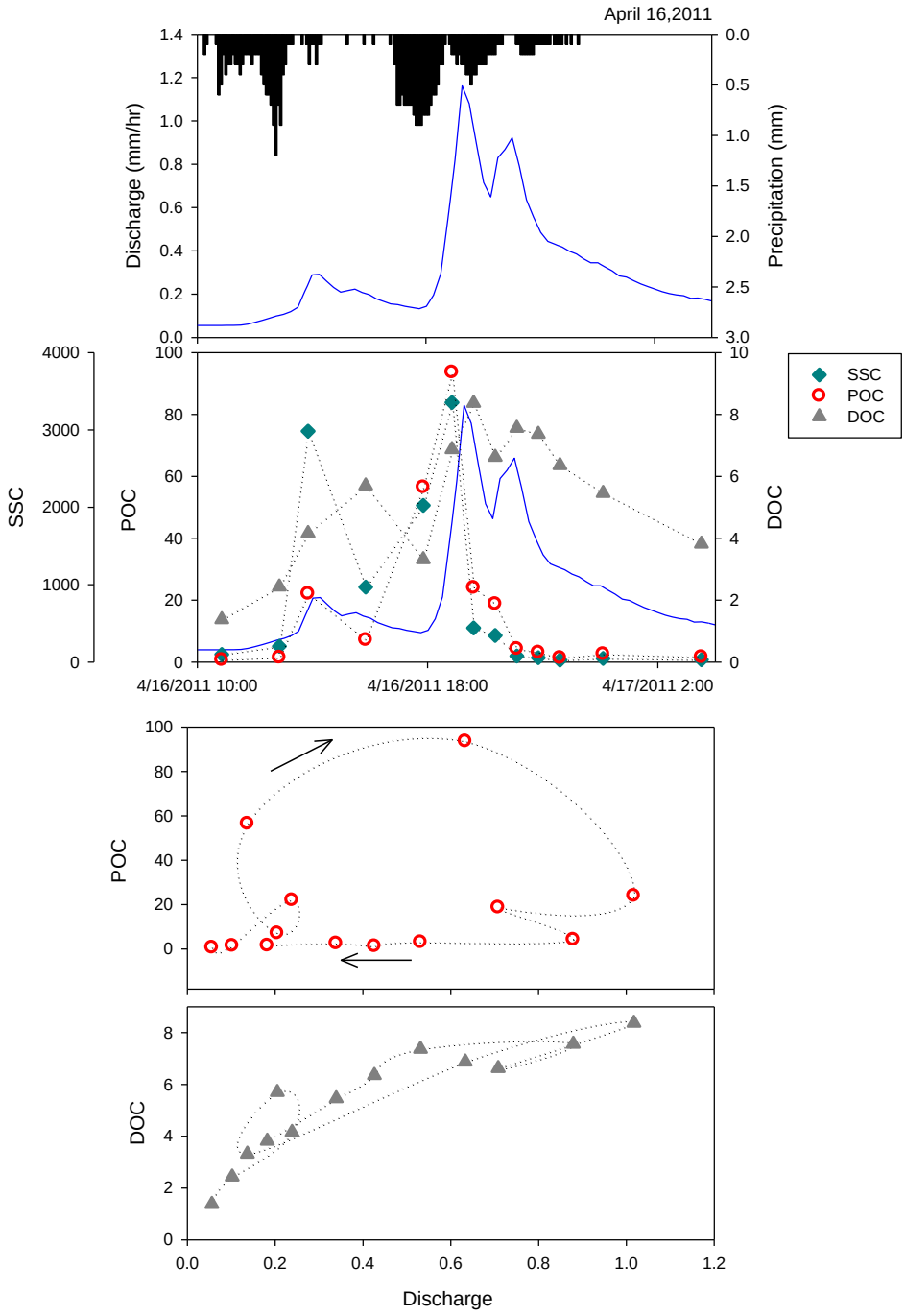


Figure 4.7 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of April 16, 2011

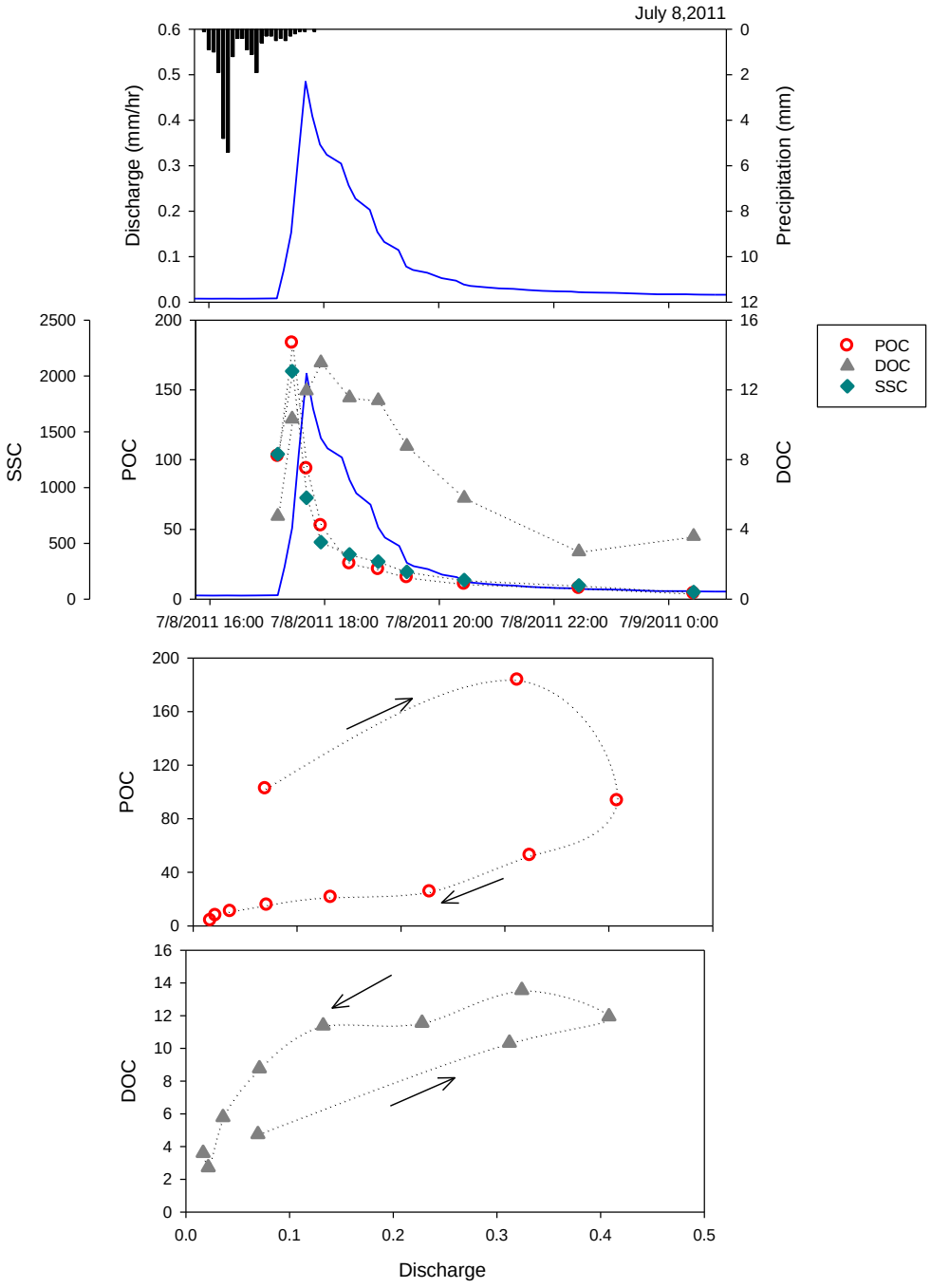


Figure 4.8 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of July 7-8, 2011

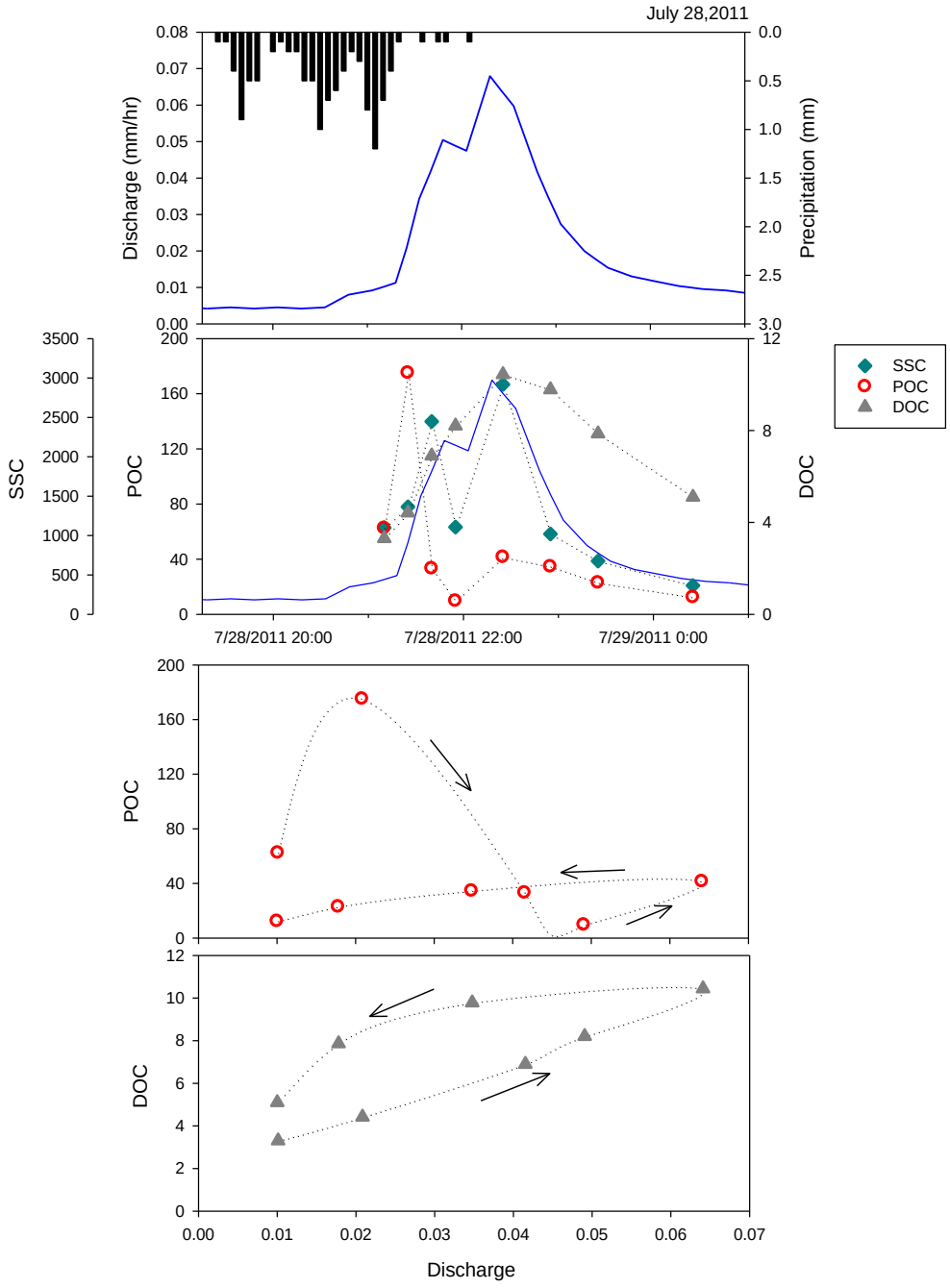


Figure 4.9 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of July 28, 2011

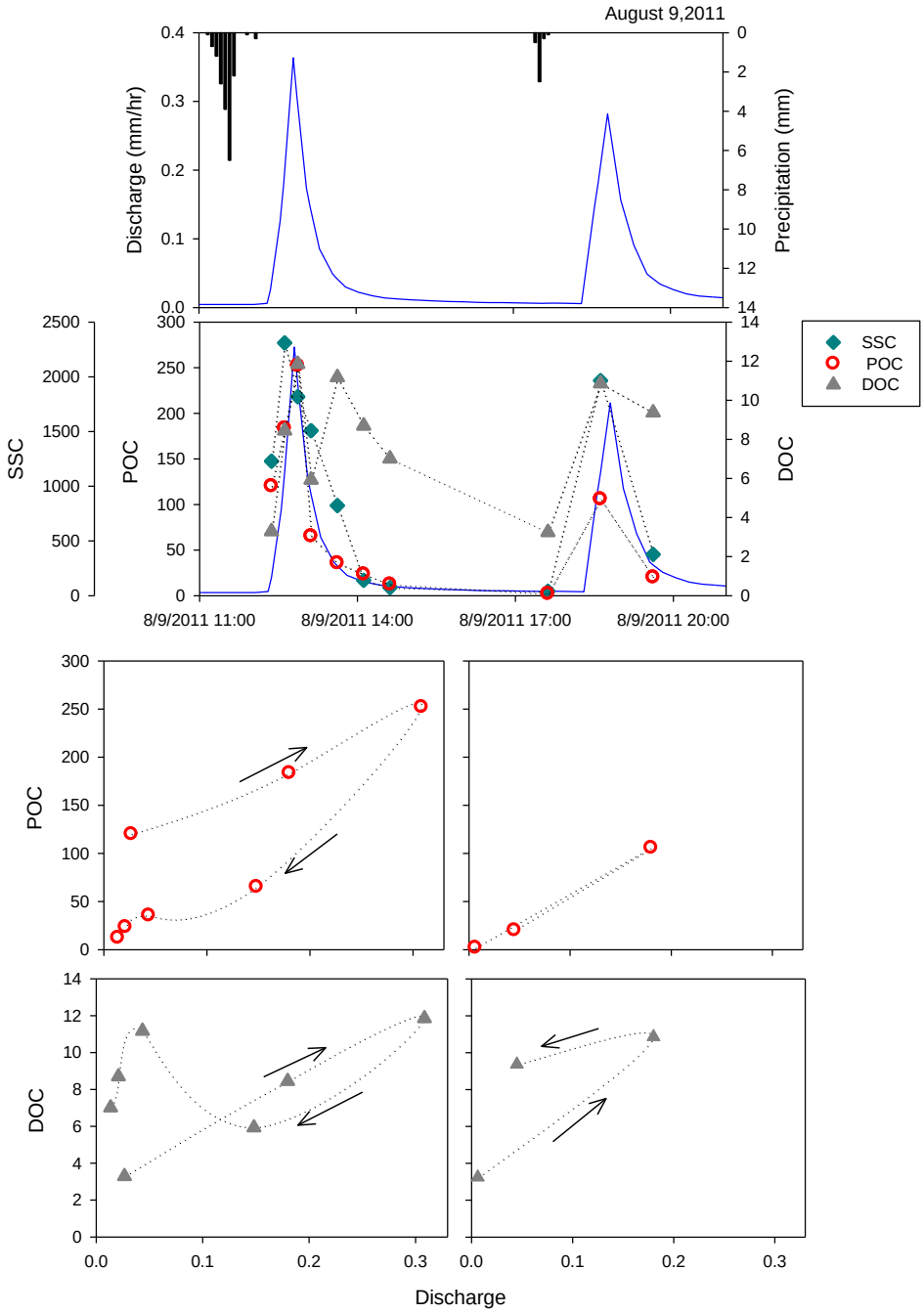


Figure 4.10 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of August 9, 2011

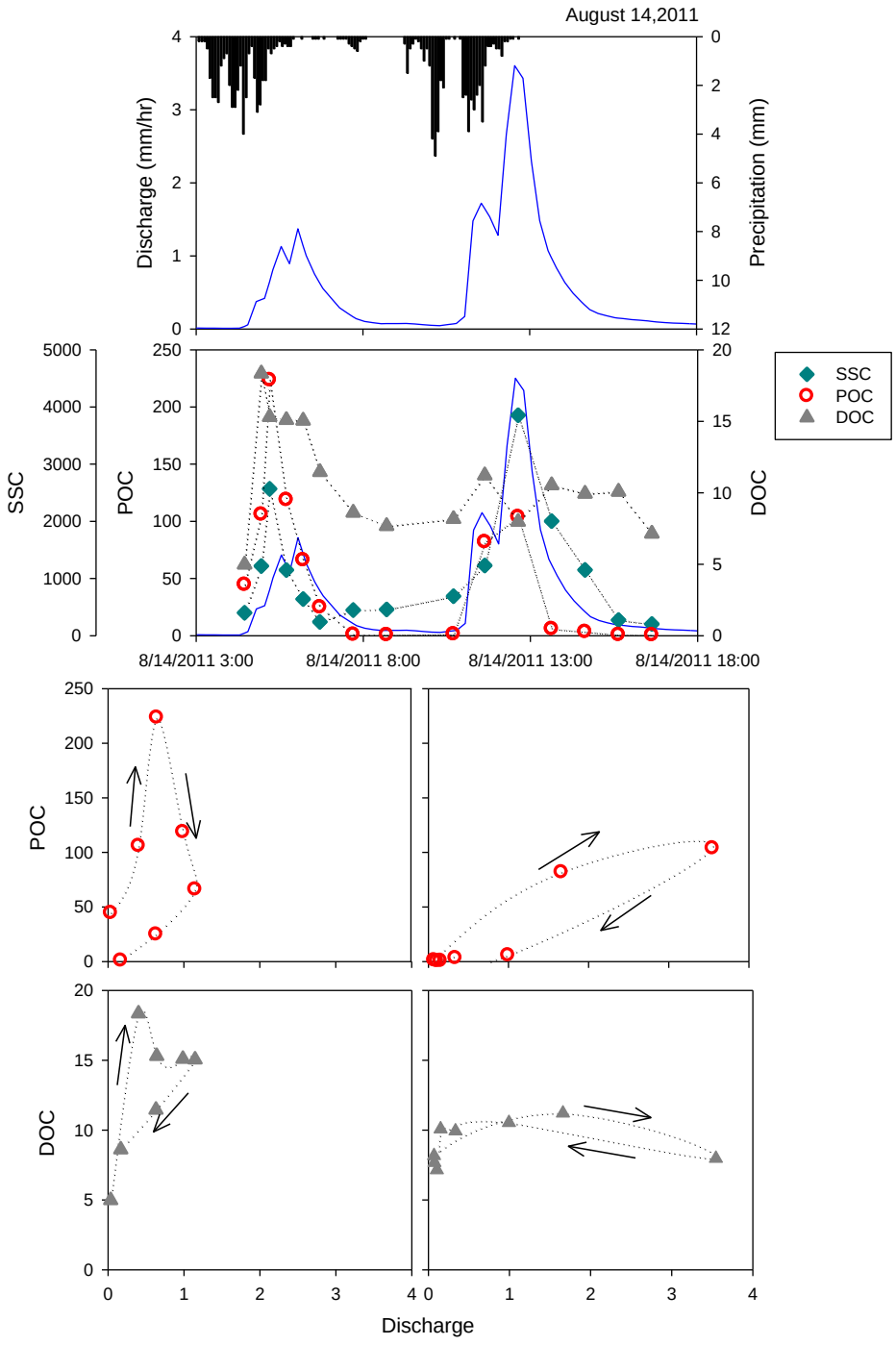


Figure 4.11 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of August 14, 2011

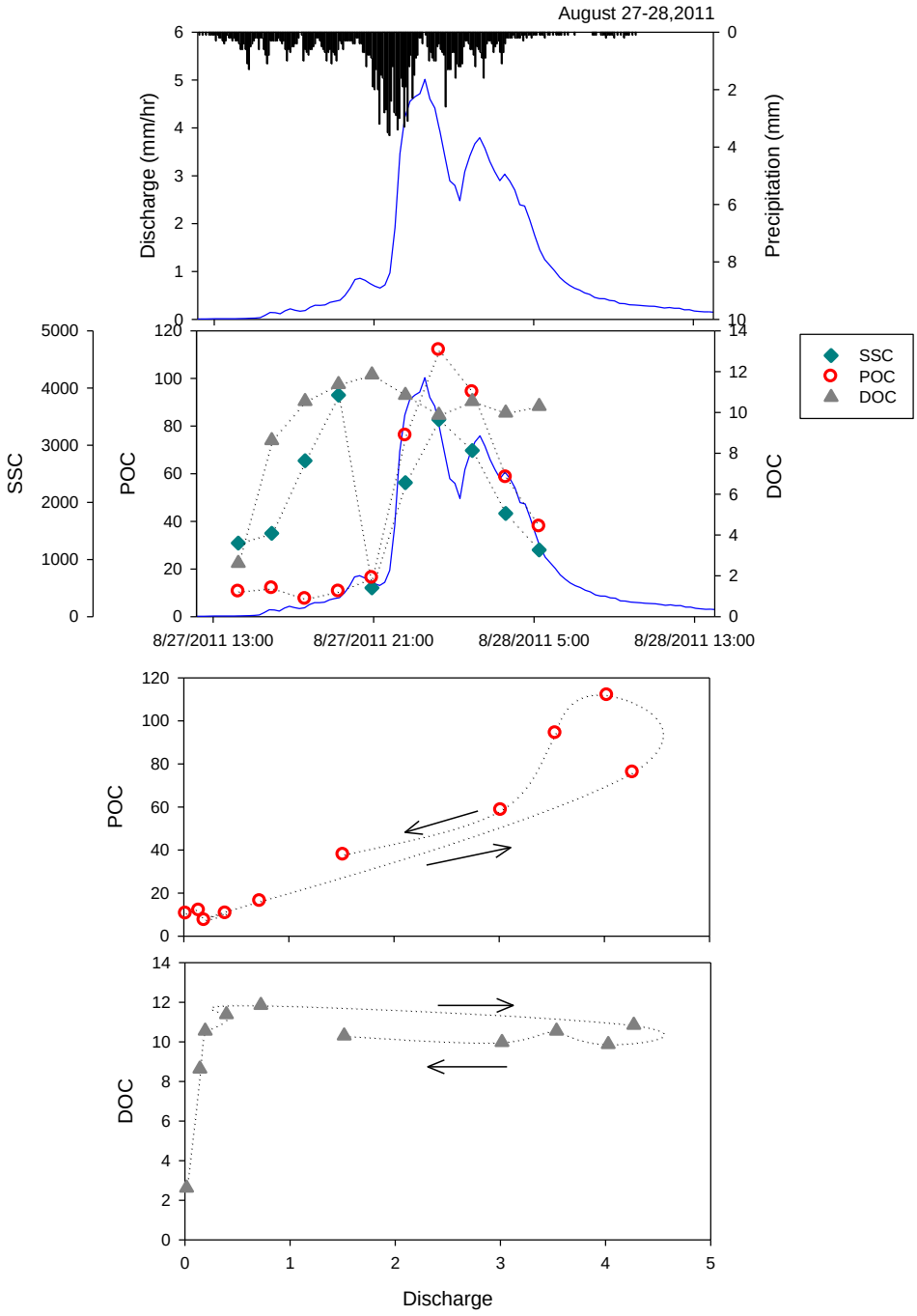


Figure 4.12 Precipitation and discharge; SS, POC and DOC concentration (mg/l) c); C-Q loops for POC and DOC for the event of August 27-28, 2011

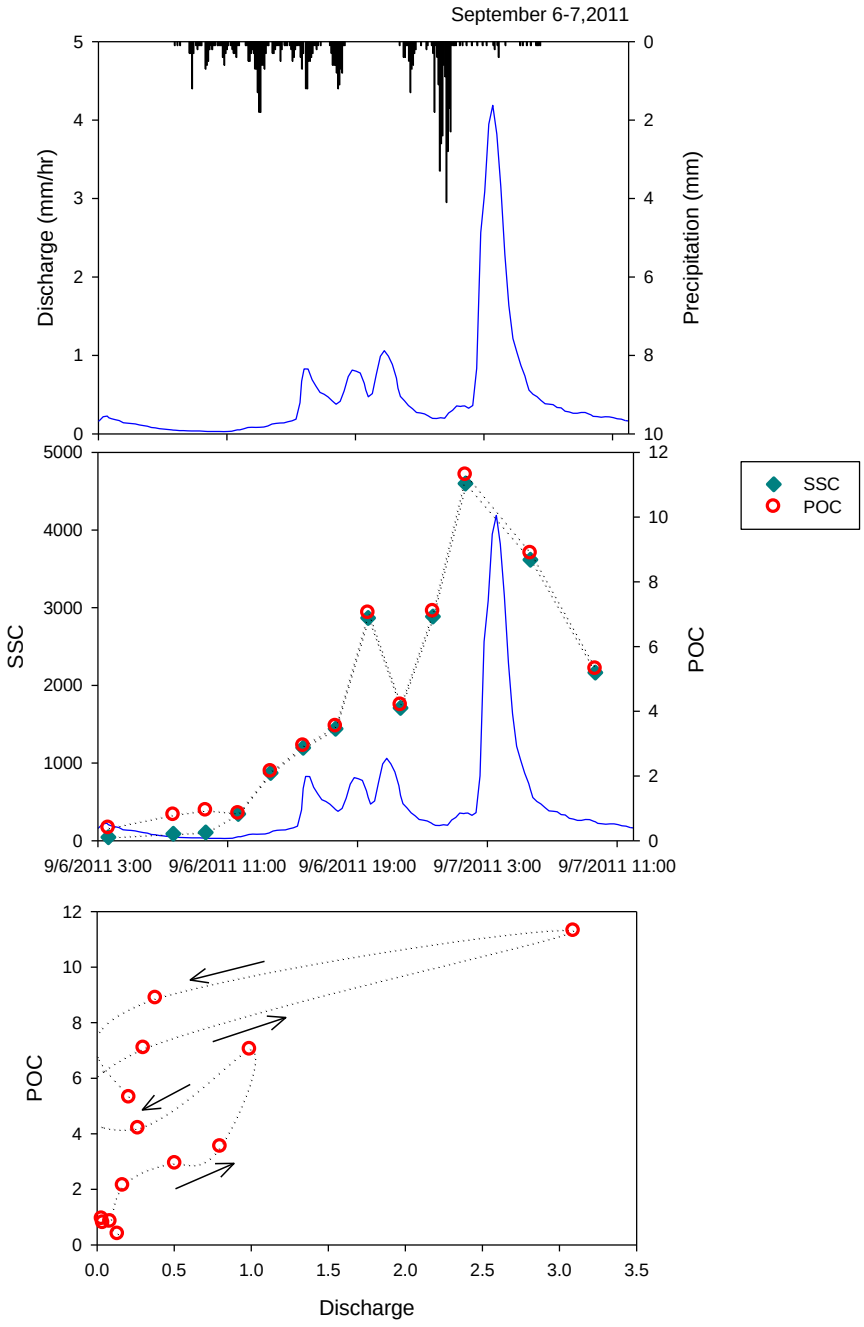


Figure 4.13 Precipitation and discharge; SS and POC concentration (mg/l) c) ; C-Q loop for POC for the event of September 6-7, 2011

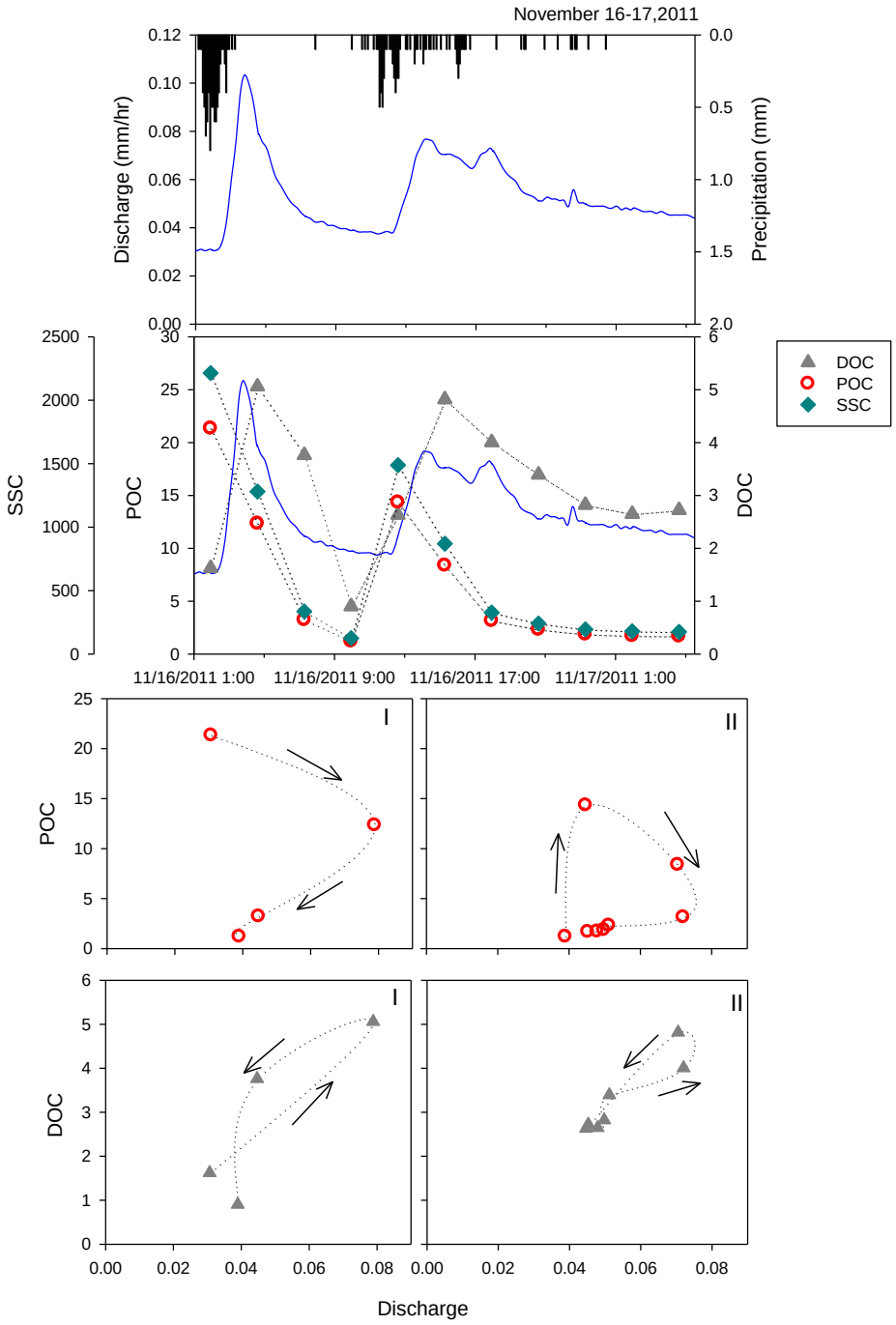


Figure 4.14 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of November 16-17, 2011

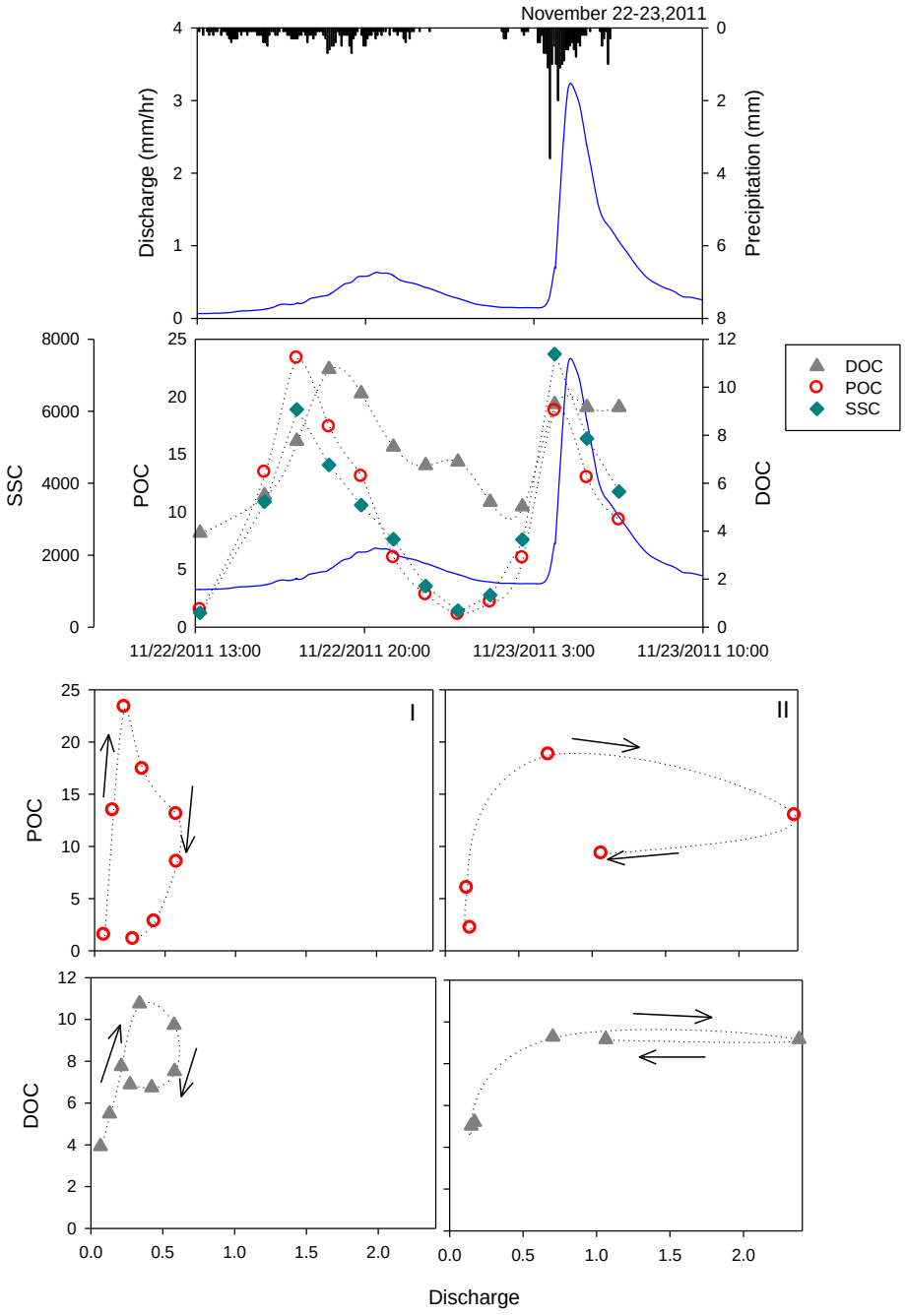


Figure 4.15 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of November 22-23, 2011

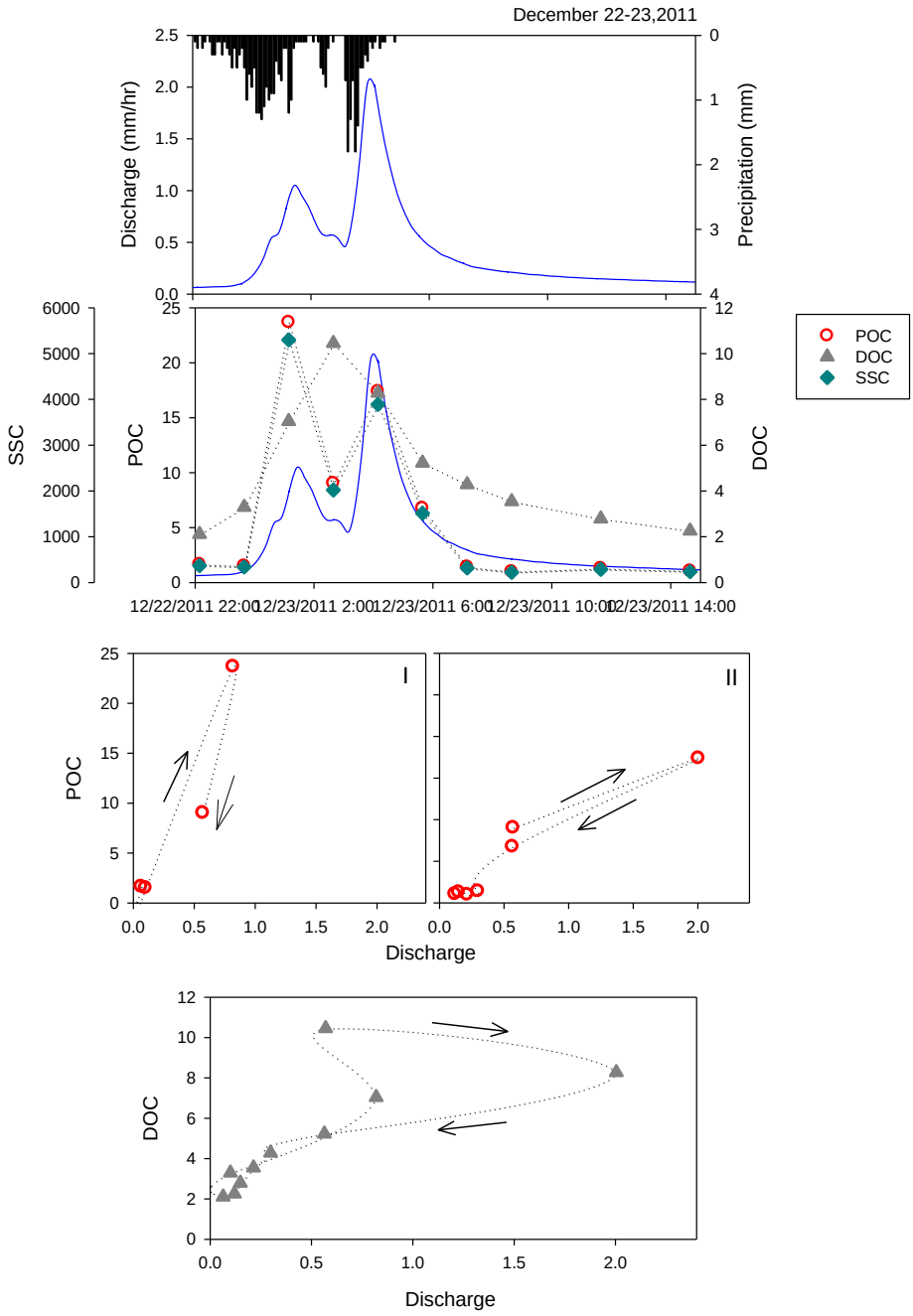


Figure 4.16 Precipitation and discharge; SS, POC and DOC concentration (mg/l); C-Q loops for POC and DOC for the event of December 23, 2011

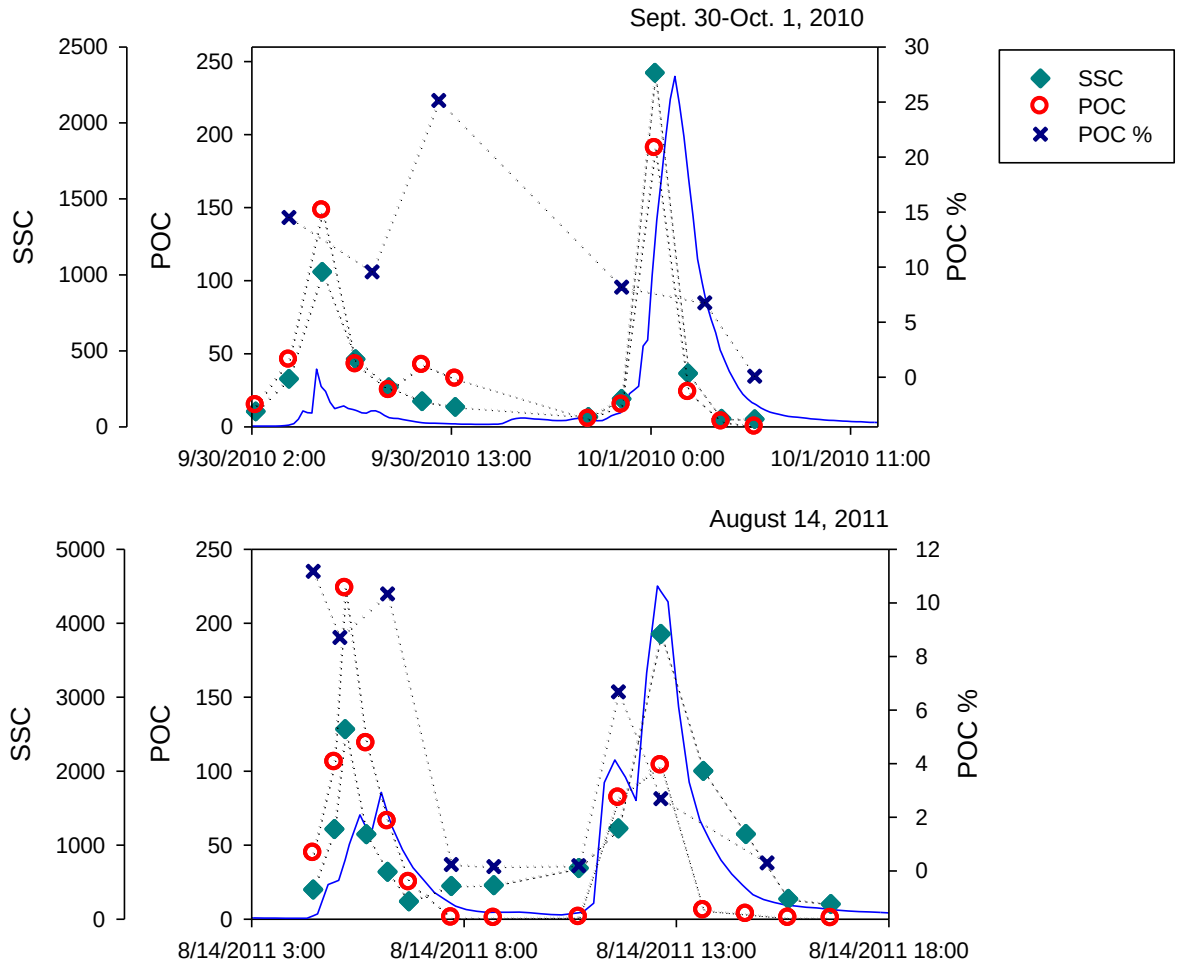


Figure 4.17 Temporal patterns of SS (mg/l), POC content (%) and POC concentration (mg/l) for the events of September 30-October 1, 2010 (above) and August 14, 2011 (below)

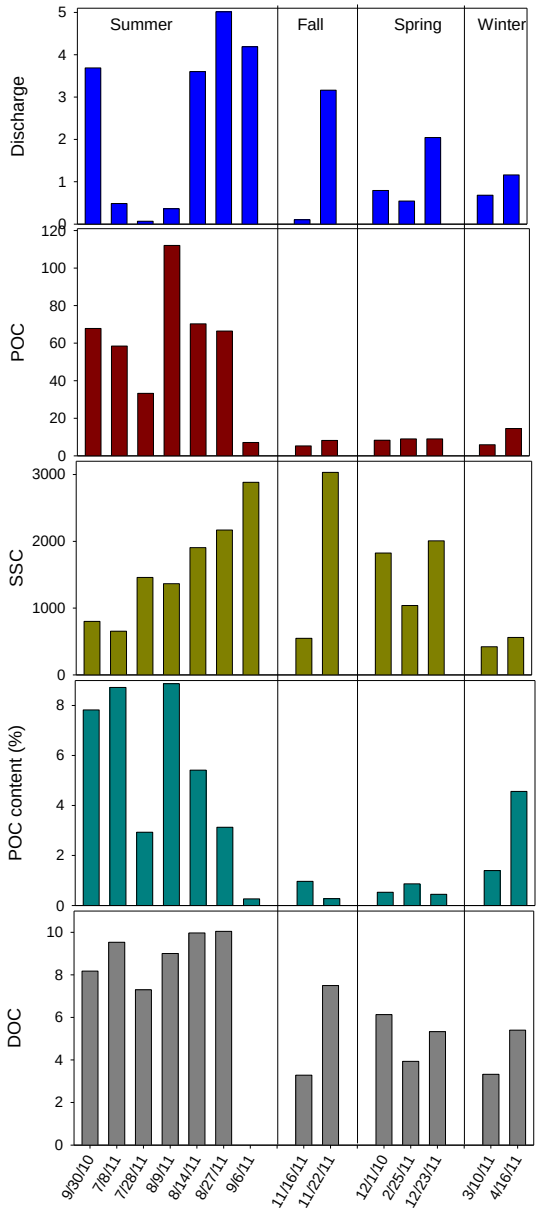
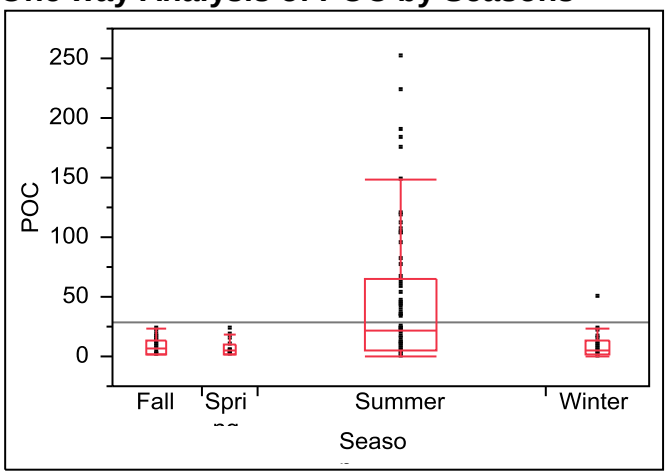


Figure 4.18 Flow-weighted mean concentrations of POC, SS, DOC (in mg/l) and POC content (%) for the sampled events at ST3 showing the effect of seasonal timing of the events on POC, SS, % POC content and DOC. The DOC data for event 11 (9/6/11) was not available.

One way Analysis of POC by Seasons



One way Anova
Summary of Fit

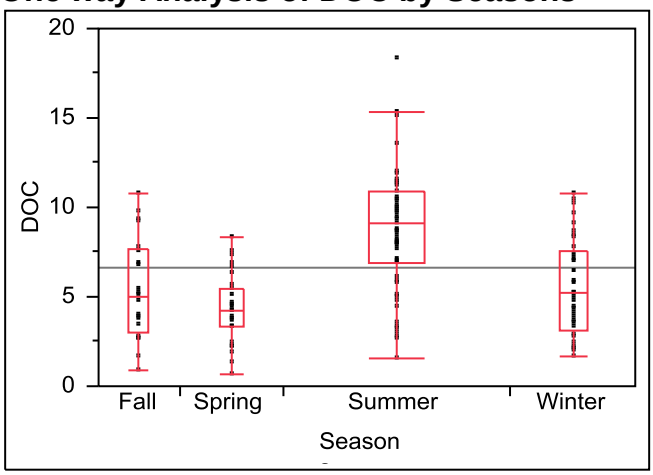
Rsquare	0.161119
Adj Rsquare	0.14327
Root Mean Square Error	43.47245
Mean of Response	28.55923
Observations (or Sum Wgts)	145

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Seasons	3	51179.22	17059.7	9.0270	<.0001*
Error	141	266469.35	1889.9		
C. Total	144	317648.56			

Figure 4.19 ANOVA on POC concentration of samples by seasons

One way Analysis of DOC by Seasons



One way Anova
Summary of Fit

Rsquare	0.294289
Adj Rsquare	0.28063
Root Mean Square Error	2.880589
Mean of Response	6.628365
Observations (or Sum Wgts)	159

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Seasons	3	536.3416	178.781	21.5456	<.0001*
Error	155	1286.1577	8.298		
C. Total	158	1822.4994			

Figure 4.20 ANOVA on DOC concentration of samples by seasons

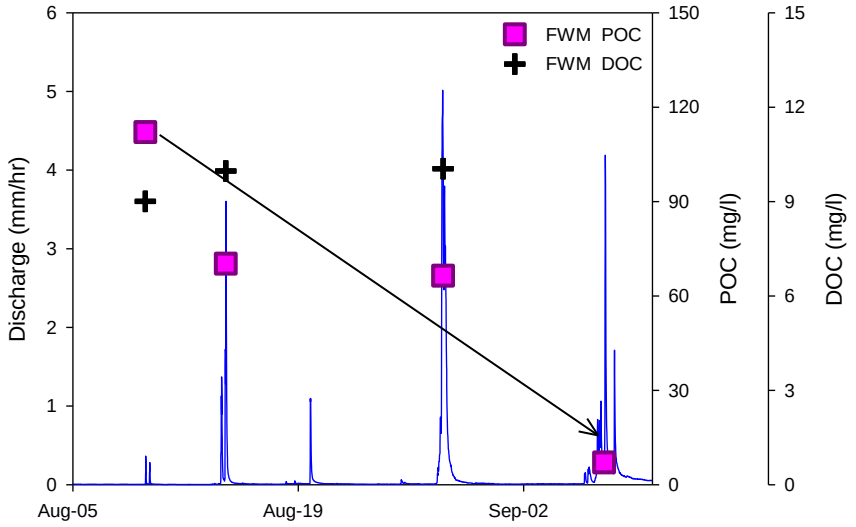


Figure 4.21 Streamflow discharge and the flow-weighted POC and DOC concentration during successive floods in summer, 2011 at ST3.

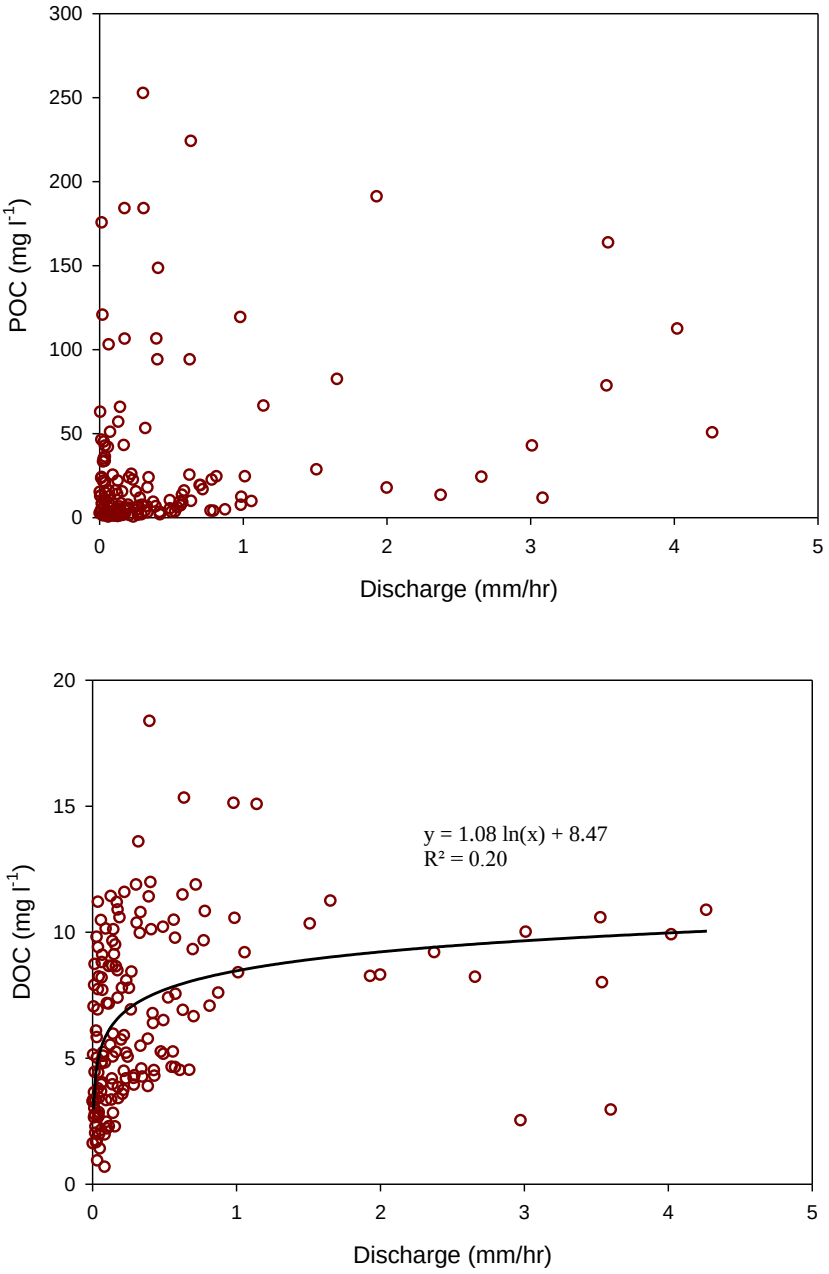


Figure 4.22 Relationship between discharge and particulate organic carbon (above) and dissolved organic carbon (below)

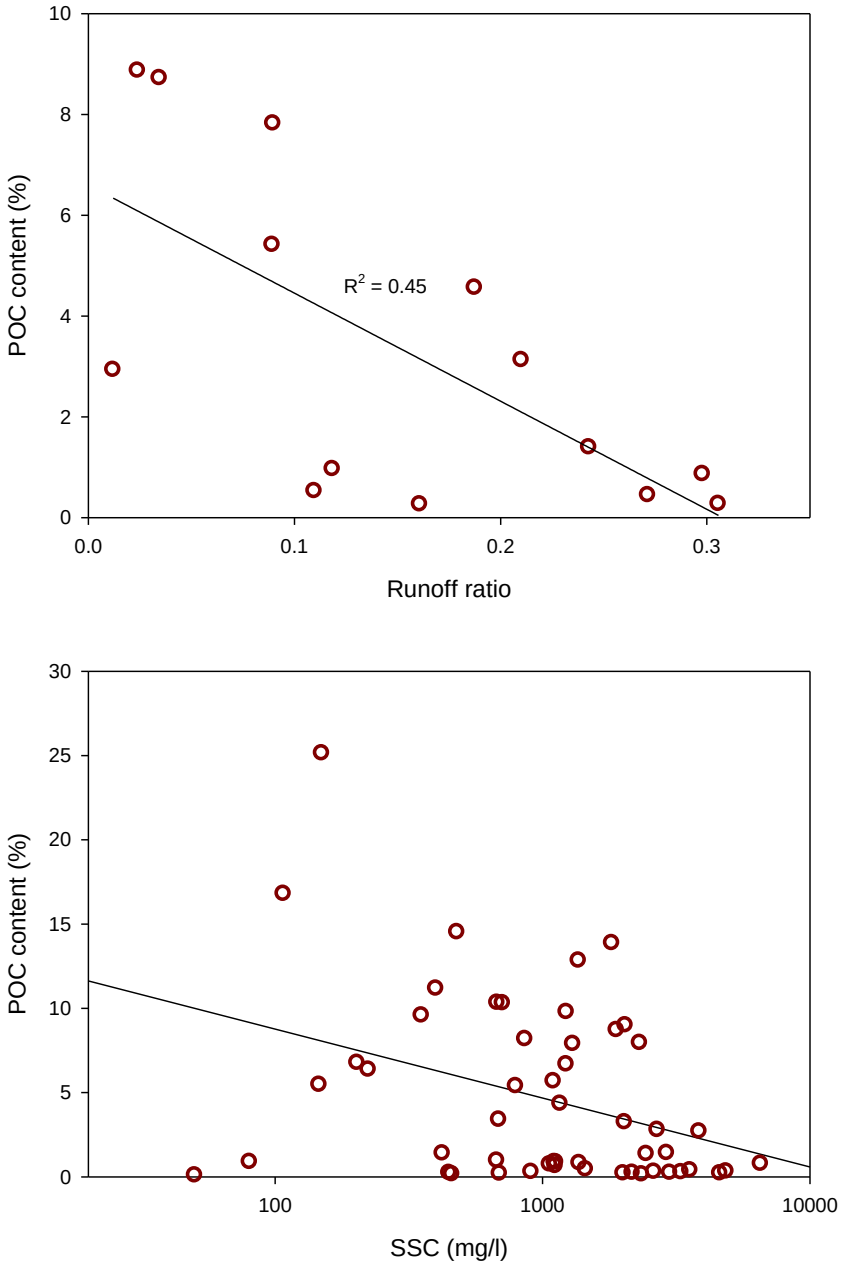
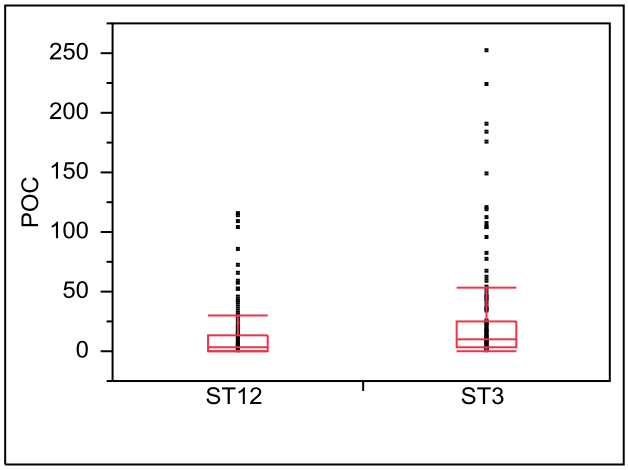


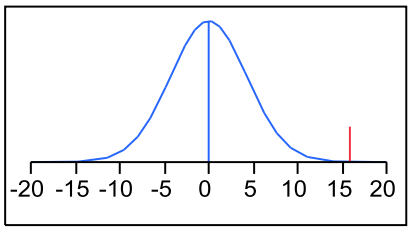
Figure 4.23 Relationship between POC content (%) and runoff ratio of sampled events (above) and concentration of suspended sediments (below)

One-way Analysis of POC by Catchment scales



t Test

Difference	15.8802	t Ratio	3.694508
Std Err Dif	4.2983	DF	291
Upper CL Dif	24.3400	Prob > |t|	0.0003*
Lower CL Dif	7.4205	Prob > t	0.0001*
Confidence	0.95	Prob < t	0.9999

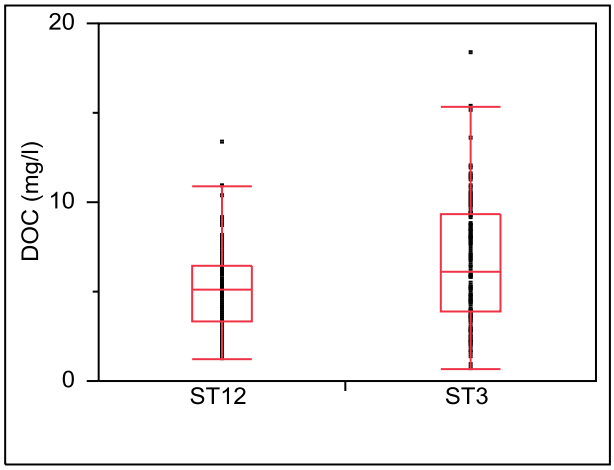


Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Column 2	1	18470.40	18470.4	13.6494	0.0003*
Error	291	393782.25	1353.2		
C. Total	292	412252.66			

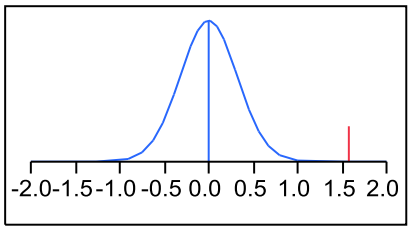
Figure 4.24 ANOVA and t test analysis on DOC concentration by catchment scales (ST3 and ST12)

One-way Analysis of DOC by Catchment scale



t Test

Difference	1.57612	t Ratio	4.916328
Std Err Dif	0.32059	DF	313
Upper CL Dif	2.20690	Prob > |t|	<.0001*
Lower CL Dif	0.94534	Prob > t	<.0001*
Confidence	0.95	Prob < t	1.0000



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Column 4	1	195.6097	195.610	24.1703	<.0001*
Error	313	2533.1045	8.093		
C. Total	314	2728.7142			

Figure 4.25 ANOVA and t test analysis on DOC concentration by catchment scales (ST3 and ST12)

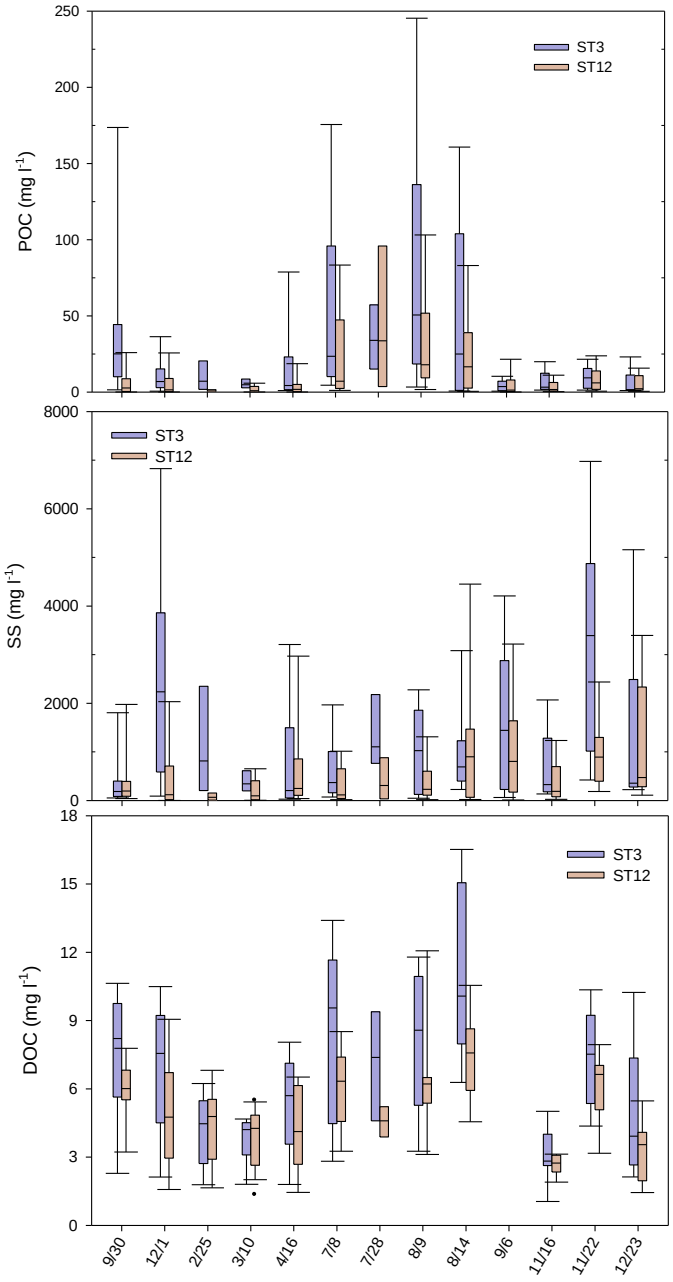


Figure 4.26 Box plots to compare the concentration of POC, SS and DOC at the ST3 and ST12 catchment

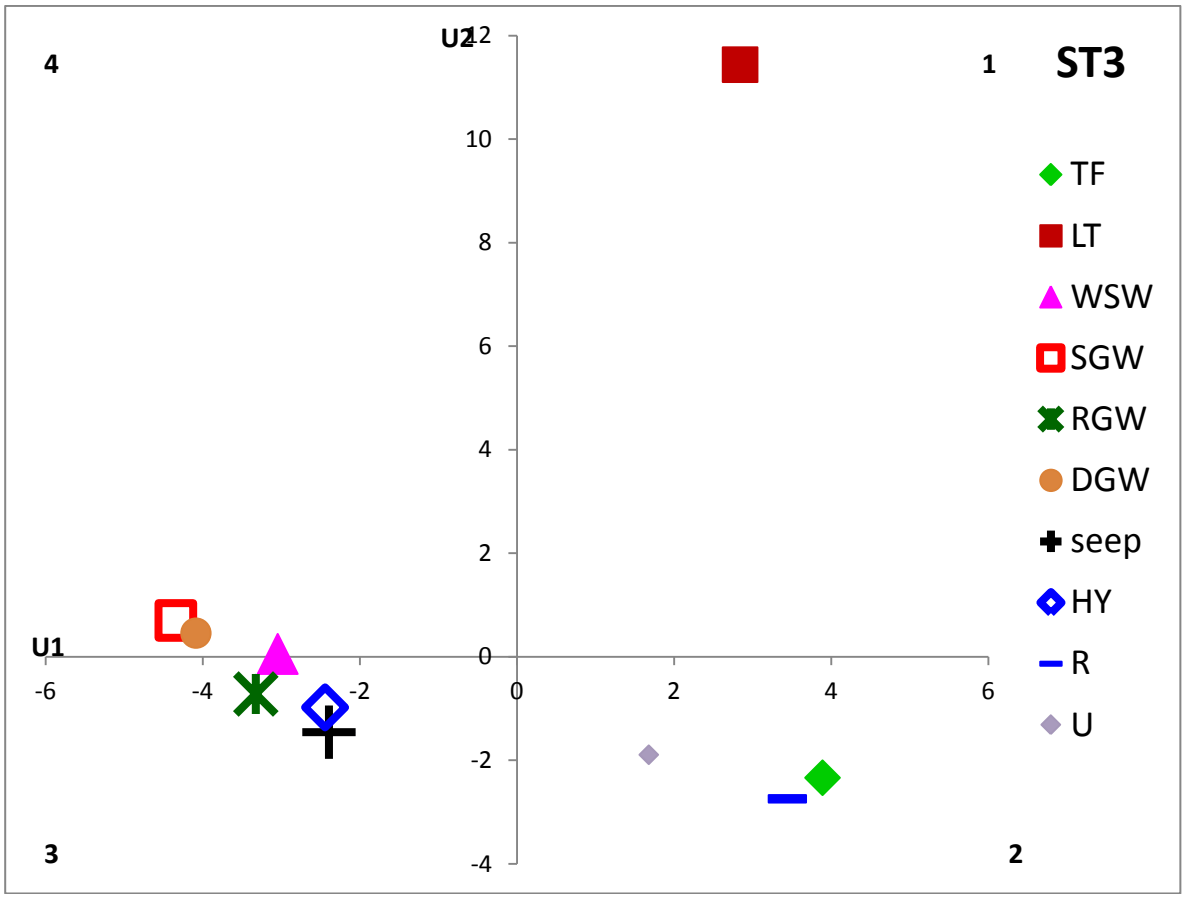


Figure 4.27 Concentrations of sampled end-members in 2-dimensional EMMA space. U1 and U2 indicate the first and second principal components. The sampled end-members are –TF- throughfall, LT-litter leachate, WSW- wetland soil water, , SGW – shallow ground water, RGW – riparian groundwater, DGW – deep groundwater, seep – groundwater seeps, HY-hyporheic water, R-precipitation, and U – tension soil water

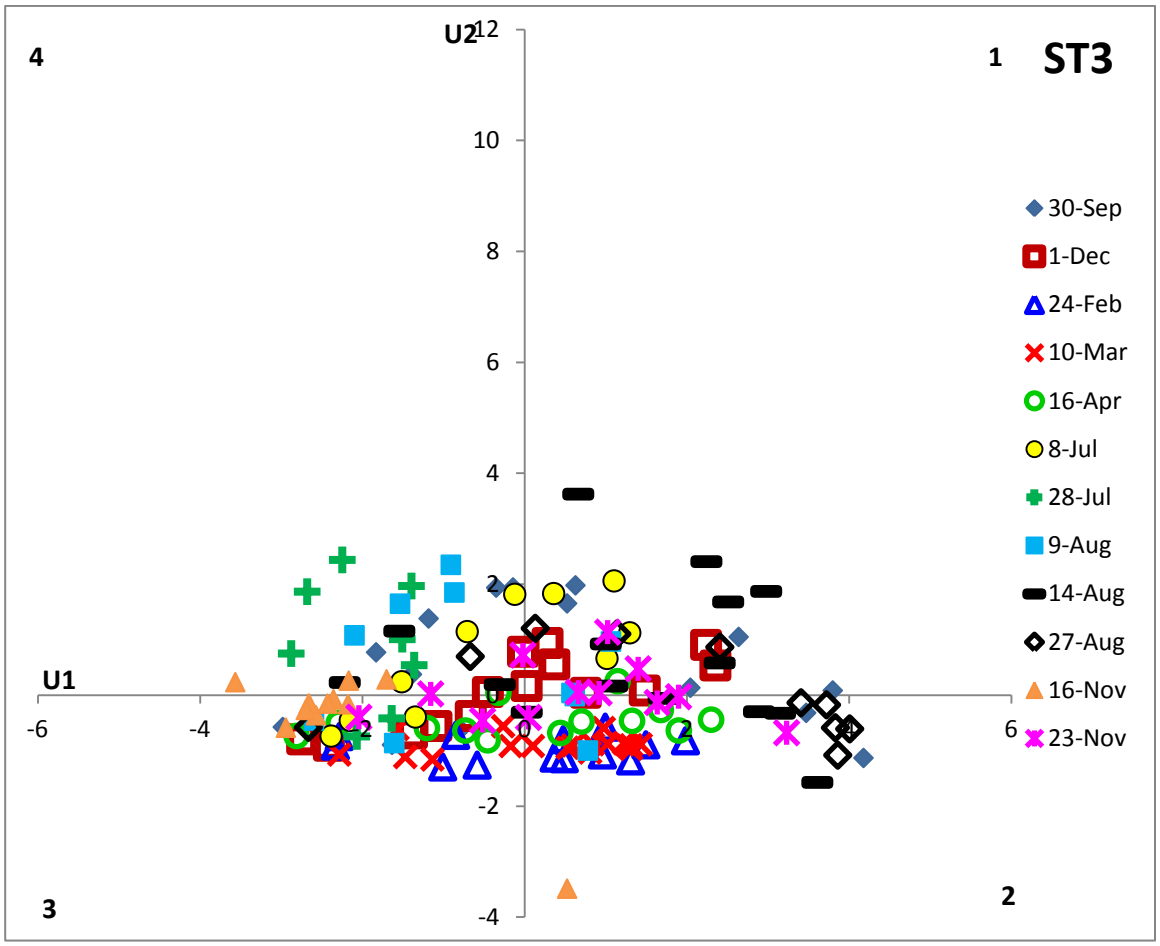


Figure 4.28 Sampled storm events in EMMA space highlighting the differences in mixing patterns among the storm events for dissolved phase constituents

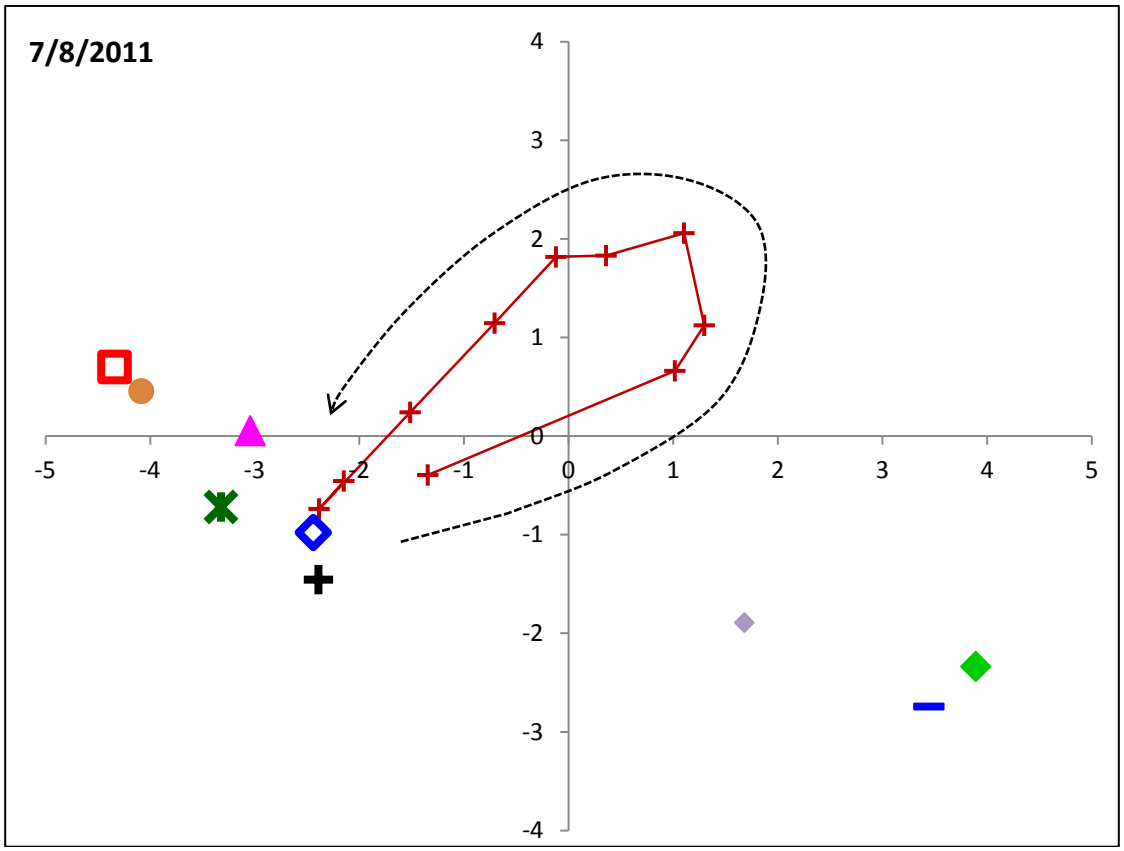


Figure 4.29 Within-event hysteresis loop for event 6 (July 8, 2011) in EMMA mixing diagrams highlighting the counterclockwise shape of the loop and the influence of end-members on stream water chemistry.

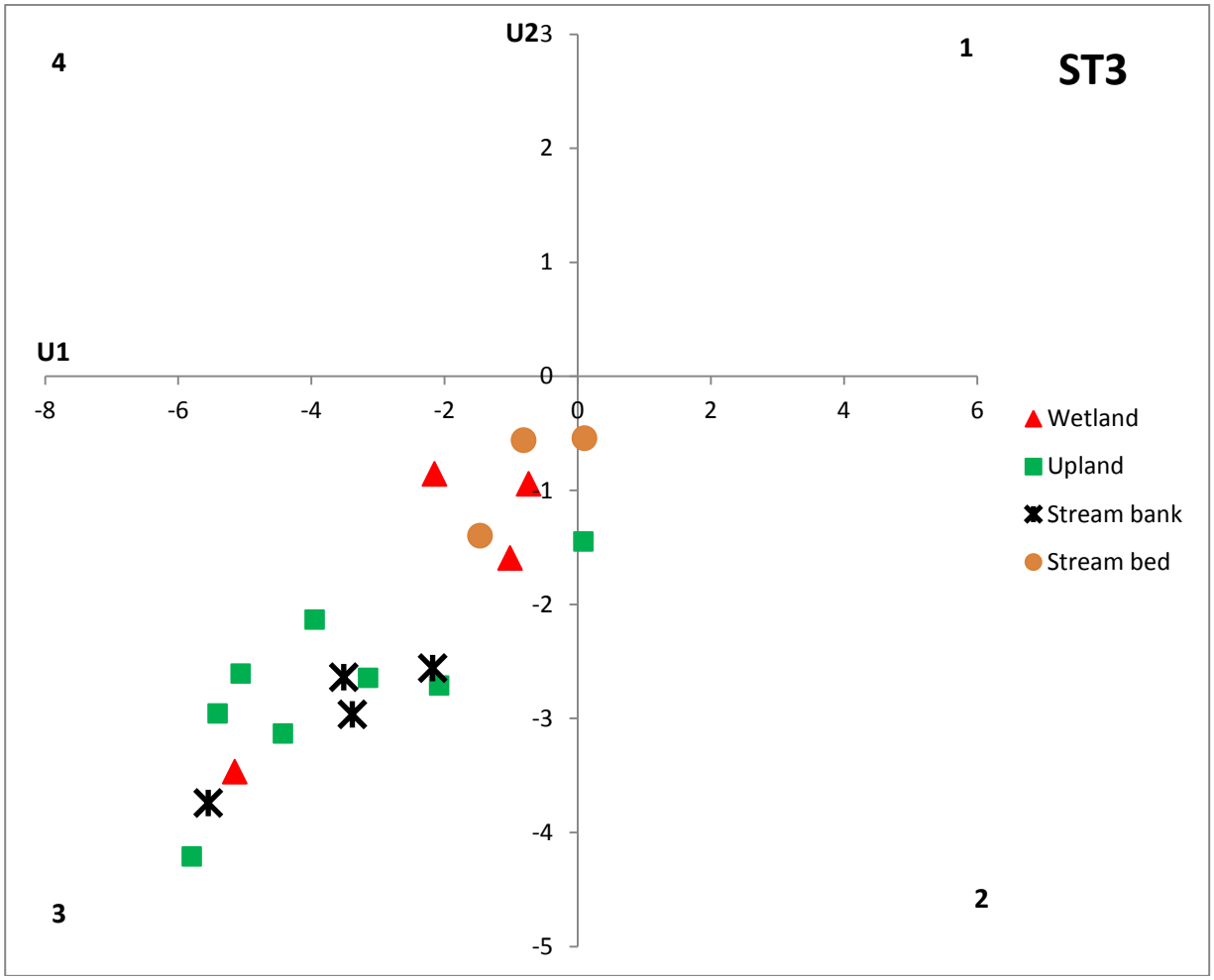


Figure 4.30 Concentrations of sampled end-members in 2-dimensional EMMA space for EMMA on particulate phase constituents of stream runoff.

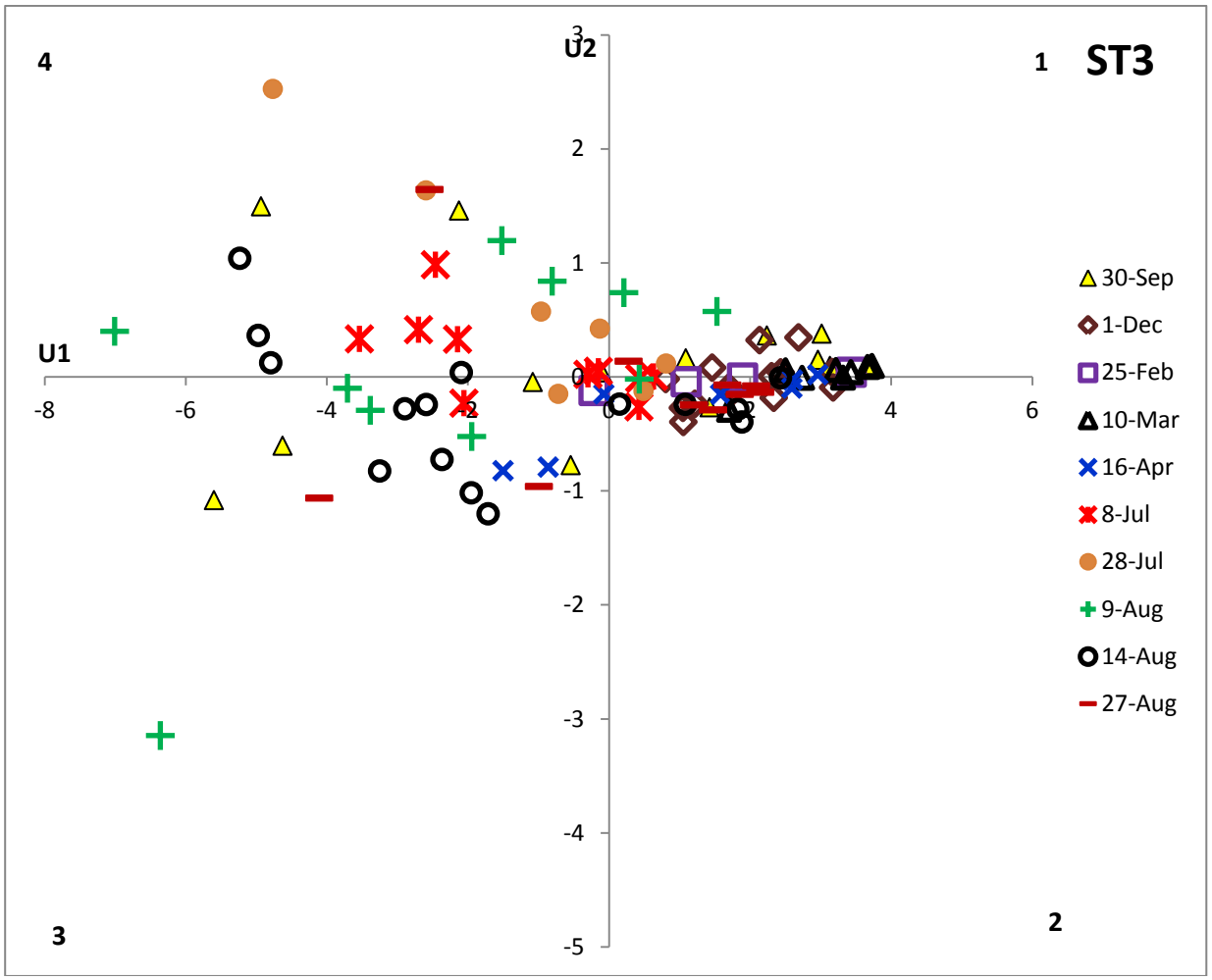


Figure 4.31 Sampled storm events in EMMA space highlighting the differences in mixing patterns among the storm events for the particulate phase constituents.

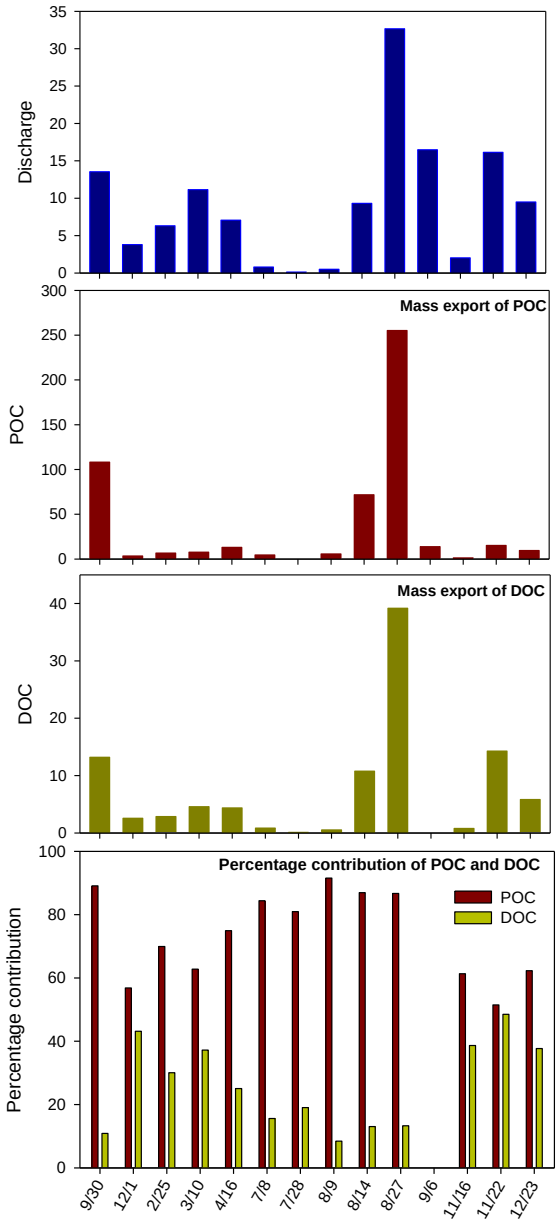


Figure 4.32 Total discharge, mass exports of POC and DOC, and percent contribution of POC and DOC to the total carbon export during storms from ST3

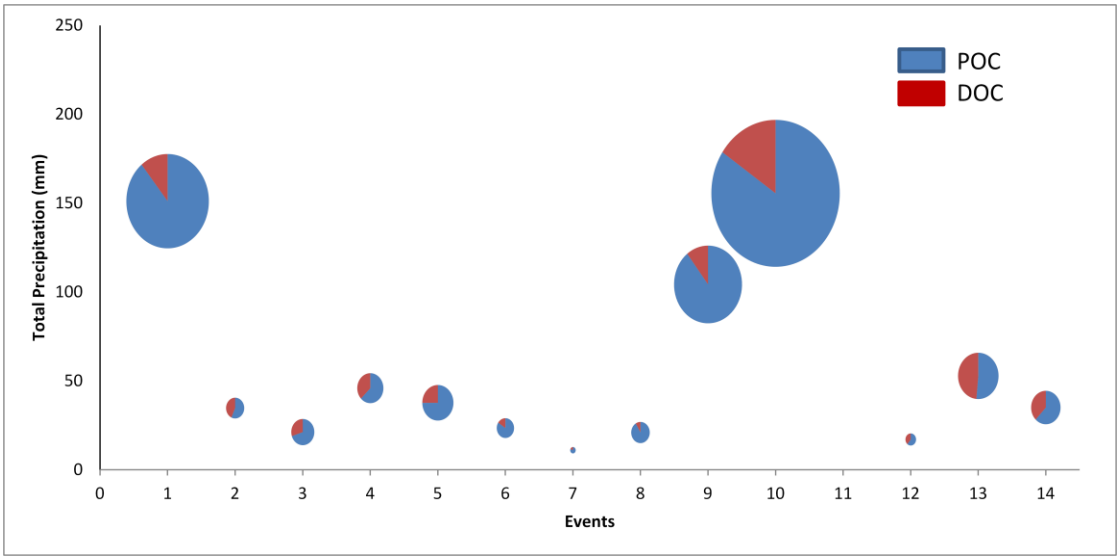


Figure 4.33 Relationship between total precipitation and total carbon export (indicated by size of circle) as well as contribution of POC and DOC in the sampled storm events at ST3

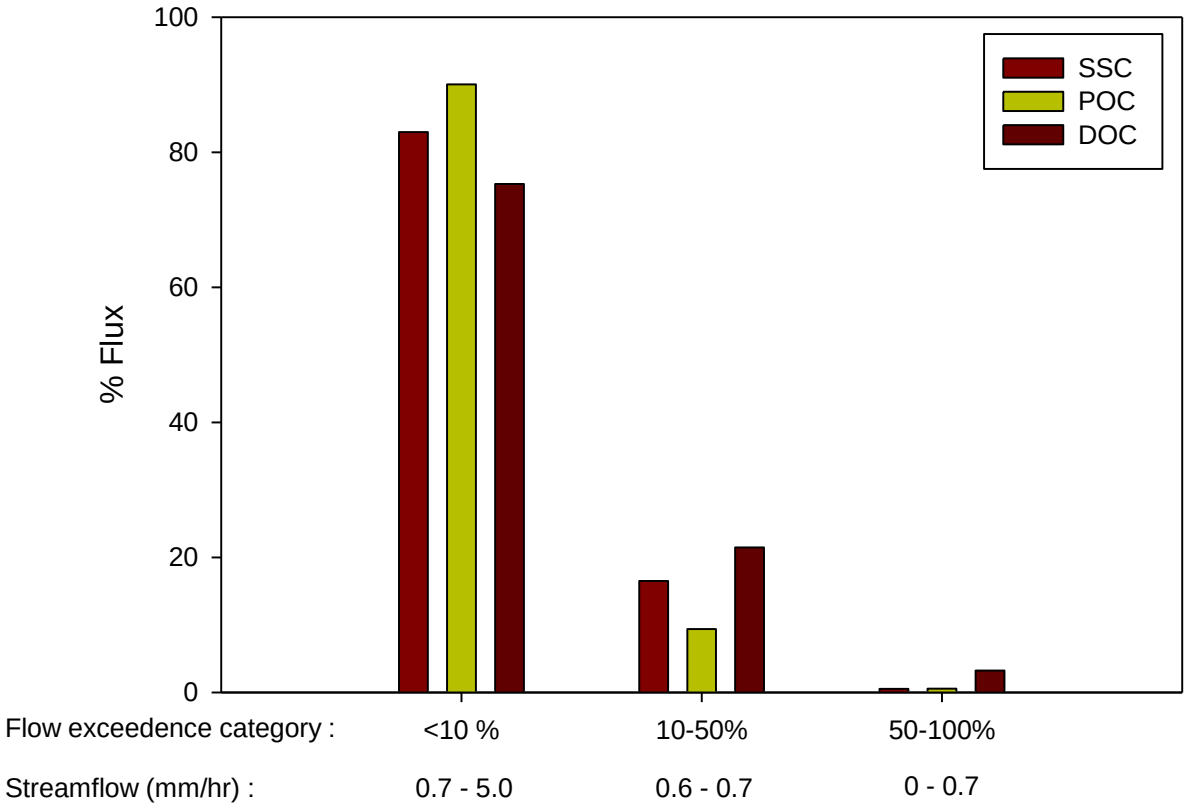


Figure 4.34 Flow-stratified distributions of SS, POC and DOC fluxes showing that major part of export occurs during high-flow conditions (i.e. flows that are exceeded less than 10 % of time)

Table 4.1 Hydrologic attributes of the sampled storm events during the study period (Sept. 2010 – Dec. 2011) for the ST3 catchment

Event	Date	Season	Duration hrs	Precipitation			Streamflow Discharge				7-day GW depth[a]		
				Amount (mm)	Intensity (mm)	API7 (mm)	Amount (mm)	Peak mm/hr	RR	AR24hrs mm	LW2 (m)	LW4 (m)	LW5 (m)
High POC concentration events [a]													
1	9/30/2010	Su	61:15	151.1	5.2	20.3	13.5	3.7	0.09	0.2	0.3	0.7	0.8
8	8/9/2011	Su	14:30	21	6.5	7.2	0.5	0.4	0.02	0.6	0.2	N/A	0.7
9	8/14/2011	Su	30:45	104.3	4.9	31.3	9.3	3.6	0.09	0.1	0.2	N/A	0.7
10	8/27/2011	Su	59:00	155.5	3.6	20.5	32.7	5	0.21	22.3	0.2	0.3	0.6
Medium POC concentration events													
5	4/16/2011	Sp	30:00	37.7	1.2	23.7	7.1	1.2	0.19	1.3	0.1	0.0	0.4
6	7/8/2011	Su	19:45	23.4	5.4	3.7	0.8	0.5	0.03	0.2	0.1	N/A	0.7
7	7/28/2011	Su	7:00	11	1.2	0.7	0.1	0.1	0.01	0.1	0.2	N/A	0.7
Low POC concentration events													
2	12/1/2010	W	56:30	34.7	3.9	4.8	3.8	0.8	0.11	0.4	0.3	0.8	0.5
3	2/25/2011	W	62:16	21.2	1	10.1	6.3	0.5	0.3	0.7	0.1	0.2	N/A
4	3/10/2011	Sp	48:30	45.9	1.2	45.4	11.1	0.7	0.24	1.7	0.1	0.2	N/A
11	9/6/2011	Su	44:00	102.5	4.1	0.9	16.5	4.2	0.16	0.3	0.2	0.2	0.4
12	11/16/2011	F	40:15	17.1	0.8	2.6	2	0.1	0.12	1.6	0.0	-0.1	0.5
13	11/22/2011	F	84:15	52.8	3.6	26.1	16.1	3.2	0.31	1.1	0.0	-0.1	0.5
14	12/23/2011	W	48:00	35	1.8	1.6	9.5	2	0.27	1.3	0.0	-0.1	0.4

[a] The storm events have been grouped based on their flow-weighted mean POC concentration (POCm) (High - POCm > 60 mg/l; Medium – POCm - 10-60 mg/l; Low – POCm < 10 mg/l).; API7 is antecedent precipitation for 7 days; AR24 is average antecedent stream discharge for 24 h; RR is the runoff ratio (ratio of discharge amount and total precipitation for event); 7-day GW depth is the average of groundwater depth for 7 days preceding the event at wells LW2, LW4 and LW5; negative values for groundwater depth indicate surface water ponding

Table 4.2 Comparison of peak POC (above) and peak DOC (below) concentrations corresponding to peak discharge values in the storm events with more than one discharge peaks.

Event		First discharge peak		Second discharge peak	
No.	Date	Qmax (mm/hr)	POCmax (mg/l)	Qmax (mm/hr)	POCmax (mg/l)
Case I – Peak POC increases with subsequent discharge peaks					
1	9/30/2010	0.6	148.1	3.7	190.6
5	4/16/2011	0.3	22.1	1.2	93.7
Case II – Peak POC decreases with subsequent discharge peaks					
2	12/1/2010	0.2	50.5	0.8	22.1
4	3/10/2011	0.7	15.5	0.6	5.7
8	8/9/2011	0.4	252.2	0.3	106.0
9	8/14/2011	1.4	223.7	3.6	103.9
12	11/16/2011	0.1	21.3	0.1	14.3
13	11/22/2011	0.6	23.4	3.2	18.8
14	12/23/2011	1.0	23.7	2.0	17.4

Event		First discharge peak		Second discharge peak	
No.	Date	Qmax (mm/hr)	DOCmax (mg/l)	Qmax (mm/hr)	DOCmax (mg/l)
Case I – Peak DOC increases with subsequent discharge peaks					
2	12/1/2010	0.2	9.6	0.8	10.8
4	3/10/2011	0.7	4.6	0.6	5.1
5	4/16/2011	0.3	5.7	1.2	8.4
9	8/14/2011	1.4	18.3	3.6	11.2
Case II – Peak DOC decreases with subsequent discharge peaks					
1	9/30/2010	0.6	11.2	3.7	9.6
8	8/9/2011	0.4	11.9	0.3	10.9
12	11/16/2011	0.1	5.1	0.1	4.8
13	11/22/2011	0.6	10.8	3.2	9.3

Table 4.3 Flow-weighted mean concentration and peak values for SS, POC and DOC in the sampled events at the ST3 catchment

Events		SSC (mg/l)		POC (mg/l)		DOC (mg/l)		% POC
No.	Date	FW Mean	Maximum	FW Mean	Maximum	FW Mean	Maximum	FW Mean
High POC concentration events [a]								
1	9/30/2010	801.7	2330.4	67.8	190.6	8.2	11.2	7.8
8	8/9/2011	1366.1	2310.0	112.1	252.2	9.0	11.9	8.9
9	8/14/2011	1905.0	3854.8	70.3	223.7	10.0	18.3	5.4
10	8/27/2011	2169.5	3874.5	66.4	112.0	10.0	11.9	3.1
Medium POC concentration events								
5	4/16/2011	560.2	3356.3	14.5	93.7	5.4	8.4	4.6
6	7/8/2011	653.7	2042.2	58.4	183.7	9.5	13.6	8.7
7	7/28/2011	1458.8	2917.8	33.3	175.2	7.3	10.4	2.9
Low POC concentration events								
2	12/1/2010	1824.9	7102.3	8.3	50.5	6.1	10.8	0.5
3	2/25/2011	1038.7	2702.2	9.0	23.4	3.9	6.5	0.9
4	3/10/2011	421.6	1113.2	5.9	15.5	3.3	5.1	1.4
11	9/6/2011	2883.9	4599.2	7.1	11.3	N/A	N/A	0.3
12	11/16/2011	546.7	2266.4	5.3	21.8	3.3	5.1	1.0
13	11/22/2011	3032.0	7589.4	8.2	23.4	7.5	10.8	0.3
14	12/23/2011	2007.1	5298.3	9.0	23.7	5.3	10.5	0.5

[a] the storm events have been grouped based on their flow-weighted mean POC concentration (POCm) (High - POCm is more than 60 mg/l; Medium – POCm is between 10-60 mg/l; Low – POCm is less than 10 mg/l). The storm events within the groups have been listed in the chronological order

Table 4.4 Pearson correlation matrix among the hydrologic variables and flow-weighted mean POC (POCm) and DOC (DOCm) concentrations

	POCm	DOCm
Qt	0.01	0.28
Qmax	0.18	**0.56**
AR24	0.22	0.32
Pt	0.33	0.52
PImax	***0.76***	***0.82***
AP7d	0.04	-0.01
AP24	0.27	0.47
RR	**-0.61**	-0.48
LW2	**0.59**	**0.55**
LW4	0.47	0.37
LW5	***0.82***	**0.67**

Correlation is significant at $P < 0.05$ level for bold numbers and $P < 0.01$ for bold italics; Qt – total discharge; Qmax – peak discharge; AR24 - average antecedent stream discharge for 24 h; Pt – total precipitation; PImax- peak 5-min precipitation intensity; AP7d – 7-day antecedent precipitation preceding the event; AP24 – 24-hour antecedent precipitation preceding the event; RR – runoff ratio – ratio of discharge amount and total precipitation for event;LW2, LW4 and LW5 - average of groundwater depth for 7 days preceding the event at wells LW2, LW4 and LW5 respectively.

Table 4.5 Mass exports of SS, POC, DOC and TOC and the relative contribution of POC and DOC towards the total carbon export for the sampled events at ST3 catchment

Event	Date	SS (kg)	POC (kg)	DOC (kg)	TOC (kg)	POC %	DOC %
High POC concentration events [a]							
1	9/30/2010	1296.8	108.2	13.2	121.4	89.1	10.9
8	8/9/2011	73.2	5.7	0.5	6.2	91.5	8.5
9	8/14/2011	2080.9	71.8	10.8	82.6	87.0	13.0
10	8/27/2011	8348.7	255.2	39.2	294.4	86.7	13.3
Medium POC concentration events							
5	4/16/2011	517.4	13.1	4.4	17.4	74.9	25.1
6	7/8/2011	52.1	4.6	0.8	5.4	84.4	15.6
7	7/28/2011	21.3	0.5	0.1	0.6	80.9	19.1
Low POC concentration events							
2	12/1/2010	749.2	3.4	2.6	5.9	56.9	43.1
3	2/25/2011	769.7	6.7	2.9	9.6	69.9	30.1
4	3/10/2011	553.1	7.7	4.6	12.3	62.8	37.2
11	9/6/2011	5629.0	13.9				
12	11/16/2011	131.0	1.3	0.8	2.1	61.3	38.7
13	11/22/2011	5623.7	15.2	14.3	29.5	51.5	48.5
14	12/23/2011	2151.1	9.6	5.8	15.4	62.3	37.7

[a] the storm events have been grouped based on their flow-weighted mean POC concentration (POCm) (High - POCm is more than 60 mg/l; Medium – POCm is between 10-60 mg/l; Low – POCm is less than 10 mg/l). The storm events within the groups have been listed in the chronological order.

Table 4.6 Export of POC, DOC and TOC on the rising limb of the discharge hydrograph and the percentage contribution of rising limb towards the total export in the sampled events at ST3

Event		Time (hours)			Discharge (mm)			POC (kg)			DOC (kg)			TOC (kg)		
No.	Date	RL	FL	% RL	RL	FL	% RL	RL	FL	% RL	RL	FL	% RL	RL	FL	% RL
High POC concentration events																
1	9/30/2010	14:15	48:30	22.7	5.8	7.8	42.7	81.9	26.3	75.7	5.7	7.5	43.4	87.7	33.8	72.2
8	8/9/2011	2:00	12:30	13.8	0.2	0.3	42.0	3.8	1.9	66.9	0.3	0.3	47.6	4.1	2.2	65.3
9	8/14/2011	7:15	53:15	12.0	4.4	4.9	47.7	51.5	20.3	71.7	5.9	4.9	54.6	57.4	25.2	69.5
10	8/27/2011	11:30	47:30	19.5	10.0	22.7	30.5	76.3	178.9	29.9	12.9	26.3	32.9	89.2	205.2	30.3
Medium POC concentration events																
5	4/16/2011	8:30	21:30	28.3	1.9	5.2	26.5	9.0	4.1	68.6	1.2	3.2	27.1	10.2	7.3	58.2
6	7/8/2011	0:30	19:15	2.5	0.1	0.7	15.8	2.3	2.3	50.5	0.1	0.7	17.6	2.5	3.0	45.4
7	7/28/2011	1:30	5:30	21.4	0.1	0.1	41.1	0.3	0.2	56.7	0.0	0.1	44.9	0.3	0.3	54.4
Low POC concentration events																
2	12/1/2010	15:00	41:30	26.5	1.5	2.3	38.6	2.5	0.9	73.6	1.4	1.2	53.9	3.9	2.1	65.1
3	2/25/2011	9:15	41:31	18.2	1.7	4.6	27.3	3.4	3.3	50.2	1.0	0.3	76.2	4.4	3.6	54.5
4	3/10/2011	10:30	35:45	22.7	3.0	8.1	27.2	4.0	3.7	51.9	1.2	3.2	27.6	5.2	6.9	43.1
12	11/16/2011	4:00	36:15	9.9	0.2	1.8	12.0	0.4	0.8	34.9	0.1	0.7	11.5	0.5	1.5	25.9
13	11/22/2011	19:30	64:45	23.1	4.9	11.2	30.7	8.2	6.9	54.3	4.8	9.5	33.5	13.0	16.4	44.3
14	12/23/2011	5:00	43:00	10.4	2.2	7.3	22.8	4.0	5.6	41.9	1.9	3.9	32.4	5.9	9.5	38.3

[a] the storm events have been grouped based on their flow-weighted mean POC concentration (POCm) (High - POCm is more than 60 mg/l; Medium – POCm is between 10-60 mg/l; Low – POCm is less than 10 mg/l)

Chapter 5

DISCUSSION

5.1 Temporal patterns of POC and DOC during storm events and hydrologic flowpaths

The concentrations of both POC and DOC increased with the increase in discharge during the storm events. This has been reported in many previous studies (Fisher & Likens, 1973, Hope *et al.*, 1994, Naiman, 1982, Oeurng *et al.*, 2011, Pawson *et al.*, 2008, Wiegner *et al.*, 2009). The increase in POC during storm events is consistent with the increased mobilization of carbon due to surface erosion by high-intensity precipitation (Coynel *et al.*, 2005, Jung *et al.*, 2012, Kim *et al.*, 2010) while the increase in DOC is attributed to the flushing out of carbon-rich soil water from the upper soil horizons (Hornberger *et al.*, 1994, Inamdar *et al.*, 2004). However, the temporal patterns of POC and DOC concentration during the storm events were noticeably different. This indicates different sources and transport mechanisms of POC and DOC in the watershed (Battin *et al.*, 2008).

While POC peaked on the rising limb of the discharge hydrograph, DOC peak was more concurrent with discharge or closely followed the discharge peak. End member mixing analysis (EMMA) on the dissolved phase of runoff constituents revealed that surficial sources such as precipitation and throughfall were the major

sources of runoff on the rising limb and soil and shallow groundwater sources dominated on the recession limb (Figure 4.29). This pattern of evolution of runoff sources within a storm event is consistent with the previous studies (Inamdar *et al.*, 2012, Inamdar and Mitchell, 2007, Rice & Hornberger, 1998). The higher contribution of surficial sources on the rising limb is in agreement with the higher POC concentration on the rising limb since the surficial sources are responsible for the transport of particulate matter from the forest floor to the stream (Bormann *et al.*, 1969). The peak in DOC concentration on the falling limb after peak discharge is explained by flushing of DOC from the upper soil into the stream by a rising water table (Hornberger *et al.*, 1994, Inamdar *et al.*, 2004, Hinton *et al.*, 1997). The groundwater depth was observed to be closest to the soil surface following the discharge peak and remained elevated through hydrograph recession in the storm events (Figure 4.2). This observation was also supported by the expression of soil and shallow groundwater sources on the falling limb of discharge hydrograph. Similar observations of delayed peak in DOC due to the rise in water table were also made by Inamdar and Mitchell (2007), Raymond and Saiers (2010) and Hagedorn *et al.* (2000).

The difference in temporal patterns of POC and DOC were also supported by different hysteresis patterns in the C-Q loops during the storm events. In case of POC, the C-Q loops were generally in the clockwise direction. Clockwise loops indicate the presence of easily erodible sources of POC located close to the watershed outlet (Williams, 1989). However, anticlockwise POC loops were observed for the events of August 27, 2011 (event 10; Figure 4.12) and September 6, 2011 (event 11; Figure

4.13), which were the last two of four successive events in summer, 2011. This may be due to the exhaustion of easily-erodible sediment sources resulting in the increased contribution of compact, erosion resistant soils in the later events (Coynel *et al*., 2005). DOC on the other hand, displayed all possible hysteresis patterns - clockwise, anticlockwise and mixed patterns. These kinds of mixed patterns for DOC have also been reported in previous studies such as Oeurng *et al*. (2011) and Butturini *et al*. (2006) while Jeong *et al*. (2012) and Carey (2003) have reported consistent clockwise patterns in DOC loops. The clockwise hysteresis patterns for POC and DOC observed by Jeong *et al.* (2012) were recorded in a steep, mountainous forested catchment in Korea where the shallow flowpaths and steep slope gradients resulted in a quick mobilization of C in catchment runoff. In contrast, Butturini *et al.* (2006) attributed the anticlockwise hysteresis patterns for DOC to the delayed peak of storm runoff. Thus, the differences in patterns of the hysteresis loops or the relative expression of POC or DOC on the rising or fall limbs of the hydrograph may be dictated by factors such as catchment topography, proximity of the POC and DOC sources to the drainage network, and the hydrologic flow paths that intersect these C pools.

5.2 Differences of POC and DOC among storm events and the role of hydrologic conditions

This study revealed that high-discharge events such as September 30, 2010 (event 1), August 14, 2011 (event 9) and August 28, 2011 (event 10) recorded high POC and DOC concentrations while low-discharge events had relatively low POC and

DOC concentrations (Table 4.3). This is not a new trend and has already been reported in many studies (Fisher & Likens, 1973, Hope *et al.*, 1994, Kim *et al.*, 2010, Oeurng *et al.*, 2011, Schlesinger & Melack, 1981). Elevated concentrations of POC and DOC for high-discharge events were primarily due to higher contribution of surficial sources such as rainfall, throughfall and litter leachate in the stormflow runoff. This was supported by the larger shift of high-discharge events towards the surficial end-members in the EMMA U-space indicating a greater expression of these end members in runoff (Figure 4.28).

The elevated POC and DOC concentrations for these storm events were also potentially influenced by storm attributes like rainfall intensity and the seasonal timing of these events during the year. It should be noted that all the storms that generated the highest POC and DOC concentrations occurred in summer – a period when convective weather systems generate high-intensity, short-duration storms as opposed to frontal systems in autumn and spring that generate long-duration low-intensity storms. Flow-weighted mean POC concentrations for storm runoff were strongly correlated to the peak precipitation intensity (Table 4.4). The high-intensity events likely facilitated greater surface runoff and erosion and thus delivered larger amounts of carbon-rich forest floor material to the stream. Jeong *et al*. (2012) also reported that rainfall intensity was a critical factor in influencing the storm event concentrations of POC. The summer events were also likely influenced by the repeated cycles of drying and rewetting of the soil surface. Repeated cycles of drying and wetting of soils have been shown to enhance mineralization rates and therefore the production and release

of carbon from the soil (Borken and Matzner, 2009, Lundquist *et al.*, 1999). It is possible that elevated summer temperatures along with drying and wetting cycles enhanced the breakdown of organic matter on the forest floor of the study catchments which was then flushed out with runoff during storms.

This study also revealed interesting among- and within-event changes in POC and DOC. For storm events with multiple discharge peaks, the peak POC concentration corresponding to the first discharge peak was higher compared to the subsequent peaks even when the subsequent discharges were greater than the first discharge peak (Events 2, 9, 13 and 14; Figures 4.4, 4.11, 4.15 and 4.16 respectively). This indicates the presence of a highly mobilizable POC stock in the catchment that is partly exhausted towards the end of the storm events. Similarly, the POC concentration as well as the POC content of suspended sediments was observed to decrease with successive storm events that occurred over a short period (e.g., events 8 to 11) (Figure 4.20). This phenomenon of exhaustion of POC for successive closely-spaced events has also been observed in previous studies such as Veyssy *et al*. (1999) and Coynel *et al.* (2005). Veyssy *et al.* (1999) explained this phenomenon through a conceptual model which proposes that the carbon-rich litter fraction is depleted in the earlier storm events resulting in the export of mineral-rich suspended sediments in the later events. This was also observed in this study as the successive storm events revealed a gradual impoverishment in the POC content of the suspended sediments for the later events (Event 8 to 11; Table 4.3).

For DOC, the decrease in concentration with successive storm events was not observed suggesting a more stable and continuous supply of DOC compared to POC. However, DOC did display a slight dilution for peak discharges associated with the largest storm events (Figures 4.3, 4.11 and 4.12). This phenomenon of dilution of DOC was especially evident for storms exceeding streamflow discharges of 3 mm/hr suggesting that a hydrologic threshold may have been reached where the supply of water outpaced the supply of DOC from the catchment. It should be noted though that at the same time that DOC experienced dilution, the POC concentrations continued to rise (Figures 4.3, 4.11 and 4.12). This suggests that while very high streamflow discharges may outpace DOC supply, erosive processes associated with these high discharges could continue to mobilize additional POC sources from the catchment.

The particulate phase EMMA analysis revealed that the high-intensity summer events showed greater diversity of sediment sources compared to the low-intensity events (Figure 4.31). This is in agreement with previous studies such as Walling *et al*., (1999) which observed that the contribution of sediment sources such as stream channel banks is significantly greater during high flows than during low flows. Similarly, while the export of carbon from the upland sources is restricted at low flows (Mcdowell & Likens, 1988), they are observed to play an important role in case of high intensity storms when overland flow is dominant (Cronan *et al.*, 1990). However, this study did not capture all the sediment sources indicating that a more extensive spatial sampling of the watershed sources may be required to capture the complete spectrum of sediment sources as well as their evolution during the storm events. While

the potential sediment sources such as streambed sediment, stream bank soils, wetland soils and upland soils were sampled, the future studies in this study catchment should include other potential sources such as unpaved roads and horse trails running through the catchment. The sampling of sediment sources may also be carried out more frequently (3-4 times a year) to account for the temporal variability in the sediment sources.

5.3 Differences in POC and DOC with catchment scale

The mean concentrations of POC and DOC in this study decreased with increase in catchment scale from ST3 (12 ha) to ST12 (79 ha). Similarly, the ratio of concentration of POC to DOC (POC: DOC) decreased from ST3 to ST12. Very few studies have compared the flux of POC and DOC across catchment scales. A recent study by Pawson *et al.* (2012) in an eroding peatland catchment reported a decrease in the flux of POC and DOC as well as a decrease in the POC: DOC ratio from headwater stream locations to the catchment outlet. This study sampled 13 nested stream locations with drainage areas ranging from 0.05 to 902 ha. Pawson *et al.* (2012) attributed the decrease in POC to the decrease in erosion-prone areas from the headwater catchments to the main outlet as well as the storage of POC within the fluvial drainage network. In-stream microbial processing of POC (Battin *et al*., 2008) may also lead to the decrease in POC concentrations downstream. Similarly, a significant amount of in-stream processing of DOC in the stream channel leading to the decrease in DOC concentration has also been reported (Dawson *et al.*, 2001,

Worrall *et al.*, 2006). While a combination of these factors may be working in this study catchment, the larger decrease in POC concentrations compared to DOC at the ST12 (indicated by the lower POC: DOC ratios) suggest that sediment deposition in the fluvial network could be one of the major factors.

5.4 Mass exports of carbon and the significance of POC

Previous reviews and studies that were primarily focused on large watersheds have reported that POC formed a minor component of carbon export (Hope *et al.*, 1994; Meybeck, 1982). In contrast, recent studies that have investigated small mountainous catchments (Jeong *et al*., 2012), erosive peatland catchments(Pawson *et al.*, 2008, Worrall *et al.*, 2003) and forested catchments (Kao & Liu, 1997, Kim *et al.*, 2010) indicate that POC is significant and could also form a major portion of the total C export. Kau & Liu (1997), Kim *et al.* (2010) and Pawson *et al*. (2008) have reported higher contributions of POC to the total annual carbon export whereas Jeong *et al*. (2012) found that POC exports during storm events exceeded the corresponding DOC values (Table 5.1).

The export of POC for the storm events sampled during 2011 was 405 kg. Assuming that POC during baseflow was small and can be neglected, the annual POC export from the catchment during 2011 was estimated to be 33.75 kg C ha^{-1} yr^{-1}. Annual DOC export was estimated to be 17.5 kg C ha^{-1} yr^{-1}. These values are within the range of annual POC and DOC exports reported by other studies in the literature (Table 5.1). POC dominated the annual C flux and accounted for 66 % of it. The

dominance of POC was even more pronounced during the stormflow conditions when it accounted for 83.5 % of the total carbon exported from the study catchment. Among the sampled storms, the large events were especially important for the POC flux. The three largest events in terms of total precipitation (63 mm out of a total 130 mm) accounted for 84% of the total POC and 63% of the total DOC exported during the sampled storm events (Figure 4.33). Similarly, flow-duration analysis (Figure 4.34) indicated that 90% of the POC and 75% of the DOC exported during the storm events was associated with the stream flows that were exceeded less than 10% of the time during the stormflow conditions. These results underscore the importance of large, intense storm events and high-flow conditions in mobilizing and exporting C from watersheds and especially the particulate form of C.

While POC accounted for the major part of annual export of carbon, it should be noted that the event of August 27, 2011 (event 10), associated with hurricane Irene, was responsible for 63% of the annual POC export, while accounting for only 19% of the annual DOC export. Hence, in the absence of such extreme events, the annual export of POC is expected to decrease much sharply compared to the drop in annual DOC export. Therefore, the contribution of POC and DOC to the annual carbon export is expected to be comparable or dominated by DOC in the absence of such extreme events. For example, while the ratio of annual POC to DOC exports during 2011 is 1.9 in this study, if we disregard the export of POC and DOC during the extreme event of August 27, 2011 the ratio of POC to DOC exports drops to 0.9. These results have special implications in light of climate-change scenarios (Karl *et al.*, 2009) that

suggest that the Northeastern US will be subject to greater intensity and magnitude of storm events in the future. The increased frequency of storm events might result in the increased export of terrestrial carbon to the oceans and an increased proportion of POC to the total C export. Increased POC in the carbon flux can affect carbon degassing from the aquatic systems into the atmosphere since POC can transform into atmospheric carbon either directly or via DOC as an intermediate step (Pawson *et al.*, 2006).

The rapid increases in POC concentrations and flux during high-flow conditions also highlights the need to perform high-frequency sampling of stormflow for the quantification of carbon export from the small headwater catchments (Bass *et al*., 2011; Jung *et al.*, 2012; Jeong *et al*., 2012). Bass *et al.* (2011) reported that weekly sampling severely underestimated the DOC export from a headwater catchment in tropics with weekly estimates 49-78% lower than those based on high-frequency sampling. The rapid and larger changes in POC compared to DOC during storms, as shown by this study, would suggest that weekly sampling (in lieu of high frequency sampling) would lead to even greater errors and underestimation of C flux from catchments.

Table 5.1 Export of organic carbon from catchments of different ecosystem types

Location & Reference	**Watershed Size (km^2)**	**Ecosystem type**	**DOC export (kg C ha^{-1} yr^{-1})**	**POC export (kg C ha^{-1} yr^{-1})**	**POC/ DOC**
Hubbard Brook,N.H.(Hobbie & Likens, 1973)	0.1	Temperate forest	11.8	3.4	0.3
Moisie River, Quebec (Naiman, 1982)	19871	Boreal forest	42.6	4.8	0.1
Haean Basin, S. Korea (Jeong *et al*., 2012)	0.38	Mountainous, deciduous forest	6.7, 3.22[a]	4.34, 3.65[a]	0.6
North Pennies, UK (Worrall *et al*., 2003)	11.4	Peatland	94	199	2.1
South Pennies, UK (Pawson *et al*., 2008)	0.38	Peatland	153.9	739.7	4.8
NE Scotland (Hope *et al.*, 1997a)	1320-2100	Temperate grasslands	13.4-115	1-85.3	
Britain (Hope *et al.*, 1997b)	159[b]	Range of catchments	7.7-103.5 (32)	57	
Humber river (Tipping et al., 1997)	381-8231	Range of catchments	23-54	7-32	
Gwangneung catchment (Kim *et al*., 2010)	0.22	Deciduous forest	40	50	1.25
Lanyang Hsi, Taiwan(Kao & Liu, 1997)	N/A	Temperate cypress forest and tropical woodlands	41	46	1.1
Jyozankei, Japan (Sakamoto *et al.*, 1998)	N/A	Temperate forest	33	21	0.63
This Study	0.12	Temperate forest	17.5	34	1.9

[a] indicates the export during storm flow conditions. [b] indicates the average value. Parentheses- ( ) indicate the median value.

Chapter 6

SUMMARY AND CONCLUSION

While many studies have studied the catchment exports and concentrations of DOC, very few studies have compared the storm event export patterns of POC and DOC, especially, for small catchments where POC exports could be significant. This study investigated the temporal patterns and fluxes of POC and DOC for 14 storm events sampled over a 16-month period extending from September, 2010 to December, 2011. The study was conducted in two (12 and 79 ha) nested forested catchments located in the mid-Atlantic, Piedmont region of USA. Runoff sampling was performed using automated ISCO samplers. Samples were filtered using 0.45 µm filter to separate into dissolved and particulate phases. Sources and hydrologic flow paths for DOC and POC were characterized using end-member mixing analysis. The relative contributions of POC and DOC to the total carbon exports from the catchment were determined. The key results and conclusions from this study were:

- The differences in the temporal patterns of POC and DOC during storm events as well as the nature and direction of C-Q hysteresis loops of POC and DOC alluded to different sources and flow paths of POC and DOC within the catchments. EMMA analysis revealed that while surficial flowpaths may be important for both POC and DOC, POC may be transported with surface runoff from proximal (near

stream) sources while DOC may be leached from runoff waters and rising groundwater into the soil horizons.

- POC and DOC responses also differed substantially for sequential storm events as well as for peak discharge conditions during large events. These differences suggest that there are important differences in the total pools and leaching rates or kinetics of these two constituents.
- While POC and DOC concentrations both decreased with increasing catchment scale – 12 to 79 ha there was a greater drop in POC concentrations. This result has important implications for computation of C fluxes for varying catchment scales.
- While there are contrasting results in the literature about the relative contribution of POC and DOC to the total C export, this study revealed that POC was the major component of the total carbon export from the study catchment. These results emphasize the need to adequately address POC export, especially in regions where small, steep watersheds subject to heavy precipitation drain directly into sensitive coastal water bodies or aquatic ecosystems.
- A major portion of the POC and DOC export for storm events occurred during large, high-intensity storms. Since the magnitude and intensity of storm events are predicted to increase under the future climate-change scenarios, it is very likely that the quantity of organic carbon, especially the particulate fraction will increase in catchment runoff.

- The sharp increases in POC concentrations during storm events and the highly episodic nature of POC export underscore the need to perform high-frequency sampling during storm events. Daily, weekly, or monthly sampling regimes will likely severely underestimate the POC export from the watershed.

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