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The application of electrical conductivity as a tracer for hydrograph separation in urban catchments

Brian A. Pellerin,[1*,†] Wilfred M. Wollheim,[1] Xiahong Feng[2] and Charles J. Vörösmarty[1]

[1] *Water Systems Analysis Group, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824, USA*
[2] *Earth Sciences Department, Dartmouth College, Hanover, NH 03755, USA*

Abstract:

Two-component hydrograph separation was performed on 19 low-to-moderate intensity rainfall events in a 4·1-km^2 urban watershed to infer the relative and absolute contribution of surface runoff (e.g. new water) to stormflow generation between 2001 and 2003. The electrical conductivity (EC) of water was used as a continuous and inexpensive tracer, with order of magnitude differences in precipitation (12–46 μS/cm) and pre-event streamwater EC values (520–1297 μS/cm). While new water accounted for most of the increased discharge during storms (61–117%), the contribution of new water to total discharge during events was typically lower (18–78%) and negatively correlated with antecedent stream discharge ($r^2 = 0{\cdot}55$, $p < 0{\cdot}01$). The amount of new water was positively correlated with total rainfall ($r^2 = 0{\cdot}77$), but hydrograph separation results suggest that less than half (9–46%) of the total rainfall on impervious surfaces is rapidly routed to the stream channel as new water. Comparison of hydrograph separation results using non-conservative tracers (EC and Si) and a conservative isotopic tracer (δD) for two events showed similar results and highlighted the potential application of EC as an inexpensive, high frequency tracer for hydrograph separation studies in urban catchments. The use of a simple tracer-based approach may help hydrologists and watershed managers to better understand impervious surface runoff, stormflow generation and non-point-source pollutant loading to urban streams. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS hydrograph separation; urbanization; electrical conductivity; impervious

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INTRODUCTION

Urbanization dramatically alters the hydrologic response of streams and rivers to rainfall, resulting in higher runoff volume and peak discharge, as well as increased rates of hydrograph rise and recession relative to streams in undisturbed watersheds (Arnold and Gibbons, 1996; Walsh *et al.*, 2005). While impervious surfaces such as roads and roofs have been implicated as the main driver of hydrologic changes in urban watersheds, the management of impervious surface runoff and urban stormflow remains a challenge (Endreny, 2005; Walsh *et al.*, 2005).

The volume of surface runoff contributing to urban stormflow is largely dependent on the connectivity of impervious surfaces to the stream channel (Brabec *et al.*, 2002; Lee and Heaney, 2003). Many field and modelling studies have used the total impervious area (TIA) in a watershed to estimate surface runoff volumes and thresholds for aquatic degradation (Mallin *et al.*, 2000; Brabec *et al.*, 2002; Jennings and Jarnagin, 2002). However, total imperviousness may result in large overestimates of runoff volume, peak flow, infiltration rates and stormwater pollutant loading to streams during hydrologic events (Alley and Veenhuis, 1983; Brabec *et al.*, 2002; Lee and Heaney, 2003). Despite advances in geospatial data (Endreny, 2005), quantifying the hydrologically-connected impervious area (HCIA) remains difficult, especially at the watershed scale.

Evaluating the role of subsurface runoff during storms is also critical for understanding rainfall-runoff patterns, but has received little attention in urban watersheds. Increased subsurface discharge of soil and groundwater is a common response to rainfall in temperate forested watersheds (Buttle *et al.*, 1995; Genereux and Hooper, 1998; Burns, 2002). While urban watershed studies often assume that stormflow is generated from impervious surface runoff during most events (Rodriguez *et al.*, 2004; Rose, 2003), increased subsurface runoff has been shown to account for a significant fraction of stormflow in some urban watersheds (Buttle *et al.*, 1995; Sidle and Lee, 1999; Gremillion *et al.*, 2000). Therefore, the relative importance of impervious surface runoff and subsurface discharge to urban stormflow generation is surprisingly unclear.

Chemical and isotopic hydrograph separation has been used extensively in forested watersheds to determine the sources of stream discharge during events, but has rarely been used in urban watersheds (Buttle, 1994; Burns, 2002). Naturally-occurring stable water isotopes (δ^{18}O and δD) are generally recognized as the preferred tracers for hydrograph separation studies (Kendall and Caldwell, 1998), but their widespread use may be limited by high

* Correspondence to: Brian A. Pellerin, Water Systems Analysis Group, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824, USA. E-mail: bpeller@usgs.gov
† Current Address: US Geological Survey, 6000 J Street, Placer Hall, Sacramento, CA 95819, USA.

analytical costs. The electrical conductivity (EC) of water has also been used as a tracer for hydrograph separation (Nakamura, 1971; Matsubayashi *et al.*, 1993; Cey *et al.*, 1998; Heppell and Chapman, 2005) and may be ideally suited to urban watersheds where groundwater EC values are commonly elevated by non-point source pollution (Paul and Meyer, 2001; Kaushal *et al.*, 2005). In addition, surface water EC measurements are simple, inexpensive and can provide high frequency, *a priori* data for model testing and watershed management.

Here we present two-component hydrograph separation results for 19 rainfall events to infer the importance of surface and subsurface runoff in stormflow generation in a 4·1-km^2 urban watershed. We focus on high frequency, low-to-moderate intensity storm events which commonly occur in temperate watersheds. Our specific objectives were to: (1) evaluate the use of EC as a tracer for urban hydrograph separation by comparison with more conventional tracers (δD and silica) for several events, (2) quantify the relative and absolute contribution of surface and subsurface discharge to stormflow generation and (3) draw inferences on the fraction of imperviousness that is hydrologically connected to the stream channel. The use of a simple tracer-based hydrograph separation approach may help hydrologists and watershed managers to better understand impervious surface runoff, stormflow generation and non-point-source pollutant loading to urban streams.

MATERIALS AND METHODS

Site description

The study watershed (Saw Mill Brook) is a 4·1-km^2 headwater catchment located in the westernmost portion of the Ipswich River basin in Massachusetts (Figure 1) and is part of the Plum Island Ecosystem Long-Term Ecological Research (LTER) project. Land use in our study catchment is largely residential (72% of the watershed area) with most of the land classified as high-density single-family lots (0·25–0·50 acres) based on 1 : 5000 orthophotography and 1 : 25 000 aerial photography (MassGIS, 1999). Smaller fractions of the watershed are in forest cover (14%), agriculture (4%), wetland (4%) and industrial/commercial (5%) land uses. The population density (1999) was 981 people km^{-2} with greater than 90% of wastewater exported out of the watershed via sanitary sewer systems. The TIA was derived from estimates of percent impervious surfaces versus land- use type (Arnold and Gibbons, 1996; Wollheim *et al.*, 2005) and accounts for approximately 25% of the watershed area. Surficial geology is dominantly till and bedrock with sand and gravel (17% of the watershed area) and fine-grained alluvial deposits (6%) generally found along stream channels. The watershed lies in the towns of Burlington and Wilmington, both of which manage storm water via municipal storm drainage networks.

Mean annual precipitation is approximately 1150 mm year^{-1} and is evenly distributed throughout the year.

Sampling method

Stream water level and EC values (corrected for temperature) were measured at 15-min intervals between August 2001 and September 2003 at the mouth of the watershed using a portable sensor with retrievable data-loggers (YSI, Inc., MA). Water levels were converted to discharge by rating-curve development over a wide range of flow conditions at the sampling location. Well-defined events (e.g. similar pre- and post-rainfall EC values and discharge volumes) were selected for hydrograph separation in our study and winter events were typically avoided because of the potentially confounding influence of road de-icing chemicals in impervious surface runoff.

Two storm events were also separated into pre-event water (hereafter referred to as old water) and rapid rainfall runoff (new water) using conventional hydrograph separation tracers (δD and silica). Stream water samples were

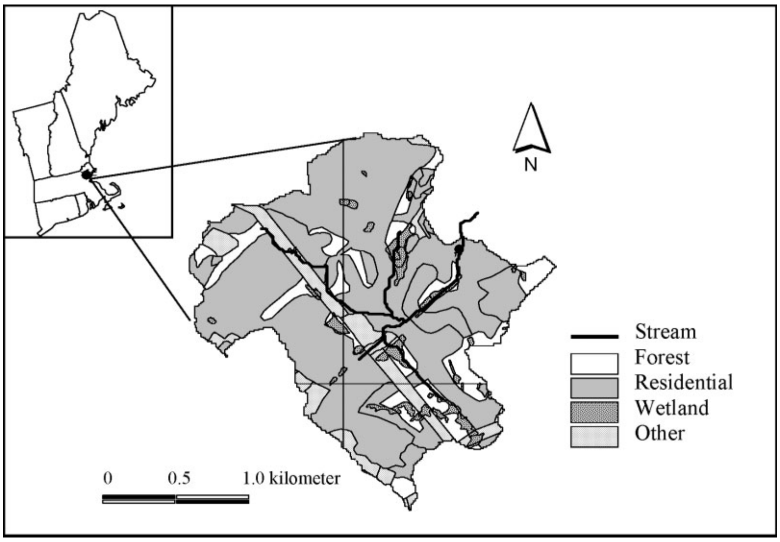

Figure 1. Location and land use of the 4·1 km^2 Saw Mill Brook catchment. Other includes open land, agriculture, recreation, commercial and industrial

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collected at intervals ranging from 20 min to 6 h for a low antecedent flow summer storm (16–21, Sept. 2002) and a higher antecedent flow winter rainfall event (January 29–31, 2002) during a snow free period. Samples were collected for comparison of intrastorm patterns of new and old water discharge using different tracers, as well as comparison of total storm event contributions. Datalogger malfunction resulted in the loss of EC data from the January 2002 event and precludes the intrastorm comparison of EC as a tracer for this event. However, silica (Si) and δD data are compared to draw inferences on the use of a conservative and non-conservative tracer during storm events. In addition, total new and old water contributions from the January 2002 storm are compared with values predicted from a regression of EC-based events to assess controls on stormflow generation.

Bulk precipitation was collected in the watershed for δD and Si concentrations using 7·5 cm funnel collectors attached to 1 HDPE bottles and placed in an open location. EC values were measured in the field shortly after rainfall and sub-samples were transported to the lab for analysis. Precipitation EC values during additional events were based on weekly data from the National Atmospheric Deposition Program (NADP/NTN) monitoring station MA13 in Lexington, Massachusetts, approximately 7 km southwest of our study site. Comparison of measured precipitation EC values, NADP weekly data at MA13 and NADP data from other nearby stations suggests that using MA13 data represents a negligible source of error (data not shown). Daily precipitation was interpolated (Shepard, 1968) from National Climatic Data Center precipitation monitoring stations in northeastern Massachusetts and southern New Hampshire and compared against NADP and USGS data near the sampling site. Intrastorm precipitation depths were obtained from USGS data recorded at 15-min intervals in South Middleton, Massachusetts (station 01101500), approximately 14 km northeast of our study catchment.

Laboratory analysis

Sub-samples of stream water and rainfall ($\approx$20 samples/event) were stored in 50-ml HDPE bottles with minimal headspace for subsequent analysis of δD using an H-device interfaced with a gas source mass spectrometer at the Stable Isotope Geochemistry Laboratory at Dartmouth College, NH. Isotopic values are reported in parts per thousand difference (‰) relative to the VSMOW standard and had an analytical precision of 0·5‰. Sub-samples for dissolved silicate concentrations (SiO_4, hereafter referred to as Si) were stored at 4 °C, filtered within 48 h through 25-mm diameter membrane filters (0·45 µm pore size) and frozen in HDPE bottles until analysed by flow injection using a Lachat QuikChem 8000 Automated Analyser.

Hydrograph separation

A two-component hydrograph separation model was used to infer the relative and absolute contributions of old and new water via the following equations:

$$Q_t = Q_o + Q_n \tag{1}$$

$$Q_t C_t = Q_o C_o + Q_n C_n \tag{2}$$

$$Q_o = Q_t[(C_n - C_t)/(C_n - C_o)] \tag{3}$$

where Q is discharge, C is the tracer value (EC, δD or Si) of the total stream flow, old water and new water (t, o and n). As in other studies, we used the tracer value in the stream prior to rainfall to characterize old water and precipitation to characterize new water (Nolan and Hill, 1990; Buttle *et al*., 1995; Heppell and Chapman, 2005). Using an integrated pre-event signature may be necessary in urban watersheds since characterizing the spatial variability in groundwater chemistry is often a significant logistical constraint (Buttle *et al*., 1995).

The use of a two-component model requires simplifying assumptions that have received considerable attention in the literature (Buttle, 1994). Important assumptions in our study require that: (1) EC values in new and old water differ significantly (2) the spatial and temporal uniformity of end-member EC values are maintained en route to the stream and (3) soil water EC values are similar to groundwater (or soil water contributions to streamflow are negligible). Violation of these assumptions may affect the interpretation of results and are discussed later.

Uncertainty in the EC-based two-component hydrograph separation results were estimated at one standard deviation by a general uncertainty propagation technique (Genereux, 1998). While the standard deviation of stream EC values over 24-h baseflow periods was typically $<5\%$ of the EC value, we assumed a standard deviation of $\pm 10\%$ ($\pm$52–130 µS/cm) for old water to account for additional unmeasured spatial and temporal variability. Intra-event rainfall EC values were also not measured and we therefore assumed a standard deviation of $\pm$10 µS/cm to account for temporal variability of EC in rainfall. The uncertainty in stream water EC values was calculated using the analytical uncertainty of the field instrument (0·5% of stream EC $\pm$1·0 µS/cm). Relationships between rainfall and runoff parameters were assessed via simple and multiple regression analyses using S-Plus version 6·1. (Insightful Corporation, Seattle, WA). All statistics were performed at the 95% confidence interval.

RESULTS

Hydrograph separation

The 19 events in our study were low-to-moderate rainfall (0·2–4·6 cm) and differences in antecedent discharge and 5-day rainfall suggest a range of watershed moisture conditions (Table I). Total discharge (e.g. baseflow plus event flow) ranged from 0·04–0·60 cm and corresponded with rainfall/runoff ratios of 0·04–0·37 during events. Annual runoff coefficients in this catchment were 0·28 for a relatively dry year (974 mm of precipitation, 2000–2001 water year) and 0·33 for a wet year

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Table I. End-member EC values, antecedent discharge, and rainfall characteristics, for 19 rainfall events in 2001–2003 at the Saw Mill Brook watershed, Massachusetts

Event dates	Rainfall EC (μS/cm)	Pre-event EC (μS/cm)	Antecedent discharge ($\times 10^{-3}$ m^3/s)	Ant. 5-day rainfall (cm)	Total rainfall (cm)	Max 1-h rainfall (cm)
Aug. 12–16, 2001	21	636	14·8	2·0	4·6	0·6
Sept. 21–24, 2001	14	1297	3·7	0·1	2·0	0·3
Jan. 29–31, 2002[a]	na	na	11·6	0·2	0·6	0·3
Apr. 22–24, 2002	27	633	28·3	0·1	0·5	0·2
May 2–5, 2002	27	520	39·7	2·2	1·2	0·3
Jun. 12–13, 2002	32	564	31·5	1·7	0·5	0·4
Jun. 15–16, 2002	32	587	28·9	0·6	2·7	0·5
Jul. 9–11, 2002	38	1151	4·1	0·0	1·0	0·3
Jul. 23–27, 2002	46	1241	2·0	1·1	2·1	0·7
Aug. 2–5, 2002	27	1274	0·7	0·2	0·2	0·2
Aug. 29–31, 2002	15	667	0·1	0·9	2·4	0·3
Sept. 15–21, 2002[b]	14	1256	0·2	0·4	0·9	0·3
Sept. 26-Oct. 4, 2002	12	1259	4·1	2·9	1·6	0·4
Oct. 16–18, 2002	25	883	7·3	2·1	3·2	0·7
Apr. 22–24, 2003	17	791	16·1	0·0	1·3	0·4
Apr. 26–29, 2003	17	789	13·8	1·3	2·7	0·3
May 28–29, 2003	24	538	60·9	6·0	1·4	1·6
Aug. 18–21, 2003	31	686	7·3	1·1	0·8	na
Sept. 19–21, 2003	28	1102	2·5	1·8	1·0	0·8

[a] δD and Si data only;
[b] δD, Si and EC data.

Table II. Two-component hydrograph separation results for 19 rainfall events in 2001–2003 at the Saw Mill Brook watershed, Massachusetts

Event dates	Total runoff (cm)	Storm runoff (cm)	New water runoff (cm)	New water (%)	Uncertainty (%)	New at peak (%)	New Water/Stormflow	New Water/Rainfall	TIA/HCIA (%)
Aug. 12–16, 2001	0·60	0·40	0·30	51	5	97	75	7	26
Sept. 21–24, 2001	0·17	0·14	0·12	68	2	90	85	6	24
Jan. 29–31, 2002[a]	0·07	na	0·02	34	na	25	na	4	15
Apr. 22–24, 2002	0·17	0·03	0·03	18	9	5	106	7	26
May 2–5, 2002	0·40	0·12	0·14	34	7	46	117	11	46
Jun. 12–13, 2002	0·10	0·03	0·03	27	8	27	106	5	23
Jun. 15–16, 2002	0·19	0·10	0·10	50	4	73	104	4	15
Jul. 9–11, 2002	0·07	0·06	0·05	72	1	83	88	5	20
Jul. 23–27, 2002	0·11	0·10	0·09	78	1	91	90	4	17
Aug. 2–5, 2002	0·06	0·05	0·04	71	2	68	78	19	70
Aug. 29–31, 2002	0·13	0·12	0·09	74	1	84	74	4	15
Sept. 15–21, 2002[b]	0·07	0·07	0·04	64	2	60	64	5	19
Sept. 26-Oct. 4, 2002	0·25	0·18	0·13	52	5	83	72	8	32
Oct. 16–18, 2002	0·25	0·21	0·16	64	3	92	75	5	20
Apr. 22–24, 2003	0·14	0·04	0·03	18	9	8	61	2	8
Apr. 26–29, 2003	0·33	0·24	0·17	52	10	81	72	6	25
May 28–29, 2003	0·21	0·07	0·05	25	8	6	82	4	16
Aug. 18–21, 2003	0·12	0·06	0·05	46	5	63	85	7	27
Sept. 19–21, 2003	0·04	0·03	0·02	66	2	61	85	2	9

[a] δD and Si data only;
[b] δD, Si and EC data.

(1360 mm, 2001–2002) as reported by Wollheim *et al.* (2005).

Precipitation EC values ranged from 12–46 μS/cm (mean = 25 μS/cm) and were one to two orders of magnitude lower than antecedent stream EC values (520–1297 μS/cm; Table I). Stormflow, defined here as discharge above baseflow volumes, is largely composed of new water based on EC hydrograph separation (61–117%; Table II). New water accounted for 18–78% of total storm discharge during events (Table II) and was negatively correlated with antecedent discharge ($r^2 = 0{\cdot}55$; Figure 2). Precipitation characteristics (5-day antecedent, total and maximum 1-h rainfall) were not significantly correlated with the percentage of new water ($p = 0{\cdot}26–0{\cdot}37$, data not shown). Peak discharge was composed of 5–97% new water (median = 68%) and was positively correlated with antecedent discharge and total precipitation ($r^2 = 0{\cdot}41$ and $0{\cdot}37$; $p < 0{\cdot}01$).

Approximately 77% of the variability in new water runoff was explained by the total rainfall (Figure 3) and was improved only slightly by adding parameters in a multiple regression (adjusted $r^2 = 0{\cdot}81$ with antecedent 5-day precipitation; data not shown). One precipitation event (August 12–16, 2001) disproportionately influenced the relationship between new water and total rainfall and excluding this point resulted in a slightly lower r^2 ($0{\cdot}63$, $p < 0{\cdot}01$). New water in the channel accounted for approximately 4–11% of rainfall in 18 of 19 events, with a higher percentage during the event with the lowest rainfall (19% from August 2–5, 2005).

While several assumptions are required to estimate uncertainty in the absence of extensive temporal or spatial EC data, these values provide additional constraint on hydrograph separation results. Uncertainty in the fraction of old and new water ranged from ±1–10% (Table II) and was generally insensitive to assumptions about temporal variability in precipitation EC values during events. For example, doubling the precipitation EC values and increasing the standard deviation to 100% increased the uncertainty in our hydrograph separation < 3% (data not shown). Standard deviations greater than ±10% of old water EC values may have a larger impact on the uncertainty estimates, but adequate data to assess this uncertainty were not available.

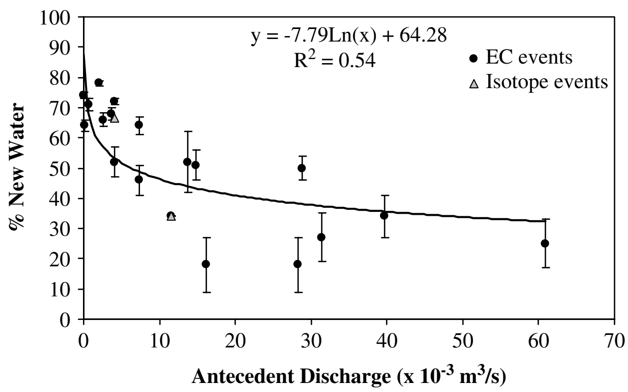

Figure 2. New water (%) versus antecedent discharge ($\times 10^{-3}$ m^3/s) for the 19 rainfall events in our study. Error bars represent uncertainty at approximately one standard deviation

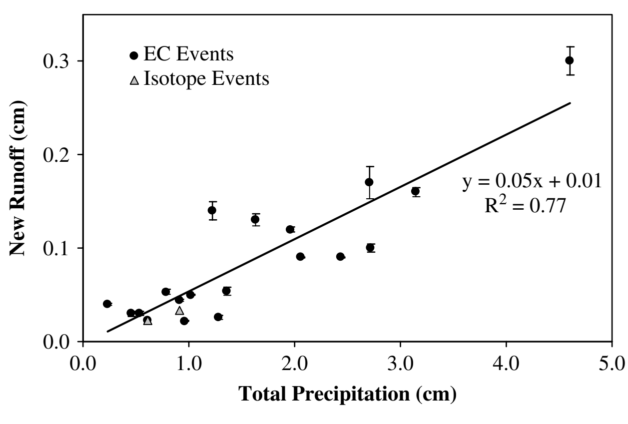

Figure 3. Depth of new water runoff (cm) versus the total precipitation (cm) for the 19 events in our study. Error bars represent uncertainty at approximately one standard deviation

Comparison of tracers (EC, δD and Si)

The contributions of new and old water and intrastorm patterns were generally comparable when calculated using δD and Si as tracers during the January 29–31, 2002 event and using EC, δD and Si during the September 16–21, 2002 event (Figures 4 and 5). Old water contributions were overestimated by less than 6% for most events due to the short-lived pulse of high EC surface runoff (data not shown). Linear interpolation between pre- and post-flush EC values resulted in nearly identical contributions of new water for the September event using δD and EC (65 and 64% new water, respectively). The contribution of new water using Si was lower in September (53%) but followed the same temporal pattern (Figure 5). Hydrograph separation results using δD and Si showed similar temporal patterns and event totals for the January 2002 event (25 and 20% new water, respectively; Figure 4).

DISCUSSION

Rationale for EC as an urban hydrograph tracer

Hydrograph separation studies using EC in forested watersheds have reported relatively small differences (<50 μS/cm) between precipitation and baseflow EC values (McDonnell *et al.*, 1991; Matsubayashi *et al.*, 1993; Laudon and Slaymaker, 1997). In contrast, EC values in old and new water differed by 1–2 orders of magnitude in our urban study watershed (Table I). Large differences in end-member EC values resulted in uncertainty estimates in the fraction of new water of ±1–10% in our study (Table II), generally not enough error to compromise the essential findings of the hydrograph separation (Buttle, 1994).

A second consideration in EC hydrograph separation is the non-conservative nature of the tracer, which may result in changes in end-member EC values en route to the stream. The use of a bulk precipitation EC value to characterize new water does not take into account intrastorm rainfall variability, throughfall-enrichment and the washoff of pollutants accumulated on impervious surfaces. However, doubling the precipitation EC value and increasing the standard deviation to 100% during events increased the uncertainty in our hydrograph separation by only 1–3%, suggesting that throughfall-enrichment would not dramatically alter our conclusions. In addition, the delivery of throughfall water directly to the channel is likely insignificant relative to impervious surface runoff in urban catchments (Buttle *et al.*, 1995) and we assume this a negligible source of error in our study. The first flush of solutes from impervious surfaces, suggested by short-lived peaks in stream EC prior to peak discharge, also has minimal impact on our overall hydrograph separation (Figure 5).

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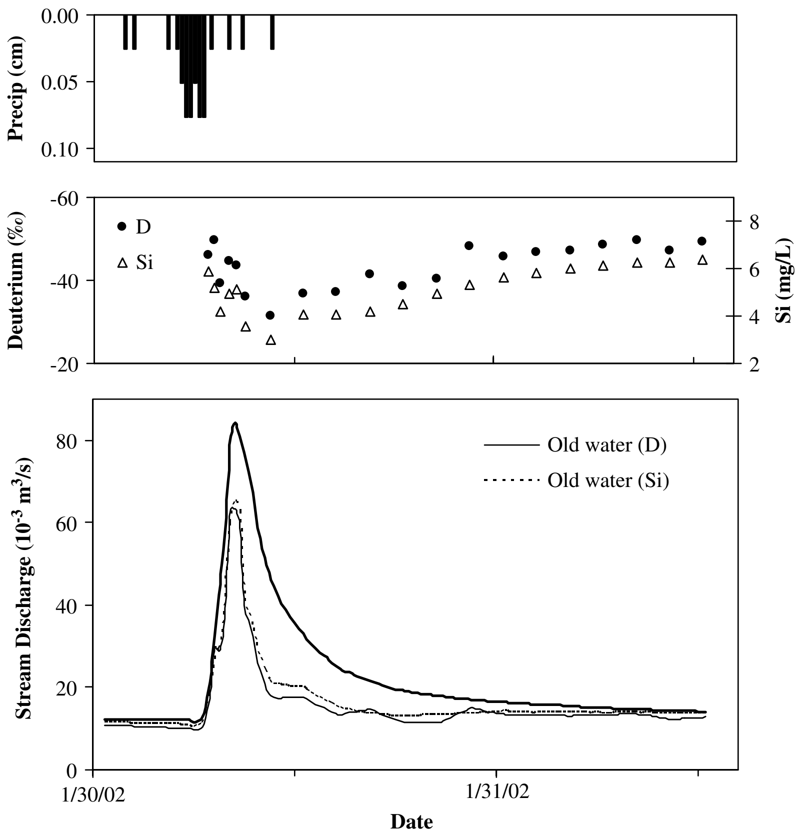

Figure 4. Rainfall depth, stream δD and Si concentrations, total discharge and old water discharge (based on δD and Si as hydrograph tracers) for the January 29–31, 2002 event

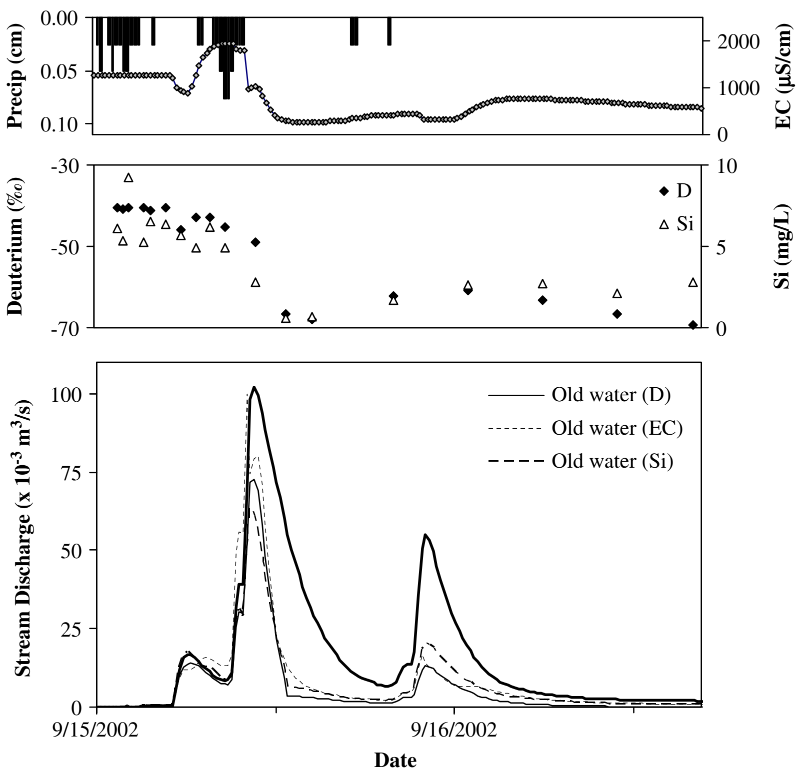

Figure 5. Rainfall depth, stream δD and Si concentrations, total discharge and old water discharge (based on EC, δD and Si as hydrograph tracers) for the September 15–21, 2002 event

The importance of unsaturated zone soil water in stormflow generation is not known in urban catchments but is usually assumed to be negligible (Rose, 2003; Berthier *et al*., 2004). Inferences from EC-discharge hysteresis loops in our study generally support the use of a two-component mixing model composed of high EC old water and low EC precipitation (C3 loop as described by Evans and Davies, 1998; Rose, 2003). Limited data in our study watershed suggest that soil water EC values were significantly lower (30–120 μS/cm) than baseflow stream EC values, possibly reflecting dissolution of mineral material rather than anthropogenic solute loading to groundwater (Paul and Meyer, 2001; Kaushal *et al*., 2005). Significant discharge of soil water is unlikely for low-intensity, low-volume precipitation events during drier periods (Nolan and Hill 1990), but may become increasingly important during periods of high antecedent moisture (Berthier *et al*., 2004). The displacement of soil water would result in an overestimate of new water, possibly explaining new water contributions of 104–117% of stormflow during four high antecedent moisture events in our study (Table II).

Comparison of EC and conventional tracers

Although the use of EC for hydrograph separation has been reported in forested watersheds (Pinder and Jones, 1969; Nakamura, 1971; Pilgrim *et al*., 1979), its use in non-forested watersheds is rare (Nolan and Hill, 1990; Cey *et al*., 1998; Heppell and Chapman, 2005). Isotopic tracers are generally considered indicators of water sources, while non-conservative chemical tracers such as EC and Si are considered flowpath tracers due to interactions with mineral material and constituents en route to the stream (Laudon and Slaymaker, 1997). A comparison of two storms indicates that intrastorm and total contributions of new and old water were similar using EC and/or Si and δD as hydrograph tracers (Figure 3), suggesting that isotopically new water largely bypasses mineral soils or does not reach near-equilibrium values for EC and Si concentrations during transport along subsurface flowpaths. Additional storms were sampled for isotopic hydrograph separation, but showed little difference between pre-event baseflow and precipitation δD values and were therefore not included in this analysis.

Results from other studies in non-forested and forested watersheds are generally inconclusive as to the widespread use of EC for hydrograph separation. For example, Cey *et al*. (1998) reported only slight differences between hydrograph separation results using δ^{18}O and EC in an agricultural watershed, while Nolan and Hill (1990) found that non-conservative tracers (EC, potassium, Si) resulted in elevated old water contributions relative to δD in the declining limb of a storm. Studies in forested watersheds have presented contradictory results with EC and isotopic tracers (McDonnell *et al*., 1991; Matsubayashi *et al*., 1993; Laudon and Slaymaker, 1997). While a lack of agreement between tracers in forested catchments may be the result of small differences in end-member EC values, additional validation of EC-based approaches with more conventional tracers and hydrometric measurements is needed in individual catchments and during a range of hydrologic and climatic conditions before widespread application.

Relative contribution of new water to stormflow generation

Hydrograph separation indicates that stormflow (e.g. discharge above baseflow) is largely composed of new water, accounting for 61–117% of elevated discharge (Table II). The importance of direct rainfall onto the stream channel and overland flow from pervious surfaces were not explicitly evaluated as part of our study, but were likely not the dominant mechanisms of new water delivery to the stream. First, the runoff efficiency from impervious surfaces is much higher than that of pervious surfaces during low-intensity or short-duration events similar to those in our study (Endreny, 2005). Second, the stream channel and near-stream saturated zones that effectively generate new water runoff during storms occupy a small percentage of the watershed and appear hydrologically-disconnected for much of the reach, a feature reported in other urban watersheds (Groffman *et al*., 2003). Finally, new water runoff coefficients were similar over a range of antecedent discharge conditions (Table II), but presumably would have been higher during wetter periods if saturated pervious surfaces generated significant runoff (Eshleman *et al*., 1993; Boyd *et al*., 1994).

While infiltration and depression storage account for a delay in new water delivery to the stream channel (Endreny, 2005), our results indicate that new water contributions lag behind the increase in discharge (Figures 4 and 5). Elevated old water discharge is observed on the rising limb using EC, δD and Si as hydrograph tracers, suggesting that this phenomenon is not related to the initial solute washoff from impervious surfaces. The same phenomenon was observed by Sidle and Lee (1999) and Nolan and Hill (1990), with the latter attributing increasing old water contributions to flood waves of baseflow water displaced by runoff from localized impervious surfaces. The rapid mobilization of water stored in near-stream zone soils or water stored in the stormwater drainage network may also account for increased old water contributions to initial stormflow, but hydrometric measurements and three-component hydrograph separation would likely be required to accurately describe this mechanism.

Our data also indicate that while the amount of new water runoff is strongly correlated with total precipitation depth (Figure 3), the relative contribution of new water is largely determined by the antecedent stream discharge (Figure 2). Despite increases in old water contributions during the initial hydrograph rise, low new water percentages during some events apparently reflect the mixing of new water with a large volume of baseflow rather than a significant increase in subsurface discharge as described

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in some forested watersheds (Buttle *et al*., 1995; Burns, 2002).

Estimating the hydrologically-connected impervious area

A comparison of new water runoff with the maximum runoff possible from impervious surfaces in the watershed (25% of total area) suggests that less than half of the TIA is hydrologically-connected to the stream channel during small to moderate rainfall events (Table II). This highlights the need to distinguish between the TIA and HCIA in urban watersheds (Brabec *et al*., 2002). One event with a higher contribution (70%, 2–5 August 2002) had very little precipitation and was therefore subject to greater potential error. Reported ratios are also subject to uncertainties in our approaches for estimating the TIA, interpolated storm event rainfall totals, and assumptions related to hydrograph separation as discussed previously. However, uncertainties of ±25% in the total storm rainfall or TIA estimates would not dramatically alter the interpretation of our results (e.g. 6–62% TIA/HCIA).

Other approaches for estimating the HCIA include linear regression of rainfall versus stormflow for small storms (Alley and Veenhuis 1983; Boyd *et al*. 1994) and the use of relationships between the HCIA and TIA or land use (Alley and Veenhuis, 1983; Booth and Jackson, 1997). While calculating the runoff coefficient based on stormflow and rainfall is less intensive than field surveys of HCIA, a key assumption in the final regression is that stormflow is generated exclusively from impervious surfaces (Boyd *et al*., 1994). While our study generally supports this assumption (Table II), its validity is not clear for all urban catchments (Sidle and Lee, 1999; Gremillion *et al*., 2000) and results with this method likely represent an upper limit to the HCIA estimate.

Site-specific relationships between the HCIA and TIA or HCIA and land use categories (Alley and Veenhuis, 1983; Booth and Jackson, 1997) may provide a better estimate of impervious surface runoff than TIA, but local differences in watershed drainage often preclude their widespread application in urban catchments. For example, Zariello and Reis (2000) reported that estimates of HCIA calibrated to summer rainfall events in the Ipswich River watershed were 20–50% lower than estimates based on published land use relationships. Using the TIA to predict impervious surface runoff would result in predicted runoff volumes 4–5 times higher on average than calculated by hydrograph separation in our study (data not shown). Similarly, site-specific relationships from Alley and Veenhuis (1983) and Schueler (1987) would have resulted in HCIA estimates of 14 and 28% for our study area, higher than HCIA estimated at 4–11% predicted by EC-based hydrograph separation for 18 of 19 storms in our study (Table II).

CONCLUSIONS

Although quantifying the ultimate fate of rainfall in a complex urban watershed is beyond the scope of this study, our results suggest that less than half of the rainfall on impervious surfaces is rapidly routed to the stream channel in our study catchment. Rainfall on non-effective impervious surfaces evaporates, infiltrates through roadways and parking lots, runs off to pervious surfaces or enters the storm drainage infrastructure. Septic system discharge (Burns *et al*., 2005), urban irrigation, and stormwater management strategies that reduce the HCIA and promote groundwater recharge may increase the relative importance of subsurface flow paths in urban watersheds. High groundwater recharge rates and rapid soil infiltration may help reconcile the large contributions of old water to stormflow generation in some urban watersheds (Buttle *et al*., 1995; Sidle and Lee, 1999; Gremillion *et al*., 2000) by maintaining a shallow water table and enhancing the rapid displacement of soil and groundwater during events. While decreasing the HCIA is widely recognized as a key to reducing non-point source pollution (Walsh *et al*., 2005), a better understanding of the relative contributions of surface and subsurface water to stormflow generation is critical for accurate hydrologic modeling, water quality management and urban design.

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