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The influence of urbanization on runoff generation and stream chemistry in Massachusetts watersheds

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THE INFLUENCE OF URBANIZATION ON RUNOFF GENERATION AND STREAM CHEMISTRY IN MASSACHUSETTS WATERSHEDS

BY

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To Anthony Cecconi – the *smartest* man I know

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ABSTRACT

THE INFLUENCE OF URBANIZATION ON RUNOFF GENERATION AND STREAM CHEMISTRY IN MASSACHUSETTS WATERSHEDS

By

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University of New Hampshire, September, 2004

The conversion of forested and agricultural land to suburban and urban landscapes is a dominant land use change dynamic in the United States and has implications for watershed hydrology and water quality. Here I evaluate the effect of integrated landscape features (e.g. percent residential or developed) and watershed-scale attributes influenced by urbanization on stream nutrient concentrations in headwater catchments in Massachusetts. In addition, I evaluate the importance of surface versus subsurface flow paths during rainfall events in stormflow generation in a small urban catchment. The percentage of residential land explains 52 % of the variability in mean annual nitrate (NO_3) concentrations in headwater catchments of the Ipswich River watershed, but is not correlated with mean annual phosphate (PO_4) or dissolved organic nitrogen (DON) concentrations. A multiple regression of wetlands plus open water percentage and septic density explains 51 % of the variability in NO_3 concentrations and highlights the potential importance of wetlands (sinks) and septic wastewater (sources) at the watershed scale. Stream DON concentrations are best predicted by the percent wetlands in the study catchments ($r^2 = 0.56$) and in a compiled dataset of northeastern U.S. watersheds ($r^2 = 0.60$; $n = 158$ watersheds). Hydrograph separation in an

intensively-studied 3.9 km^2 catchment indicates that surface flow paths are critical to stormflow generation during rainfall events in urbanizing catchments. Elevated discharge is largely composed of new water, with total precipitation depth describing most of the variability in new water runoff volumes. However, only about 20 % of the impervious surface area contributes direct runoff to the stream during hydrologic events with the other 80 % presumably exported from the watershed, evaporated or entering the groundwater. Impervious surfaces increase surface runoff of water and contaminants to streams, but may also result in reduced groundwater recharge. Reduced recharge may decrease wetland abundance and denitrification potential, in addition to increased runoff bypassing wetlands. Discharge from septic systems may compensate by providing some recharge, but with elevated subsurface NO_3^- inputs below the rooting zone. Understanding the simultaneous and interacting influence of these components will be critical for managing the impacts of urbanization on stream hydrology and water quality.

INTRODUCTION

Land use change has significantly altered the landscape of the northeastern United States over the past three hundred years. Shortly after European settlement in the mid-18th century, a significant fraction of the forested landscape was transformed for agricultural production (Foster et al., 2003; Francis and Foster, 2001; Howarth et al., 1996). By the mid-19th century, over 70 % of Massachusetts land area was identified as pasture (Francis and Foster, 2001). However, agriculture was largely abandoned by the 20th century as U.S. crop production increased in mid-western states and rural populations began migrating to urban and suburban areas. Forest re-growth became the dominant feature of the New England landscape following the abandonment of agriculture (Francis and Foster, 2001; Roman et al., 2000; Matlack, 1997), but the regional vegetation patterns of the pre-agricultural period have not been re-established (Foster et al., 2003).

Rapid population growth and urbanization since the 1950's continue to alter the landscape in many parts of the northeastern United States (Hopkinson and Vallino, 1995; Howarth et al., 1996). Urbanization is a dynamic spatial phenomenon associated with increases in energy consumption and landscape modification (McDonnell and Pickett, 1990) and is one of the major forces in land use change in the United States and has largely taken place in watersheds formerly dominated by forests and agriculture. Approximately 12 million hectares of land were converted to developed land in the U.S. between 1982 and 1997, with a significant fraction in prime farmland (Hasse and

Lathrop, 2003). The rate of conversion has also increased from 1.4 million acres per year between 1982-1992 to 2.2 million acres per year between 1992-1997 (NRCS, 2000). Urban areas are home to a large fraction of the U.S. and global population although they only account for 2 % of the earth's land surface (Grimm et al., 2000). Low-density growth (e.g. "urban sprawl") is also a feature of urban land use change in which large amounts of land resources are lost in relation to human population growth (Hasse and Lathrop, 2003). Estimates of urban population growth suggest that greater than 80 % of the U.S. population will reside in urban areas by 2025 (McDonnell et al., 1997).

Categories such as urban, suburban, and rural are typically based on population density, but are poorly defined quantitatively (Theobald, 2004). For example, definitions of urban range from > 386 people / km^2 (U.S. Census Bureau) to > 620 people / km^2 (McDonnell and Pickett,1990; McDonnell et al., 1997) or > 1000 people / km^2 (Marzluff et al., 2001, cited in Theobald, 2004). However, dynamic land use change may not be adequately described by a single aggregated variable like population density, percent residential, or impervious surface area (Theobald, 2004; Alberti et al., 2003). Urbanization as a land use change is multidimensional and highly variable across the rural-to-urban gradient (Alberti et al., 2003). Urbanizing areas vary in terms of individual components like the type of infrastructure, populations, physical and chemical environments, and human cultures (Zandbergen, 1998; McDonnell and Pickett, 1990). The spatial and temporal complexity of these features typically do not correlate with a simple rural-to-urban gadient based on population density (McDonnell et al., 1997). Understanding the distribution and role of landscape attributes as components of urbanization is critical for understanding both ecological impacts and the social drivers of land use change (Alberti et al., 2003; Grimm et al., 2000). In addition, evaluating the simultaneous and interacting influence of these components is critical for understanding the impact of urbanization on stream hydrology, water quality, and ecological impacts (McDonnell et al., 1997).

Here I present a review of several important landscape attributes introduced during urbanization (e.g. impervious surfaces, artificial drainage networks, wastewater) and natural features influenced by urbanization (wetlands and surface water). Impacts occur on the hydrology, biogeochemistry, water quality, and biotic integrity of urbanizing watersheds and this represents only a partial review of the topic focusing on nutrient biogeochemistry. The majority of published literature on urbanization is from temperate watersheds, although recent papers (McDowell, 2001; Grimm et al., 2000) have discussed land use change in other regions.

The Role of Impervious Surfaces - The increase in impervious surface area is a ubiquitous feature of urbanizing watersheds. Impervious surfaces used for transportation are typically the dominant type and include roads, parking lots, driveways, and sideways (Arnold and Gibbons, 1996). Rooftops and compacted soils are also considered impervious surfaces in many cases. Impervious surfaces are a relatively recent phenomenon and are often considered an indicator of urbanization (Brabec et al., 2002). In the 1904 U.S. census, approximately 93 % of all roads were unpaved (Arnold and Gibbons, 1996). Currently, the impervious surface covers approximately 112,000 km^2 of the conterminous U.S., an area slighter larger than all herbaceous wetlands in the U.S. (Elvidge et al., 2004). Impervious surface area continues to grow at a rapid pace (>

10,000 miles per year) and will continue to be a key issue in watershed management and planning (Elvidge et al., 2004; Brabec et al., 2002) and influences watershed hydrology, heat fluxes, carbon sequestration, geomorphology, surface and groundwater quality, wetland abundance, biotic diversity, and fish and invertebrate abundance (Morse et al., 2003; Nowak and Crane, 2002; Brabec et al., 2002; Groffman et al., 2002; Jennings and Jarnigan, 2002; Paul and Meyer, 2001; Arnold and Gibbons, 1996).

Impervious surfaces act to integrate a number of simultaneous interactions that alter stream watershed hydrology (Jennings and Jarnigan, 2002). Decreased permeability associated with urban development is known to influence runoff and alter the hydrologic response of streams and rivers to precipitation and snowmelt events. Increased runoff volume, higher peak storm flows, and increased overland or channelized flow are all commonly attributed to urbanization and may have important impacts in the watershed (Kang et al., 1998; Hopkinson and Vallino, 1995). Higher flow volumes increase scouring and stream channel erosion (Booth and Jackson, 1997) and impact stream geomorphology (Paul and Meyer, 2001). In addition, the ration of annual stream runoff to rainfall increases in comparison to forested watersheds. Groffman et al. (2004) found that 17-34 % of annual rainfall ran off in suburban and urban watersheds in Baltimore in comparison to < 5 % in forested watersheds. Burges et al. (1998) reported 44-48 % of rainfall ran off from forested catchments in comparison to 12-30 % in forested watersheds. Zariello and Barlow (2002) found that runoff increased from 20-80 % of precipitation in catchments ranging from 11-86 % impervious in Massachusetts. The increased delivery of surface runoff to stream via stormwater pipes may also reduce groundwater recharge, resulting in a lowering of the water table, reduced baseflow volumes, and changes in riparian wetland areas (Groffman et al., 2002; Gremillion et al., 2000; Arnold and Gibbons, 1996).

Thresholds for impacts on watershed hydrology are evident at about 10-20 % impervious (Jennings and Jarnigan, 2002; Paul and Meyer, 2001; Arnold and Gibbons, 1996). A common assumption in urban rainfall-runoff modeling studies, however, is that all impervious surfaces contribute runoff directly to the stream (Beighley et al., 2003; Jennings and Jarnigan, 2002; Booth and Jackson, 1997). A number of studies suggest that about 30 – 75 % of the total impervious area (TIA) is directly-connected to the stream (Taylor, 1977; Alley and Veenhuis, 1983; Ku et al., 1992; Booth and Jackson, 1997; Brun and Band, 2000; Zariello and Reis, 2000; Lee and Heaney, 2003). Modeled estimates using both the TIA and intensively-measured effective impervious area (EIA) have been shown to result in total and peak runoff differences of about 265 % (Lee and Heaney, 2003). The EIA is the major source of urban storm runoff to streams and is therefore the most critical parameter for many urban rainfall-runoff models. However, few studies use this parameter because it is difficult to measure accurately (Lee and Heaney, 2003; Jennings and Jarnigan, 2002). Site-specific relationships between EIA and TIA (Alley and Veenhuis, 1983) or land use (Dinicola, 1989) have been used as a surrogate, while other studies have estimated the EIA through model calibration (Anderson et al., 2002; Valeo and Moin, 2001). However, field verification is normally not performed and these assumptions are therefore not evaluated.

Isotopic and geochemical hydrograph separation studies in forested watersheds usually indicate that increased flow is largely due to the discharge of groundwater and soil water stored in the watershed prior to the event (Genereux and Hooper, 1998; Buttle, 1994). Although increased stream discharge in urban watersheds is assumed to be the result of impervious surface runoff, at least one urban hydrograph separation study has found a large fraction of increased streamflow was due to the discharge of groundwater (Sidle and Lee, 1999). Subsurface discharge could account for a significant fraction of streamflow in other urban watersheds, particularly during wetter antecedent periods (Taylor, 1977), but the role of subsurface flow in urban watersheds has not been adequately addressed (Burns, 2002).

Understanding the contribution of direct surface runoff to streams is important because the short residence time along a surface flow path often limits the abiotic and biotic retention of contaminants. While surface runoff in forested watersheds may result in the rapid runoff of atmospheric pollutants to stream, surface runoff in urban watersheds also results in the delivery of heavy metals (Rose et al., 2001; Callender and Rice, 2000; Bannerman et al., 1993), suspended sediments (Carpenter et al., 1998), nutrients (Taylor et al., 2004; Baker et al., 2001; Driver, 1989), pathogens (Mallin et al., 2000) and other anthropogenic sources directly to streams (Paul and Meyer, 2001; Arnold and Gibbons, 1996). Therefore, a shift to surface flow paths during events will likely have a major impact on streamwater quality in urban watersheds where sources of pollutants are abundant and sinks may be bypassed.

The threshold for impacts on aquatic biota is typically reported at about 4-15 % impervious surface cover (see Morse et al., 2003; Brabec et al., 2002; Paul and Meyer, 2001), while abiotic impacts (e.g. water quality, stream habitat, geomorphology) have been reported at a greater range of impervious values (4-50 %; Brabec et al., 2002). Both the spatial typology and connectedness of impervious surfaces are likely critical features for impacts on stream health, but have received only limited attention (Taylor et al., 2004; Brabec et al., 2002). While detention ponds and soakaways provide some mitigation of stormwater impacts, the role of these structures in groundwater recharge and contaminant retention is difficult to measure in urban watersheds (Lerner, 2002).

Role of Wastewater Inputs - Urbanization has increased the rates of land-derived nutrient loading to estuaries and coastal ecosystems (Bowen and Valiela, 2001; Roman et al., 2000). Increased nitrogen (N) and phosphorus (P) flux is of particular concern for coastal eutrophication, which reduces aquatic biodiversity, increases toxic algal blooms, and may lead to fish kills (Carpenter et al., 1998). Howarth et al. (1996) estimate that wastewater N inputs from the northeastern U.S. to the North Atlantic Ocean account for 26 % of the total N inputs (0.13 Tg yr^{-1}). Roman et al. (2000) estimated that approximately 60 % of the total N load to urban estuaries in the northeastern U.S. between 1988 and 1994 was from wastewater discharge. Similarly, the authors found that wastewater accounted for 90 % of the total P loading into urban estuaries in the northeastern U.S. Trench (2000) estimated that point source inputs account for 59-76 % of the total N load and 75-83 % of the total P load to rivers in several urban watersheds in the northeastern U.S. Driscoll et al. (2003) found that wastewater accounted for 36-81 % of N loading to estuaries from eight large watersheds in the northeastern U.S. Caraco and Cole (1999) found that direct human wastewater inputs helped explain a large fraction of the variability in NO_3^- flux from large river basins globally. Castillo et al. (2000) found that soluble reactive P concentrations were best predicted by geologic substrate and wastwater treatment plant loading for 17 river sampling locations in Michigan, but NO_3^- was best described by the upstream ratio of agricultural to forested land.

Non-point sources of N and P such as septic systems are often difficult to measure and regulate but may be important sources of nutrients to rivers and streams (Carpenter et al., 1998). In a developed coastal watershed in Massachusetts (Bowen and Valiela, 2001), septic wastewater inputs to the watershed increased by a factor of 17 between 1938 and 2000 and account for nearly half of the current N load to the estuary. Significant watershed N retention also likely occurs (Valiela et al., 1997), with an estimated 65 % of the septic wastewater N input retained. In contrast to dissolved organic N and NH_4^+ (Robertson and Cherry, 1992), NO_3^- is relatively mobile in soils and likely represents the largest septic N loss to the estuary. However, direct wastewater discharges and runoff from intensive agricultural activity may contain elevated concentrations of dissolved organic N (DON) (Westerhoff and Mash, 2002). Seitzinger et al. (2002) reported that a higher proportion of anthropogenically-derived DON was bioavailable to estuarine bacteria relative to forest-derived DON. Therefore, urban and agricultural activity may not only alter the importance of DON in hydrologic N losses, but they may also have serious implications for our understanding of estuarine and coastal eutrophication.

Fertilizer and P-detergent use resulted in peak riverine P loads in the 1970's in many rivers (Billen et al., 2001; Roman et al., 2000; Smil, 1990), with significant decreases since. Despite low concentrations of P in most rivers today, human activity has increased the global waterborne P flux by at least 50 %, with developed areas exported approximately 85 % of the global total (Smil, 1990). Soils may significantly retain P from septic systems, but the long-term retention capacity of P is not well known (Bennett et al., 2001).

The Role of Wetlands and Open Water - A large body of evidence collected over the past twenty years in agricultural and forested watersheds has focused on the role of wetlands as nitrogen sinks due to denitrification, which is generally recognized as the dominant riparian process altering N fluxes to streams. "Hot spots" for denitrification (the conversion of NO_3^- to N_2O or N_2 gas) occur where organic carbon and NO_3^- are available to bacteria in anaerobic environments (McClain et al., 2003). Numerous studies have shown that wetlands are effective NO_3^- sinks (Hill, 1997; Vought et al., 1994) with no current evidence indicating that chronic N loading reduces the potential for riparian zones to function as nitrogen sinks (Hanson et al., 1994). Hydrologic events (e.g. rainfall and snowmelt) reduce water residence times and may therefore result in drainage waters largely bypassing riparian soils. In addition, seasonal or human-induced lowering of the water table may cause a disconnect between carbon-rich shallow soils and anoxic zones, reducing the denitrification potential in riparian soils (Groffman et al., 2002). The small number of studies that have examined the quantitative significance of riparian and hyporheic processes at the reach or watershed scale suggest that their importance is disproportionate to the relatively small area they occupy in the landscape (Billen and

Garnier, 2000; Chestnut and McDowell, 2000). However, few studies have specifically addressed the role of riparian wetlands and N retention in urban watersheds (Groffman et al., 2002). Historical wetland loss over the past 200 years has been significant in the U.S. and the areal extent of wetlands may limit N removal (Gleick, 1993; cited in Galloway et al., 2003).

Unlike N, P is not converted to a gas in riparian wetlands and therefore riparian P removal is via soil retention and biotic uptake (i.e. accumulation within the system). Riparian zones typically function as sinks for sediment-bound P in surface runoff via sediment deposition and infiltration (Vought et al., 1994; Osborne and Kovacic, 1993). Results of dissolved P retention in surface runoff and groundwater is more variable and the riparian zone can range from a sink (Vought et al., 1994) to a source for streams (Carlyle and Hill, 2001). Devito et al. (1989) found that < 20 % of total P was retained with five wetlands in Canada with the conversion of inorganic to organic P likely. The potential long-term P sink in riparian zones is not clear, although the role of anaerobic conditions and iron leaching appear to be important factors regulation P retention (Carlyle and Hill, 2001).

Recent evidence suggests that riparian zones may also play an important role as sources of DON and DOC to forested (Fölster, 2000; McHale et al., 2000) and urban streams (Pellerin et al., 2004; Raymond and Hopkinson, 2003). Leaching and decomposition of organic matter in the riparian zone provides a ready source of organic C and N and reduced conditions in wetland riparian zones (i.e. reductive dissolution of Fe-oxides known to bind dissolved organic carbon in mineral soils) may allow for transported through the riparian zone and delivery to the stream channel (Hagedorn et al., 2000). The role of wetlands as DON sources or sinks is not clear, however, since some forested riparian zones are sites where DON is retained or passes through unaltered (McClain et al., 1994).

Rivers, streams and lakes (including reservoirs) may be significant sources of N and P retention via sedimentation, denitrification (N only) or incorporation into biomass (Galloway et al., 2003; Peterson et al., 2001; Behrendt and Opitz, 2000). The residence time of water is a critical parameter for N retention and is typically lower in rivers and streams than in lakes, reservoirs or wetlands (Howarth et al., 1996). Many upland rivers and streams have been subjected to human modifications such as channelization, damming of rivers and removal of riparian vegetation (Pinay et al., 2002). The construction of reservoirs and dams has a significant impact on water regimes by reducing the magnitude and frequency of flood events (Pinay et al., 2002; Vörösmarty et al., 1997). The damming of rivers increased by nearly 700 % globally between 1950 and 1986 (Vörösmarty et al., 1997) and may counteract some deleterious effects of channelization by accumulating sediments and retaining inorganic nutrients (Howarth et al., 1996). However, damming may also result in negative effects, such as losses of downstream floodplains and riparian forests, reduced coastal deltaic buildup, increased organic matter decomposition and inorganic nutrient supply, and alterations in the quality of organic matter exported downstream (Pinay et al., 2002; Vörösmarty et al., 1997; Hopkinson and Vallino, 1995).

CHAPTER 1

ROLE OF WETLANDS AND DEVELOPED LAND USE ON DISSOLVED ORGANIC NITROGEN CONCENTRATIONS IN NORTHEASTERN U.S. RIVERS AND STREAMS

Abstract

Previous studies have shown that watersheds with significant human development (i.e. urban and agricultural land use) generally have higher concentrations and fluxes of dissolved inorganic nitrogen (DIN) in comparison to less developed or forested watersheds. However, the impact of watershed development on dissolved organic nitrogen (DON) concentrations in drainage waters has received little attention. We present data from 39 watersheds in Massachusetts (Ipswich River watershed) encompassing a gradient of developed land use (0-92 % urban plus agriculture) and wetland abundance (0-32 %) to assess controls on mean annual DON concentrations and DON / total dissolved nitrogen (TDN) in drainage waters. In addition, we compiled published data from 119 northeastern U.S. watersheds to evaluate broader-scale relationships between DON, developed land use, and wetlands. The percentage of developed land is a poor predictor of DON concentrations in the Ipswich watersheds (r^2 = 0.09) and the compiled dataset (r^2 = 0.27). In contrast, wetland percentage explains 56 % of the variability in DON concentrations in the Ipswich watersheds and 60 % when all literature data are included. Excluding watersheds with direct wastewater inputs to surface waters improves the regional relationship significantly (r^2 = 0.79). The DON /

TDN ratio is best explained by a multiple regression of wetland percentage and developed land use percentage for both the Ipswich watersheds ($r^2 = 0.73$) and the compiled dataset ($r^2 = 0.50$). Watersheds with abundant wetlands may therefore have high DON concentrations and DON / TDN ratios despite elevated anthropogenic N inputs associated with human development.

Introduction

Humans have significantly altered the global nitrogen (N) cycle in the temperate northeastern United States (Howarth et al., 1996; Boyer et al., 2002) via elevated atmospheric N deposition and inputs of anthropogenic N associated with land use change. As a result, current riverine N exports from the region are estimated to be 5-15 times higher than pre-industrial exports (Howarth et al., 1996). Previous studies have assessed the potential influence of atmospheric N deposition on the concentration and relative fractions of dissolved inorganic (DIN) and dissolved organic N (DON) in stream export from temperate forested watersheds (Hedin et al., 1995; Perakis and Hedin, 2002; Goodale et al., 2000; Campbell et al., 2000). Several studies have also evaluated the impact of urbanization and agriculture on DIN concentrations and fluxes from temperate rivers and streams (Jordan et al., 1997; Valiela et al., 1997; Herlihy et al., 1998; Boyer et al., 2002). Few studies, however, have evaluated the impact of human development (i.e. urbanization and agricultural development) on DON concentrations and DON / TDN ratios in drainage waters.

Urban and agricultural land use within watersheds has been linked to increased inorganic N concentrations in drainage waters via wastewater, fertilizer use, cultivation of N-fixing crops, and atmospheric deposition (Howarth et al., 1996; Jordan et al., 1997; Herlihy et al., 1998; Boyer et al., 2002). In addition to elevated DIN concentrations, wastewater discharge and runoff from intensive agricultural activity may contain elevated concentrations of DON (Westerhoff and Mash, 2002). Seitzinger et al. (2002) have reported that a higher proportion of anthropogenically-derived DON was bioavailable to estuarine bacteria relative to forest-derived DON. Therefore, urban and agricultural activity may not only alter the importance of DON in hydrologic N losses, but also may have serious implications for our understanding of estuarine and coastal eutrophication.

Our current knowledge of relationships between natural landscape features and DON concentrations in streams and rivers is also critically lacking. Wetlands have been shown to function as sinks for inorganic N through denitrification (Hill, 1996), as well as sites where inorganic N may be converted to organic N (Devito et al., 1989). Although regional studies linking DON to natural landscape features have had limited success (Clair et al., 1994), relationships between streamwater dissolved organic carbon (DOC) (Mulholland and Kuenzler, 1979; Eckhardt and Moore, 1990; Raymond and Hopkinson, 2003) and wetland abundance suggest that wetlands may play an important role in hydrologic DON losses from forested and developed watersheds.

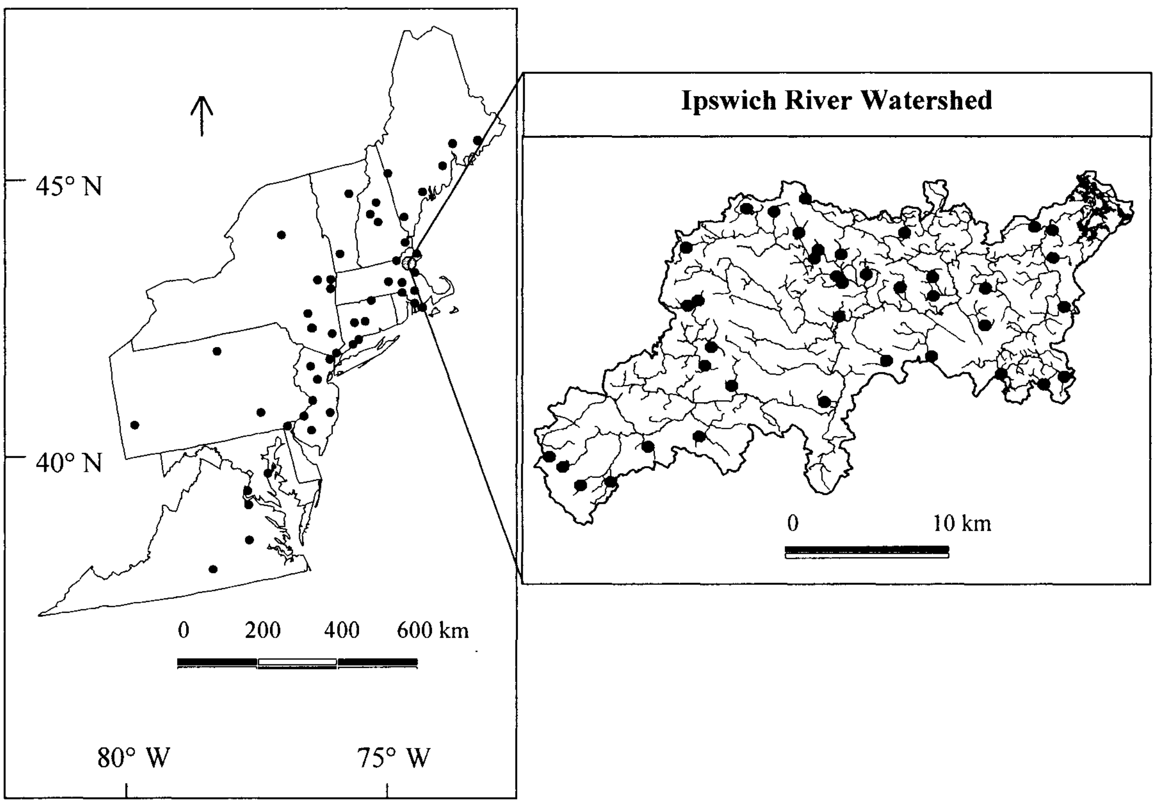
Here we present data from forested and developed watersheds in northeastern Massachusetts to assess the importance of DON in hydrologic N losses. The specific goals of this paper are to: (1) determine the concentration and proportion of DON in total N losses from 38 sub-catchments and the mouth of the Ipswich River watershed, (2) assess the influence of wetlands and developed land use on DON concentrations and DON as a fraction of total N in drainage waters, and (3) incorporate results from previously published studies in forested and mixed land use watersheds to assess the role of wetlands and human development on DON losses in the northeastern U.S.

Methods

Site Description – Samples for N analysis were collected from 38 sub-catchments and the mouth of the 404 km^2 Ipswich River watershed in northeastern Massachusetts (Figure 1). The watershed is one of three that drain into the Plum Island Sound estuary and is part of the Plum Island Ecosystem Long Term Ecological Research (LTER) project. The Ipswich River watershed lies within the coastal lowland section of New England and is characterized by low to moderate relief and relatively poor drainage. Bedrock is mainly igneous and sedimentary rock (Paleozoic and Precambrian) and shallow soils are developed largely on surficial till, gravel and sand deposits (Baker et al., 1964). Average annual precipitation is 1180 mm yr^{-1} and is uniformly distributed throughout the year. Mean monthly air temperature ranges from –2 °C in winter to 23 °C in summer. Atmospheric N deposition (inorganic, wet plus dry) is approximately 700-800 kg N km^{-2} yr^{-1} (Ollinger et al., 1993). Organic N wet deposition is assumed to be a minor component (< 5 %) of total N deposition in eastern North America (Keene et al., 2002), although some studies in northeastern U.S. watersheds have considered DON to be as high as 15 - 30 % of N deposition (Boyer et al., 2002). Land use in the Ipswich River watershed (in 1999) is 37 % forest, 35 % urban, 7 % agricultural and 16 % wetlands.

Wetland area and land use were delineated from 1:5000 orthophotography and 1:25000 aerial photography (MassGIS) and were analyzed using GIS software. Urban land use in our study included land classified as residential, commercial, industrial and transportation.

Figure 1. Location of watersheds sampled within the 404 km^2 Ipswich River watershed and the location of watersheds included in our compiled dataset. Points outside of the Ipswich River watershed may represent more than one sampled catchment.



Sub-watersheds sampled as part of this study are all headwater catchments (0.5-4.2 km^2) ranging from 0-92 % developed (urban plus agriculture). Residential land use is the dominant form of development, with agriculture (mainly as pasture) totaling < 10 % of the land area in most watersheds. Wastewater from developed areas is released to septic systems or to municipal sewer systems that discharge directly to the Atlantic Ocean. Wetlands account for 0-32 % of the watershed area in the sub-catchments (MassGIS) and are typically located along stream channels and in scattered small upland depressions.

Sampling Frequency – River water samples for N analysis were collected monthly at the mouth of the Ipswich River (42° 39'35" N, 70° 53'39" W) from 1998 – 2002, with higher frequency sampling (≈ biweekly) from February 1999 - September 2000. In the 38 sub-watersheds, samples were collected on 4-5 sampling dates from February 1999 - September 2000 and were distributed throughout the sampling period (February, April, September, and November). The number of samples collected from each site is a limitation in our dataset, but one that is often required when using spatially extensive sampling to discern broad scale patterns (Hedin et al., 1995; Lovett et al., 2000; Perakis and Hedin, 2002). However, intensive sampling at the mouth of the Ipswich River was used to determine if averaging N concentrations from the reduced sampling frequency provided a reasonable estimate of volume-weighted mean (VWM) DIN and DON concentrations.

VWM concentrations were calculated as:

$$\text{VWM} = (\Sigma C_i Q_i) / \Sigma Q_i$$

Where C_i is the measured nutrient concentration at time i, Q_i is the discharge volume for the period with the sample collection date as the midpoint, and ΣQ_i is the sum of the annual discharge.

For the Ipswich River, arithmetic mean concentrations of DON collected on the 5 sampling dates and VWM concentrations based on approximately biweekly samples differed by 5 % in 1999-2000 (477 vs. 452 $\mu g\ L^{-1}$). Similarly, DIN concentrations differed by only 8 % (202 vs. 188 $\mu g\ L^{-1}$). This suggests that reduced sampling was adequate to characterize mean annual DON and DIN concentrations in our sub-watersheds. Discharge was not measured from sub-watersheds during the sampling period and differences in land cover preclude estimating discharge based on discharge from the mouth of the Ipswich River (USGS gauging station 02102000). Fluxes are therefore not calculated for the sub-watersheds in this study.

<u>Sample Collection and Analysis</u> – Samples from the mouth of the Ipswich River were collected in 1-L polyethylene bottles or 10-L polyethylene carboys and filtered within 12 hours of collection through pre-combusted Whatman 24 mm GF/F glass-fiber filters (pore size = 0.7 μm). Samples were stored on ice until transported to the laboratory and frozen in acid-washed polyethylene bottles until analysis. Similar methods were used for sub-watershed sampling except that all bottles were filtered into acid-washed polyethylene vials in the field.

NO_3^- and NO_2^- were measured using the cadmium reduction method on a Lachat QuikChem 8000 flow injection analyzer. NH_4^+ was measured colorimetrically by the indophenol method. Total dissolved N (TDN) was determined via persulfate oxidation with subsequent measurement of NO_3^- following the methods of Valderrama (1981). DON is quantified as TDN minus DIN ($NH_4^+ + NO_3^- + NO_2^-$). Analytical precision for NH_4^+ and NO_3^- is ± 5 % and instrument detection limits are typically < 1.5 μg L^{-1} (C. Hopkinson, pers. comm.). The reported percent N recovery following persulfate digestion generally ranges from 90-110 % (Merriam et al., 1996; Bronk et al., 2000; Sharp et al., 2002; Westerhoff and Mash, 2002).

Statistical Analysis – Watersheds in this study were grouped by the fraction of developed land use (0-20 %, 21-40 %, 41-60 %, and > 60 %) to describe DON and DIN in each category. Since data were generally not normally distributed, significant differences in mean N concentrations and DON percentages were determined via the non-parametric Wilcoxon signed rank test at an alpha level of 0.05. In addition, N concentrations and DON percentage were regressed on developed land use and / or wetland fractions to evaluate relationships in our data. All statistics were performed using JMP software (version 4.04; SAS Institute, Inc.).

Results

Land Use Influence – Estimated VWM annual DON concentrations from the Ipswich River and 38 sub-catchments ranged from 170 – 825 μg L^{-1} and did not differ statistically among land use categories (Figure 2). DON concentrations for individual watersheds had a weak but significant negative correlation with the percentage of developed land use ($r^2 = 0.09$, $p = 0.04$; Table 1). In contrast to DON, watershed DIN concentrations varied by 2 orders of magnitude (16 – 1314 μg L^{-1}) and were correlated with the percent of development ($r^2 = 0.51$, $p < 0.01$). Higher DIN concentrations in developed watersheds were largely due to NO_3^-, which accounted for half of the DIN in the least developed category and increased to 90 % of DIN in the most developed land use category (data not shown). The high standard deviation in the 21-40 % developed category (Figure 2) is due to one outlier with consistently high DIN concentrations (mean = 1233 μg L^{-1}, range for other 11 sites in this category = 13 – 239 μg L^{-1}). The DON percentage (as a fraction of TDN) ranged from 17 – 97 % in individual watersheds and decreased as developed land use increased ($r^2 = 0.63$, $p < 0.01$). DON was the dominant form of N in watersheds with little to moderate development, accounting for 87 % (± 7 %) and 73 (± 24 %) of TDN in the two categories with < 40 % developed land (Figure 2). DON was a smaller fraction of TDN in more developed categories, accounting for 46 % (± 18 %) and 32 (± 10 %) of TDN.

Figure 2. Mean concentrations and standard deviations of DON and DIN in stream and river water at the Ipswich River watershed sampling locations. Watersheds are grouped by the percentage of developed land use.

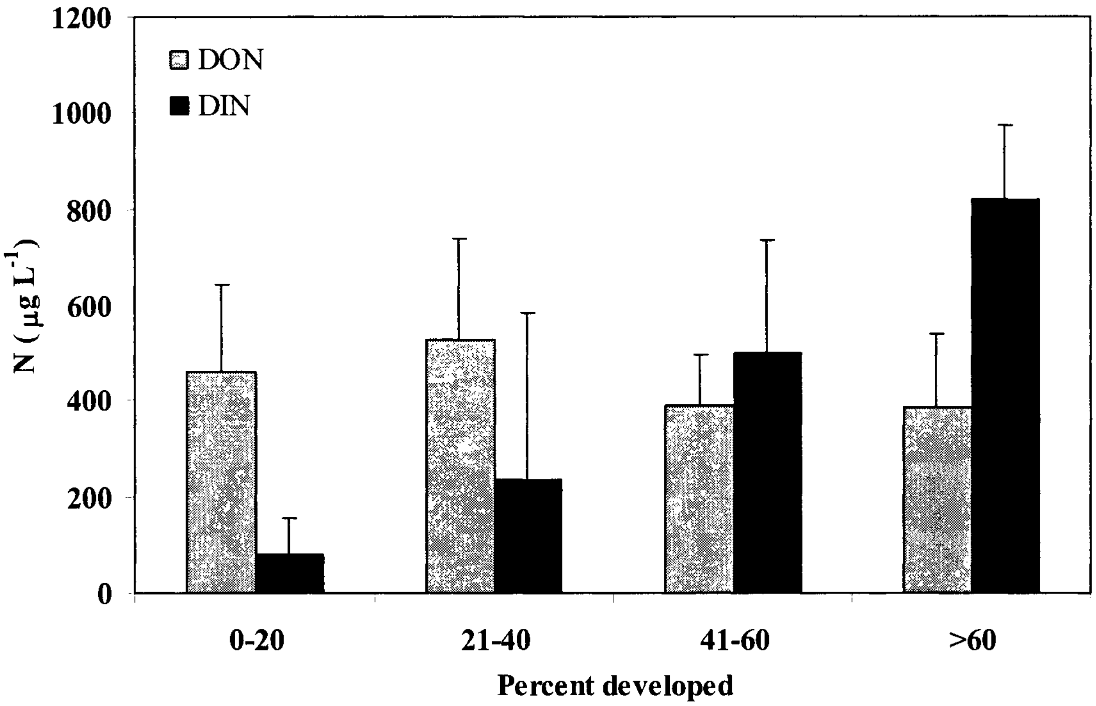


Table 1. Number of watersheds, watershed type, method of DON determination, and references for all data compiled for the northeastern U.S. Watershed types: For = entirely forested, Dev = developed (range in %). DON is calculated as TDN (measured by thermal oxidation or persulfate digestion) minus DIN or Kjeldahl N minus NH_4^+.

Number of watersheds	Watershed types	DON method	Source
10	For	thermal oxidation	Goodale et al.(2000)
1	For	persulfate digestion	McHale et al. (2000)
1	For	NA	Valiela et al. (1997)
15	For	thermal oxidation	Campbell et al. (2000), Campbell (1996)
39	For	persulfate digestion	Lovett et al. (2000)
5	For, Dev (< 20 %)	Kjeldahl nitrogen	Clark et al. (2000)
15	Dev (2 - 30 %)	Kjeldahl nitrogen	Boyer et al. (2002), USGS (2000)
12	Dev (3 - 30 %)	thermal oxidation	Daley and McDowell (unpubl.)
2	Dev (38 - 53 %)	thermal oxidation	Hopkinson et al. (1998)
14	Dev (45 - 99 %)	Kjeldahl nitrogen	Heinz Center (2002)
5	Dev (14 - 70 %)	Kjeldahl nitrogen	USGS (2003), Chalmers (2002)

Table 2. Adjusted r^2 values and p values (*in italics*) for DON, DIN, and DON/TDN as a function of percent wetlands and percent developed land use (simple regressions) and a multiple regression including both variables. Compiled regional data include Ipswich River watershed data. Regional sites without wastewater lack direct agricultural and human wastewater inputs. * indicates $p < 0.01$.

				Compiled data			
		Ipswich only		**W/out wastewater**		**All sites**	
	Variable	***(n= 39)***		***(n= 139†)***		***(n= 156‡)***	
DON ($\mu g\ L^{-1}$)	wetlands	0.56	*	0.79	*	0.60	*
vs.	developed	0.09	*(0.04)*	0.26	*	0.27	*
	wetlands, developed	0.55	*	0.80	*	0.65	*
DIN ($\mu g\ L^{-1}$)	wetlands	0.27	*	-0.01	*(0.69)*	0.01	*(0.20)*
vs.	developed	0.51	*	0.38	*	0.35	*
	wetlands, developed	0.55	*	0.53	*	0.45	*
DON/TDN	wetlands	0.42	*	0.39	*	0.38	*
vs.	developed	0.63	*	0.01	*(0.11)*	0.02	*(0.04)*
	wetlands, developed	0.73	*	0.50	*	0.50	*

† wetland n = 112 (114 for DON); ‡ wetland n = 139 (141 for DON).

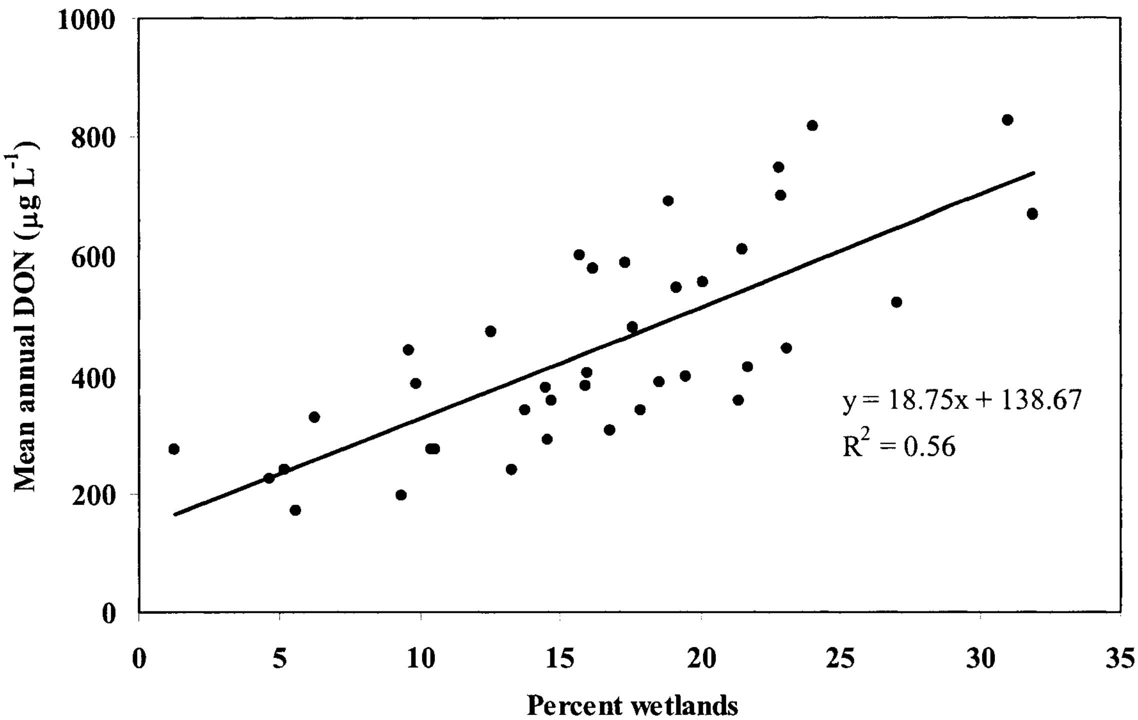
Wetland Influence – Watersheds in this study had a range of wetland percentages (0-32 %), allowing for an assessment of the wetland influence on concentrations of DON and DIN and the DON percentage. Mean annual DON concentrations were significantly correlated with wetland percentage in Ipswich River sub-watersheds ($r^2 = 0.56$, $p < 0.01$; Figure 3, Table 1). DIN concentrations had a weak, but significant negative correlation with wetland percentage ($r^2 = 0.27$, $p < 0.01$). Wetland percentage has a significant positive correlation ($r^2 = 0.42$, $p < 0.01$) with DON as a fraction of TDN in streamwater. Multiple regression analyses including both wetland percentage and the percentage of developed land improved the r^2 for DON as a fraction of TDN ($r^2 = 0.73$), but did little to improve relationships with DON and DIN concentrations. Including agriculture as a separate land use rather than including it in "developed" did not substantially improve our results (data not shown).

Discussion

DON Dynamics in the Ipswich River Watershed

In this study, DON accounted for over half of the hydrologic TDN losses from 54 % of the watersheds sampled and more than one-third of TDN losses from 77 % of the watersheds. Therefore, our data clearly indicate that DON can be a significant and often dominant fraction of TDN losses from watersheds influenced by moderately high atmospheric deposition and human development (Figure 2). However, both land use and wetlands are critical landscape features for understanding the role of DON in hydrologic N losses.

Figure 3. Percent wetlands versus mean streamwater DON concentrations (μg L^{-1}) from watersheds draining into the Ipswich River.



Effect of land use on DON – Individual watershed (Valiela et al., 1997; Williams et al., unpublished) and regional studies (Howarth et al., 1996; Boyer et al., 2002) in the northeastern U.S. have shown wastewater and fertilizer inputs to be important sources of inorganic N to surface waters. In addition, elevated surface water DON concentrations have been linked to wastewater treatment discharge and intensive agricultural activity in the U.S. (Westerhoff and Mash, 2002). Our results, however, indicate that DON concentrations in streams are not strongly influenced by urban and agricultural land use in the Ipswich River watershed despite significant anthropogenic N inputs (Figure 2, Table 1). In the Ipswich River watershed, wastewater is either discharged via septic systems or exported out of the catchment. In addition, fertilizer is mainly applied to urban lawns, which may leach a significant fraction of deposited N to subsoils (Valiela et al., 1997). Mineral forest soils are a major sink for DON (Aitkenhead-Peterson et al., 2003) and we therefore hypothesize that significant abiotic soil retention of human-loaded DON is occurring in our watersheds. Long-term N-fertilization studies at the Harvard Forest in Massachusetts have shown, however, that DON concentrations in the forest floor (McDowell et al., 1998) and mineral soil solutions (Currie et al., 1996) increased as a result of experimentally-elevated inorganic N deposition. The conversion of NO_3^- to DON in soils and the subsequent leaching of DON is possible in developed watersheds with high anthropogenic N inputs, but is not indicated by our data.

Although the percentage of developed land use is a poor predictor of DON concentrations in streams at our sites, it does explain a significant percentage of the variability in streamwater DIN concentrations ($r^2 = 0.51$; Table 1) and therefore influences the ratio of DON / TDN. Mean DON concentrations across all land use categories varied by only 27 %, while DIN concentrations increased by over an order of magnitude with increasing development (Figure 2). As a result, DON accounted for 32 - 87 % of TDN, on average, with the highest values in the least developed land use categories.

Effect of wetlands on DON – Wetlands are important sources of dissolved organic matter to streams and rivers, particularly when they fringe stream channels or discharge directly into streams (Mulholland and Kuenzler, 1979; Eckhardt and Moore, 1990; Fiebig et al., 1990; Fölster, 2000; Raymond and Hopkinson, 2003). Shallow flow paths from wetlands to streams bypass most mineral soils, which are known to retain DON as well as dissolved organic C (DOC) (Aitkenhead-Petersen et al., 2003). In addition, the refractory nature of wetland-derived DON and DOC (Stepanauskas et al., 1999) likely limits its biological utilization en route to and in the stream channel. Several studies have related streamwater DOC concentrations to the fractional area of wetlands in multiple watersheds (Mulholland and Kuenzler, 1979; Ekhardt and Moore, 1990). However, previous attempts to link hydrologic DON losses to landscape characteristics have been less successful. For example, Clair et al. (1994) found that basin slope and precipitation, both of which are factors in wetland development, explained only 30 % of the variability in DON fluxes from Canadian watersheds.

Our results show that the percentage of wetlands within the Ipswich River watershed and sub-catchments explains 56 % of the variability in DON concentrations (Figure 3). Wetland percentage also had a significant negative relationship with DIN concentrations in our study watersheds ($r^2 = 0.27$, Table 1). Although weak, this relationship suggests that wetlands at our study sites may be transforming inorganic N via denitrification (Hill, 1996) or the conversion of inorganic N into organic forms (Devito et al., 1989). However, the relationship between DIN and wetlands might also be an artifact of a weak but significant ($r^2 = 0.20$) negative relationship between developed land use percentage and wetland percentage in our watersheds. The DON / TDN ratio increased as wetland percentage increased, although the relationship was not as strong ($r^2 = 0.42$) as that using developed land use as a predictor of DON percentage ($r^2 = 0.63$). However, combining both land covers in a multiple regression explains 73 % of the variability of mean annual DON percentage for the Ipswich catchments.

Based on our data, the mean percentage contribution of DON to TDN losses from watersheds with up to 40 % urban and agricultural land (78 ± 20 %; $n = 19$) was comparable to that reported by Perakis and Hedin (2002) for unpolluted, temperate old-growth forests in South America (mean = 80 % DON). DON was only a small fraction of total N export from five eastern U.S. old-growth watersheds studied by the same authors, suggesting that chronic atmospheric N inputs may have caused a shift over time from organic to inorganic N (largely as NO_3^-) as the dominant N species in drainage waters. Our results suggest that watersheds receiving elevated N inputs due to urbanization and agriculture (in addition to nearly 10 times higher atmospheric N deposition relative to the unpolluted South American watersheds; Hedin et al., 1995) may still overwhelmingly export N in the form of DON if wetlands occupy a significant fraction of the watershed.

Regional Patterns of DON and DIN Losses

In order to assess the role of land use and wetlands on hydrologic DON losses regionally, we compiled a dataset of 119 watersheds in the northeastern U.S. from various sources in the literature (Figure 1, Table 2). Watersheds ranged in size from < 1 - 70,000 km^2 and included 69 forested watersheds and 50 watersheds with developed land use (defined as urban plus agricultural). Mean annual precipitation ranges from 900-1250 mm yr^{-1} and mean annual temperatures range from approximately 13°C in the south to 4°C in the north (Boyer et al., 2002). The gradient of atmospheric N deposition (inorganic, wet plus dry) generally decreases from about 1200 kg N km^{-2} yr^{-1} in southwestern Pennsylvania to 500 kg N km^{-2} yr^{-1} in northern Maine (Ollinger et al., 1993). Sites were characterized by 0-99 % development and 0-12 % wetlands. Land use and wetland cover data were taken from the published literature or obtained via personal communication (J. Campbell, C. Goodale, M. McHale) and may differ slightly in terms of data collection and land use classification.

Methodological issues – Different sampling methodologies are inherent in compiled datasets and need to be addressed before comparisons are made. Sampling frequencies ranged from weekly or biweekly (Campbell, 1996; Campbell et al., 2000; Clark et al., 2000; McHale et al., 2000) to monthly (Goodale et al., 2000; Daley and McDowell, unpublished) or seasonally in spatially extensive studies (Lovett et al., 2000). DON concentrations for the SCOPE study sites (Boyer et al., 2002) and the New England Coastal Basins (NECB) study sites (Chalmers, 2002) were not available in the literature and were therefore calculated from USGS data at the stations reported in the literature. Volume-weighted mean DON and DIN concentrations were calculated for 1988 -1992 at sites described by Boyer et al. (2002) and 1998-2000 for NECB study sites (Chalmers, 2002). Sampling frequency varied by sites, but most samples were collected on a monthly basis. Volume weighted N concentrations were calculated as previously described for the Ipswich River watershed. At all other sites except those in the Catskills (Lovett et al., 2000), discharge was either measured or modeled by the authors and used to calculate mean annual flow-weighted N concentrations. With the exception of two studies (Campbell et al., 2000; McHale et al., 2000), all samples were filtered through 0.45 – 0.7 μm pore size filters before analysis. Both authors estimated that total organic N equaled DON (based on the lack of turbidity in unfiltered samples) and we therefore refer to total organic N from these studies as DON.

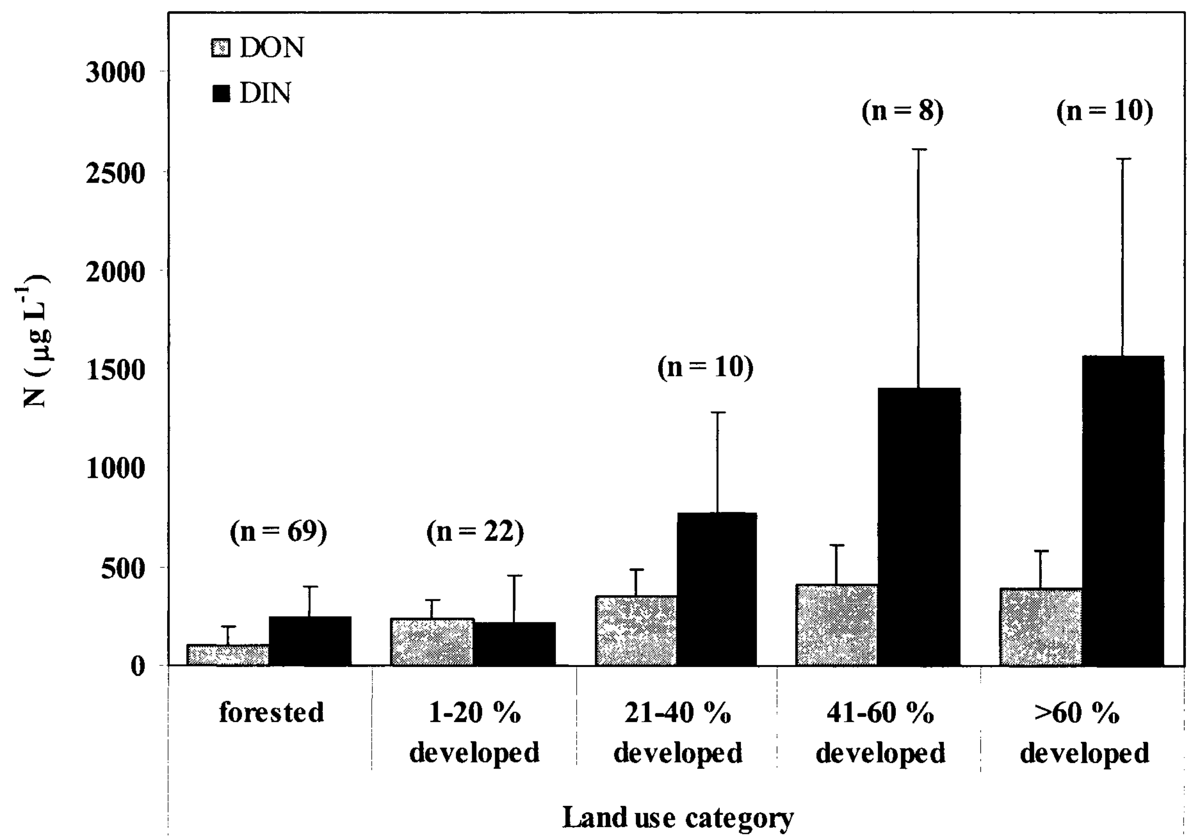
Analytical methods – A consideration for compiling data on DON is the lack of a standard analytical methodology. In our dataset, DON was either determined as the difference between TDN and DIN (NO_3^- + NH_4^+) or as the difference between Kjeldahl N (NH_4^+ + organic N) and NH_4^+ (Table 2). Inorganic N was measured colorimetrically or by ion chromatography, while TDN was measured by persulfate digestion or high-temperature catalytic oxidation. Method comparisons for TDN analysis indicate that both persulfate digestion and high-temperature oxidation typically produce similar results for freshwater and seawater samples, with N recoveries of 90 – 110 % (Merriam et al., 1996; Bronk et al., 2000; Sharp et al., 2002; Westerhoff and Mash, 2002). Cornell et al. (2003)noted that there were no clear differences in rainfall DON concentrations generated by Kjeldahl, UV, or oxidation methods, suggesting that concerns over different analytic methods may be overestimated.

The major uncertainty in DON concentrations comes from the TDN analysis and typically results in an underestimation of DON concentrations (Cornell et al., 2003). Cornell et al. (2003) found the precision and reproducibility of DON concentrations in rainwater improved as the DON / TDN ratio in samples increased. In samples with DON / TDN greater than 0.25, the percent standard deviation of DON concentrations was less than 25 % (Cornell et al., 2003). Approximately 70 % of the watersheds in our compiled dataset had DON / TDN ratios > 0.25, suggesting that the uncertainty in DON concentrations in our database should not dramatically alter our conclusions.

Effect of land use on regional DON and DIN losses – Our literature dataset of 119 watersheds indicates that DON concentrations were higher on average from developed watersheds than forested watersheds in the northeastern U.S. (Figure 4). Most forested watersheds in this study did not have wetlands, which may explain lower DON concentrations (as will be discussed in the following section). Combining the literature data with our Ipswich River watershed data shows that developed land use explains only a small percentage (27 %) of the variability in mean DON concentrations in northeastern U.S. rivers and streams. Although there was a general trend of increasing DIN concentrations with development in both the Ipswich River watersheds (Figure 2) and the literature data (Figure 4), the percentage of urban plus agricultural land was not a strong predictor of DIN concentrations ($r^2 = 0.35$, $p < 0.01$) or DON / TDN ($r^2 = 0.02$) at the regional scale. A multiple regression with agricultural and urban land use as separate cover types improves these relationships only slightly (data not shown).

There are several possible factors influencing our ability to predict DIN and therefore DON / TDN based on land use in our compiled dataset. These include: (1) data limitations, (2) use of a simple predictive model, (3) land use history, and (4) confounding land cover – land use relationships. Nearly 60 % of the watersheds in our literature dataset are entirely forested. The limited amount of published N data for developed watersheds in the northeastern U.S. likely contributes to the high standard deviation in DIN concentrations in the literature data (Figure 4). However, this observation also highlights the importance of our Ipswich River watershed data, which includes 39 watersheds influenced by human development.

Figure 4. Mean DON and DIN concentrations from watersheds in the northeastern U.S. based on the percentage of developed land use. Error bars are standard deviations. *n* = number of watersheds. See Table 1 for data references.



The use of a single land feature (percentage of developed land) to predict DIN concentrations is another challenge in our analysis. Caraco et al. (2003) found that a simple model based on population density failed to explain NO_3^- export for watersheds less than 100 km^2 in size. In contrast, they found that a simple loading model based on fertilizer, wastewater, and atmospheric inputs was a good predictor of NO_3^- export in watersheds ranging from 0.1 to over 1,000,000 km^2. For the Ipswich River sites, developed land use percentage is strongly correlated with population density (Wollheim et al., unpublished). In addition, our compiled dataset incorporates a wide range of watershed sizes and N inputs. Therefore, our simple model based on developed land use percentage may be inadequate at broad spatial scales. Quantifying N loads to watersheds in our compiled dataset may improve our ability to predict DIN concentrations and therefore DON / TDN at the broader scale, but is beyond the scope of this paper.

Data from forested watersheds in our study highlight the potential role of land use history on our ability to predict hydrologic N losses. While DON fluxes from forested watersheds are typically low, DIN fluxes are variable and may account for 0-100 % of atmospheric N inputs (Galloway et al., 2003). In our data, the DON / TDN ratio was particularly low in Catskill Mountain watersheds studied by Lovett et al. (2000), many of which show symptoms of N saturation (Aber et al., 1989). Although these sites receive high N deposition and lack wetlands, the authors attribute high streamwater NO_3^- concentrations (319 ± 119 $\mu g\ L^{-1}$) from many watersheds to forest species composition and forest history. Other forested watersheds in the northeastern U.S. generally have lower NO_3^- concentrations (104 ± 95 $\mu g\ L^{-1}$) and higher DON / TDN ratios despite differences in forest type, successional status, and atmospheric deposition (Campbell et al., 2000; Goodale, 2000; McHale et al., 2000; Clark et al., 2000; Campbell, 1996). Therefore, the role of land use history in determining hydrologic DIN losses is unclear, but we assume that our compiled dataset will allow for us to discern general land use trends without directly considering past land use.

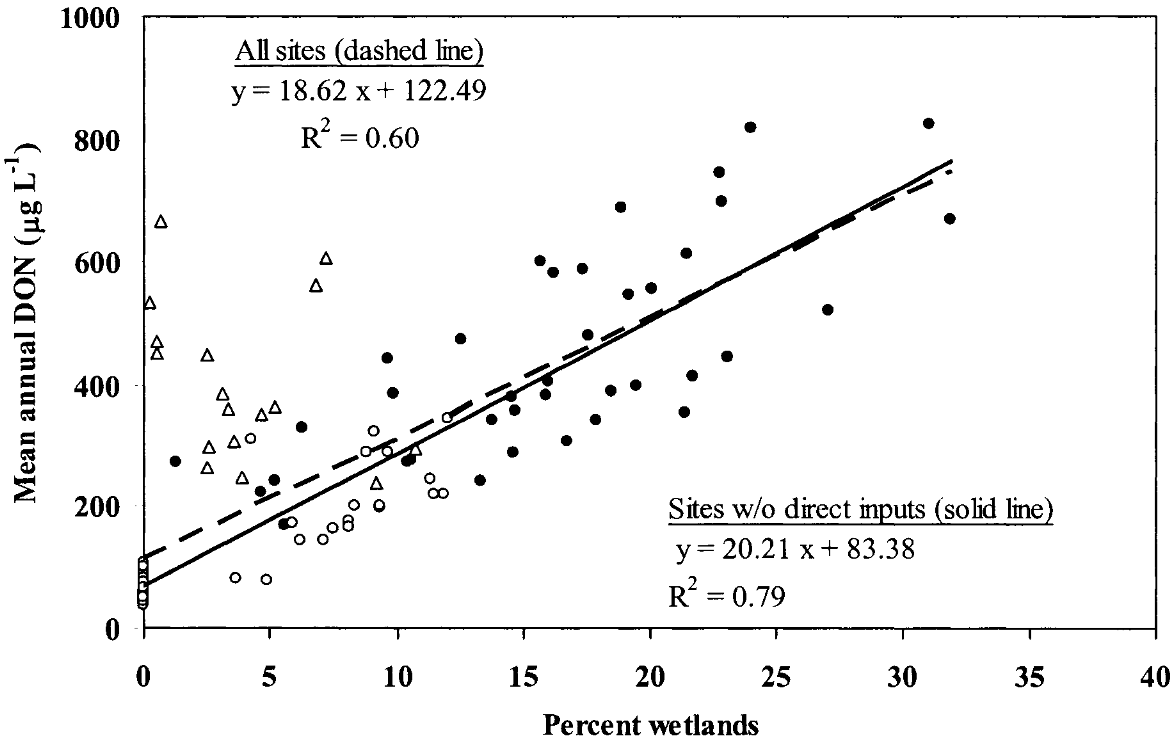
Interrelated land cover – land use relationships may also influence the interpretation of our DIN and DON values. Human development in the northeastern U.S. is concentrated in coastal lowlands, which are also typically characterized by low slopes and abundant wetlands. Although urbanization is historically associated with wetland loss, an analysis of the percentage of wetlands and population in the Gulf of Maine indicates that approximately 80 % of the population and 50 % of the wetlands are located within 100 km of the coast (data not shown). Wetlands act as both sources of DON and sinks of DIN, and may confound relationships between human development and N concentrations. However, these results indicate that in areas with significant urban development, DON may still be a large fraction of TDN losses due to the influence of wetlands on stream water chemistry.

<u>Effect of wetlands on regional DON losses</u> – Our literature dataset included 95 northeastern U.S. watersheds for which wetland data were available. Watersheds were 0-12 % wetlands, with many forested sites (n = 57) lacking wetlands. This limited range in wetland percentage also highlights the value of our Ipswich River data, which has 0-32 % wetlands in the sub-catchments studied. Despite challenges inherent in compiling datasets, our results indicate that the percentage of wetlands within a watershed explains a significant proportion ($r^2 = 0.60$, $p < 0.01$) of the variability in mean annual DON concentrations in drainage waters from forested and developed watersheds in the

northeastern U.S. (Figure 5). The observation that forested watersheds lacking wetlands had low streamwater DON concentrations (range = 39 – 127 $\mu g\ L^{-1}$) is particularly interesting. In a recent review, Aitkenhead-Peterson et al. (2003) reported mean DON concentrations of 1100 – 1560 $\mu g\ L^{-1}$ in organic soil solutions from cool deciduous and coniferous forests. The 1-2 order of magnitude reduction in DON concentrations between organic soil solution and stream water supports significant mineral soil adsorption in forested watersheds. In forested watersheds without wetlands, the transport of DON (and DOC) to streams therefore largely depends on shallow hydrologic flow paths through organic-rich soils during hydrologic events (Aitkenhead-Peterson et al., 2003).

Data used for this analysis also included 17 developed watersheds with direct anthropogenic N inputs to the rivers as human and animal wastewater (Boyer et al., 2002; Daley and McDowell, unpublished). We assume that entirely forested watersheds do not have significant wastewater inputs. Developed watersheds without direct wastewater inputs to the rivers either discharge wastewater via septic systems or discharge wastewater outside of the watershed. DON concentrations from the watersheds with direct wastewater inputs were typically higher than predicted by the wetland – DON relationship (open triangles, Figure 5), suggesting that wastewater represents a significant input of DON directly to some streams and rivers. The quantity of wastewater N inputs as estimated by Boyer et al. (2002) explained 74 % of the difference between wetland-predicted DON concentrations and measured DON concentrations at these sites (data not shown). The relationship between wetland percentages and mean annual DON concentration is strong (r^2 = 0.79) when sites with direct wastewater inputs are excluded

Figure 5. Percent wetlands versus mean streamwater DON concentrations (μg L^{-1}) in the northeastern U.S. Watersheds with direct human and animal wastewater inputs to rivers (Boyer et al., 2002; Daley and McDowell, unpubl.) are indicated by open triangles. Black circles represent our Ipswich River watershed data while open circles are literature data from watersheds without significant direct wastewater inputs (Campbell, 1996; Campbell et al., 2000; Goodale et al., 2000; Lovett et al., 2000; McHale et al., 2000; Daley and McDowell, unpubl.; Chalmers, 2002).



from our analysis. Adding the fraction of developed land use in a multiple regression explains little additional variability (Table 2), suggesting that wetlands are the primary landscape feature determining riverine and streamwater DON concentrations.

Extrapolating the slope of the DON-wetland relationship to a 100 % wetland watershed indicates that as a land use, wetlands contribute approximately 25 times more DON than other combined land uses. Seitzinger et al. (2002) reported that a substantially higher percentage of anthropogenically-derived DON was bioavailable to estuarine microbes as compared to agricultural- and forest-derived DON. Wetland-derived DON may be even less bioavailable than forest-derived DON, with only 8-15 % of the bulk DON from a wetland in Sweden taken up by estuarine bacteria (Stepanauskas et al., 1999). Therefore, additional research on the quantity and bioavailability of anthropogenic and wetland-derived DON is needed to better understand the current and future eutrophication of coastal waters.

CHAPTER 2

QUANTIFYING EVENT WATER CONTRIBUTIONS TO URBAN STORMFLOW USING ELECTRICAL CONDUCTIVITY AND ISOTOPIC TRACERS

Abstract

The relative contribution of surface and subsurface water to stormflow has received considerable attention in forested watersheds, but much less in urban watersheds. Here we quantify the role of surface (new) water and subsurface (pre-event) water to stormflow during 14 rainfall events in a 3.9-km^2 urban catchment. Two-component hydrograph separation was used with both isotopes (δD) and electrical conductivity (EC) as tracers. Comparison of results from one storm suggest that EC is a useful tracer in our urban catchment because of large differences in new and pre-event water EC (12-46 vs. 520-1297 μS/cm). Elevated discharge is largely composed of new water, with total precipitation volume describing 77 % of the variability in new runoff volumes for the range of events studied. Similar results during wet and dry periods suggests that saturation overland flow was not important during these events. New water accounted for 18-78 % of total streamflow, with differences between storms a function of new water mixing with a range of pre-event baseflow volumes rather than displacement of pre-event soil and groundwater. Results show that only about 5 % of the total precipitation volume runs off as new water, indicating that a large fraction of rainfall is either evaporated,

becomes groundwater recharge, or is exported from the watershed via the storm water infrastructure. The role of impervious surface runoff in groundwater recharge is not clear, but it may have implications for both the relative stormflow generation and long-term water quality.

Introduction

Quantifying the relative role of surface and subsurface flow paths to stormflow generation is critical for understanding the delivery of water and contaminants to surface waters. A number of studies in temperate forested watersheds have shown that subsurface discharge of soil and groundwater (e.g. pre-event water) dominates the hydrograph response to rainfall inputs (Burns, 2002; Genereux and Hooper, 1998). While urban development is known to increase peak and total stream runoff via increased imperviousness (Arnold and Gibbons, 1996), the relative importance of rapid surface runoff to stormflow generation is surprisingly unclear. For example, several studies have reported that pre-event water accounted for as much as 50-76 % of peak discharge during snowmelt or rainfall events in urbanizing catchments (Gremillion et al., 2000; Sidle and Lee, 1999; Buttle et al., 1995).

Understanding the contribution of direct surface runoff to streams is important because the short residence time along a surface flow path limits the abiotic and biotic retention of nutrients, sediments and other contaminants. While surface runoff in forested watersheds may result in the rapid runoff of atmospheric pollutants to streams, surface runoff in urban watersheds also results in the direct delivery other anthropogenic pollutants such as road runoff and domestic fertilizers to streams (Paul and Meyer, 2001;

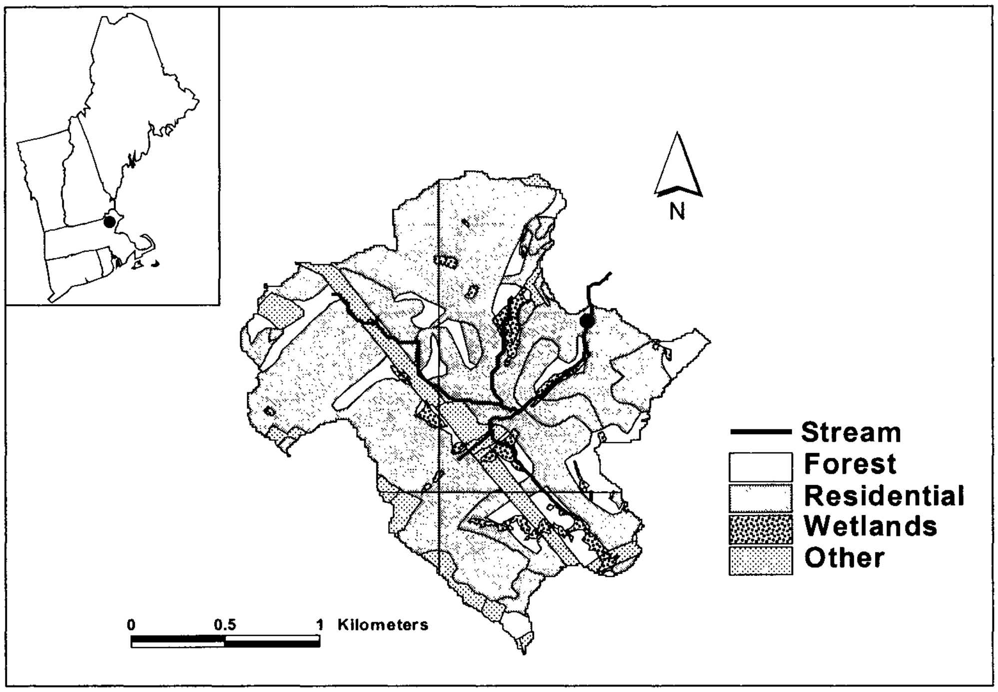
Arnold and Gibbons, 1996). Therefore, increased runoff along surface flow paths during events has a major impact on streamwater quality in urban watersheds where sources of pollutants are abundant and sinks may be bypassed. Increased surface flow paths may also reduce groundwater recharge, altering the role of riparian zones and ultimately leading to long-term declines in stream water quality (Groffman et al., 2004; Gremillion et al., 2002).

Chemical and isotopic hydrograph separation techniques have been used extensively in forested watersheds to determine the sources of stream runoff, but have received little attention in urban watersheds (Burns, 2002; Sidle, 1998; Buttle, 1994). Here we quantify the relative contribution of surface and subsurface water to stormflow generation in an urban catchment using two-component hydrograph separation. Stable water isotopes ($\delta^{18}O$ and δD) are generally recognized as the preferred tracers for hydrograph separation studies (Kendall and Caldwell, 1998), but their use in watershed-scale studies may be limited by high analytical costs and intensive sample preparation. We therefore supplement isotopic tracer data by using the electrical conductivity (EC) of water as an inexpensive, easily-measured alternative tracer for hydrograph separation. Urban watersheds may be ideally suited to EC-based hydrograph separation studies when (1) stream runoff during events is largely composed of two end-members (impervious surface runoff and groundwater discharge; Buttle, 1994; Rose, 2003), and (2) end-member EC values often differ significantly as a result of non-point source pollution of groundwater and soil water (Paul and Meyer, 2001). In addition, the use of EC as a tracer allows for the collection of high temporal resolution data for a larger number of storm events than is typically achievable using isotopes alone (Matsubayashi et al., 1993).

Although the use of EC as a hydrograph tracer in forested watersheds has been questioned due to its non-conservative nature (Laudon and Slaymaker, 1997), several studies comparing EC and isotope-based hydrograph separations have reported good agreement between the two tracers (Cey et al., 1998; Matsubayashi et al., 1993; McDonnell et al., 1991).

In this study, we present two-component hydrograph separation results for 14 rainfall events in a 3.9-km^2 urban watershed to evaluate the relative role of surface and subsurface flowpaths to stormflow. Our specific objectives were to: (1) quantify the volume and percentage of surface and subsurface discharge to stormflow, (2) validate the use and assumptions of EC as a tracer for urban hydrograph separation studies, and (3) evaluate the role of antecedent moisture conditions and precipitation characteristics on the variability in surface and subsurface runoff. In addition, we discuss the role of effective impervious surfaces in urban stormflow generation to better understand the implications of urbanization on event-based and long-term stream hydrology and chemistry.

Figure 1. Location and land use of the 3.9 km^2 study catchment. "Other" includes open land, agriculture, recreation, commercial and industrial.



Methods

Site Description - The study site (Saw Mill Brook) is a 3.9 km^2 headwater catchment located in the westernmost portion of the Ipswich River watershed (Figure 1). The Ipswich River watershed is one of three watersheds that drain into the Plum Island Sound estuary 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 land classified as high-density single-family lots (0.25-0.50 acres) based on 1:5000 orthophotography and 1:25000 aerial photography (MassGIS, 1999). The population density is 981 people km^{-2} with greater than 90 % of the population's wastewater exported out of the watershed via sewer systems. Smaller fractions of the watershed are in forest cover (14 %), agriculture (4 %), wetlands (4 %) and industrial / commercial (5 %) land uses. Total impervious area, as estimated by land use (Arnold and Gibbons, 1996), accounts for 25 % of the watershed area and includes transportation-related impervious areas (roads, parking lots, driveways) and rooftops. Watershed slopes are generally moderate (2-15 %) and 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, Massachusetts, both of which manage storm water via municipal separation storm sewer systems.

Sampling Method - Stream discharge and EC values (corrected for temperature) were measured at 15-minute intervals between August 2001 and November 2002 at the mouth of the Saw Mill Brook catchment using a YSI portable sensor probe with retrievable dataloggers (YSI, Inc., MA). Based on our dataset, we selected 13 storms with similar pre- and post-event EC and discharge values for further analysis (Table 1). Storm events during the winter and early spring were not selected because of the potential confounding influence of road deicing chemicals on EC values. One EC-based event (September 16-21, 2002) and one winter event (January 29-31, 2002) were also studied using deuterium isotope (δD) samples collected with a Sigma (American Sigma, Co.) autosampler at intervals ranging from 20 minutes on the rising limb to six hours at the end of the runoff event.

Bulk precipitation samples were collected within the watershed for the two δD events using 7.5-cm plastic funnel collectors attached to 1-L HDPE bottles and placed in an open location. Samples were measured for EC values in the field shortly after rainfall ended and later transported to the lab on ice for isotopic analysis. Precipitation EC values were estimated for the other events studied based on weekly samples collected at the National Atmospheric Deposition Program (NADP/NTN) monitoring location MA13 in Lexington, Massachusetts, approximately 7 km south / southwest of our study catchment. Comparison of our measured precipitation EC values and NADP weekly data suggests that differences in concentrations were small (≈ 4-30 μS/cm) and would have a negligible impact on hydrograph separation results. High temporal resolution data for precipitation volumes were recorded by the USGS at the gauging station in South Middleton, Massachusetts (station 01101500), approximately 14 km northeast of our study catchment. High temporal resolution data were validated against daily National Climatic Data Center (NCDC) precipitation data from Middleton and daily NADP data from Lexington and found to be comparable for most events.

Isotopic Analysis - Sub-samples of stream water and rainfall from two events were stored in 50-ml HDPE bottles with minimal headspace for analysis of naturally-occurring hydrogen (δD) isotopes. Analysis was conducted on a gas source mass spectrometer at the Stable Isotope Geochemistry Laboratory at Dartmouth College, Hanover, NH. Samples were reported in parts per thousand (‰) relative to VSMOW with an analytical precision of δD measurements of 0.5 ‰.

Hydrograph Separation - Hydrograph separation techniques were used to separate the relative contributions of pre-event or old water (stored soil and groundwater) and new water (precipitation and surface runoff) in our study. We used a two-component mass balance model to calculate the time varying sources of runoff via the following equations:

$$Q_s = Q_p + Q_n \quad (1)$$

$$Q_sC_s = Q_pC_p + Q_nC_n \quad (2)$$

$$Q_p = Q_s\,[(C_n - C_s)/(C_n - C_p)] \quad (3)$$

where Q is discharge, C is the tracer concentration (EC or δD), and s, p and n stand for stream water, pre-event water and new water. The use of a two-component model requires several simplifying assumptions that have received considerable attention in the literature (Buttle, 1994) and are further discussed in this paper.

Uncertainty Analysis - Uncertainty in the EC-based two-component hydrograph separation results were estimated according to Genereux (1998):

$$W_{fp} = \{[f_p/(C_n-C_p)*W_{cp}]^2 + [f_n/(C_n-C_p)*W_{cn}]^2 + [-1/(C_n-C_p)*W_{cs}]^2\}^{0.5} \quad (4)$$

where n = new water, p = pre-event water, s = stream water, W = uncertainty value at the 80^{th} percentile, f = the fraction of n, p and s, and C = the tracer concentration in n and p.

The EC value of pre-event baseflow was used as an integrated measure of the soil and groundwater end-member signature. While the 24-hour EC standard deviation was ≈ 2-4 % of baseflow EC values, we assumed a higher estimate (10 % of baseflow EC) to account for additional unmeasured spatial and temporal variability. New water EC values were estimated from bulk precipitation values measured at the NADP station in Lexington, MA (Table 1) with an assumed standard deviation of 10 μS/cm to account for temporal variability during events. We also assumed $n = 3$ in order to estimate the W_{ce} (e.g. standard deviation x student t-value), but results were relatively insensitive to the number of samples. The uncertainty in stream water values during the event (W_{cs}) was calculated using the analytical uncertainty in EC measurements (0.5 % of stream EC ± 1.0 μS/cm; YSI, Inc.).

Results

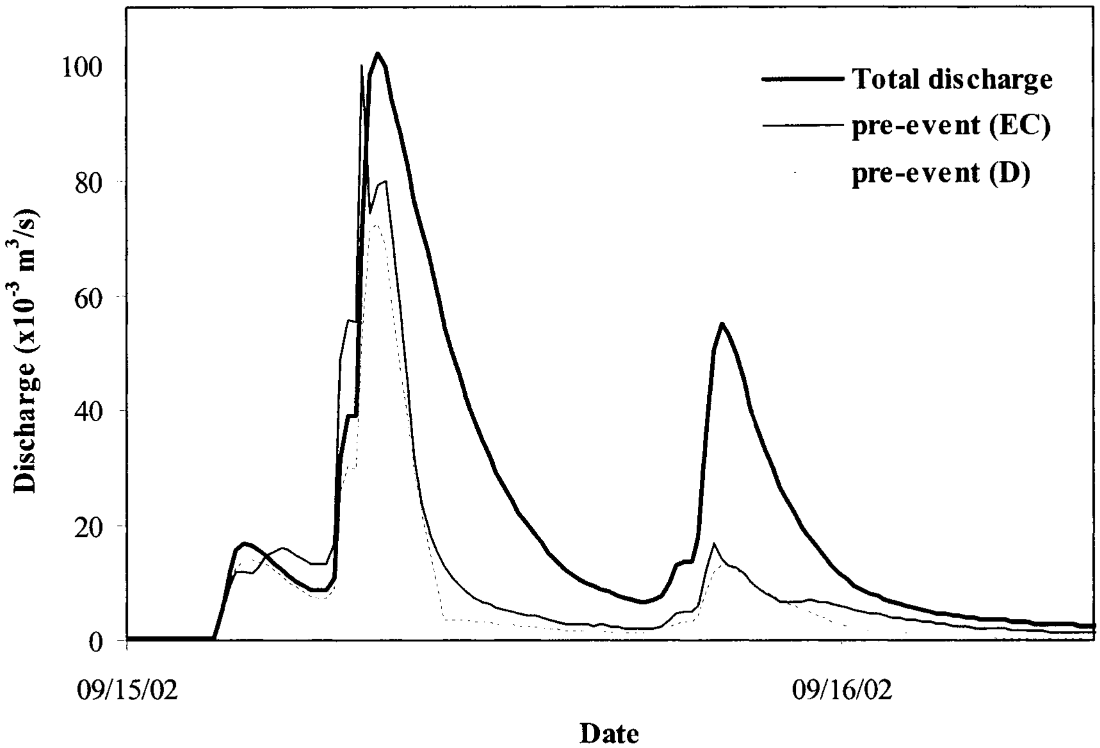
Comparison of Tracers (δD and EC) - Similar temporal patterns in new water contributions are calculated using both δD and EC as hydrograph separation tracers during the September 16-21, 2002 event (Figure 2). The first flush of solutes results in an overestimate of the pre-event water contribution to stormflow and hence differences in the percentage of new water for the event (65 % for δD vs. 48 % for EC). The fraction of peak discharge composed of new water is similar using both tracers (29 and 22 %) as the first flush occurs prior to peak flow. Accounting for the first flush by linear interpolation between pre- and post-flush EC values results in new water volumes of 0.05 cm for δ D (65 % new water) and 0.04 cm for EC (64 % new water).

Table 1. Rainfall characteristics, antecedent discharge, and end-member EC concentrations for 14 precipitation events. * indicates storms with δD isotope data.

Event Dates	Rainfall EC (μS/cm)	Pre-Event EC (μS/cm)	Antecedent Discharge (x 10^{-3} m^3/s)	Ant. 5-day Rainfall (cm)	Total Rainfall (cm)	Max 1-hr Rainfall (cm)
Aug. 12-16, 2001	21	636	14.8	2.5	4.6	0.6
Sept. 21-24, 2001	14	1297	3.7	0.0	2.0	0.3
Jan. 29-31, 2002*	na	na	11.6	0.3	0.6	0.3
April 22-24, 2002	27	633	28.3	0.1	0.5	0.2
May 2-5, 2002	27	520	39.7	2.4	1.2	0.3
June 12-13, 2002	32	564	31.5	1.9	0.5	0.4
June 15-16, 2002	32	587	28.9	0.8	2.7	0.5
July 9-11, 2002	38	1151	4.1	1.8	1.0	0.3
July 23-27, 2002	46	1241	2.0	1.0	2.1	0.7
Aug. 2-5, 2002	27	1274	0.7	0.3	0.2	0.2
Aug. 29-31, 2002	15	667	0.1	1.6	2.4	0.3
Sept. 16-21, 2002*	14	1256	0.2	0.0	0.9	0.3
Sept. 26-Oct. 4, 2002	12	1259	4.1	3.3	1.6	0.4
Oct. 16-18, 2002	25	883	7.3	1.8	3.2	0.7

* Storms with δD data. January 2002: rainfall δD = -18.6 ‰, pre-event δD = -52.1 ‰; September 2002: rainfall δD = -68.5 ‰, pre-event δD = -40.4 ‰.

Figure 2. Total discharge and pre-event discharge using both EC and deuterium (δD) tracers for hydrograph separation (September 15-21, 2002 event).



EC-Based Hydrograph Separation - The 14 events studied had low-to-moderate total rainfall depths (0.23 – 4.57 cm) (Table 1). Differences in antecedent discharge conditions (0.05 – 39.65 x 10^{-3} m^3/s) and antecedent 5-day precipitation (0 – 3.3 cm) suggest differences in antecedent watershed moisture conditions for the 14 events. Total stream runoff depths ranged from 0.07 – 0.60 cm for the individual events (Table 2) and corresponded to rainfall-runoff ratios (e.g. total runoff / precipitation) of 0.05 – 0.37. Total annual runoff during roughly the same period (2001-2002 water year) accounted for approximately 28 % of rainfall at this site (data not shown).

Hydrograph separation results indicate that the percentage of new water ranged from 18-78 % (median = 58 %) of total discharge. New water accounted for 50-78 % of total flow during low antecedent discharge events ($< 5 \times 10^{-3}$ m^3/s), indicating that most elevated discharge was new water in these events (Figure 3). In contrast, new water was a smaller fraction (18-50 %) of total stream discharge during events with higher antecedent baseflow (Figure 4). The antecedent stream discharge explained 65 % of the variability in new water percentages across the range of events at this site ($p < 0.01$; Figure 5). At peak discharge, the percentage of new water ranged from 5-97 % (median = 78 %) and was best explained by a multiple regression with antecedent discharge and the total precipitation depth ($r^2 = 0.73$, $p < 0.01$; Figure 6). The depth of new water runoff ranged from 0.02-0.30 cm (mean = 0.09 cm) was largely determined by the amount of total precipitation during the event ($r^2 = 0.77$, $p < 0.01$) (Figure 7). Included the antecedent 5-day precipitation depth with the total precipitation depth in a multiple regression improved the r^2 but only slightly ($r^2 = 0.81$). One high precipitation event (August 12-16, 2001) is partly responsible for the high r^2 in new runoff volumes and the relationship between new water depth and total precipitation decreases to 0.57 ($p < 0.01$) when this point is excluded from the multiple-regression. New water runoff volume ranged from 4-11 % of total precipitation in 13 of 14 events, with one higher event (19 % on August 2-5, 2002 event) potentially due to high uncertainty (based on the percent error) during very low precipitation volume precipitation events (e.g. 0.23 cm).

Table 2. Two-component hydrograph separation results for 14 storms events. * indicates storms with δD isotope data.

Event Dates	Total Runoff (cm)	New Water Runoff (cm)	New Water (%)	Uncertainty (%)	New at Peak (%)	New Water/ Rainfall
Aug. 12-16, 2001	0.60	0.30	51	5	97	7
Sept. 21-24, 2001	0.17	0.12	68	2	90	6
Jan. 29-31, 2002*	0.07	0.02	34	na	25	4
April 22-24, 2002	0.17	0.03	18	9	5	7
May 2-5, 2002	0.40	0.14	34	7	46	11
June 12-13, 2002	0.10	0.03	27	8	27	5
June 15-16, 2002	0.19	0.10	50	4	73	4
July 9-11, 2002	0.07	0.05	72	1	83	5
July 23-27, 2002	0.11	0.09	78	1	91	4
Aug. 2-5, 2002	0.06	0.04	71	2	68	19
Aug. 29-31, 2002	0.13	0.09	74	1	84	4
Sept. 16-21, 2002*	0.07	0.04	64	2	60	5
Sept. 26-Oct. 4, 2002	0.25	0.13	52	5	83	8
Oct. 16-18, 2002	0.25	0.16	64	3	92	5

Figure 3. Total discharge and old (pre-event) water discharge for eight events with antecedent discharge < 10 x 10^{-3} m^3/s. Only events with EC as a tracer are shown.

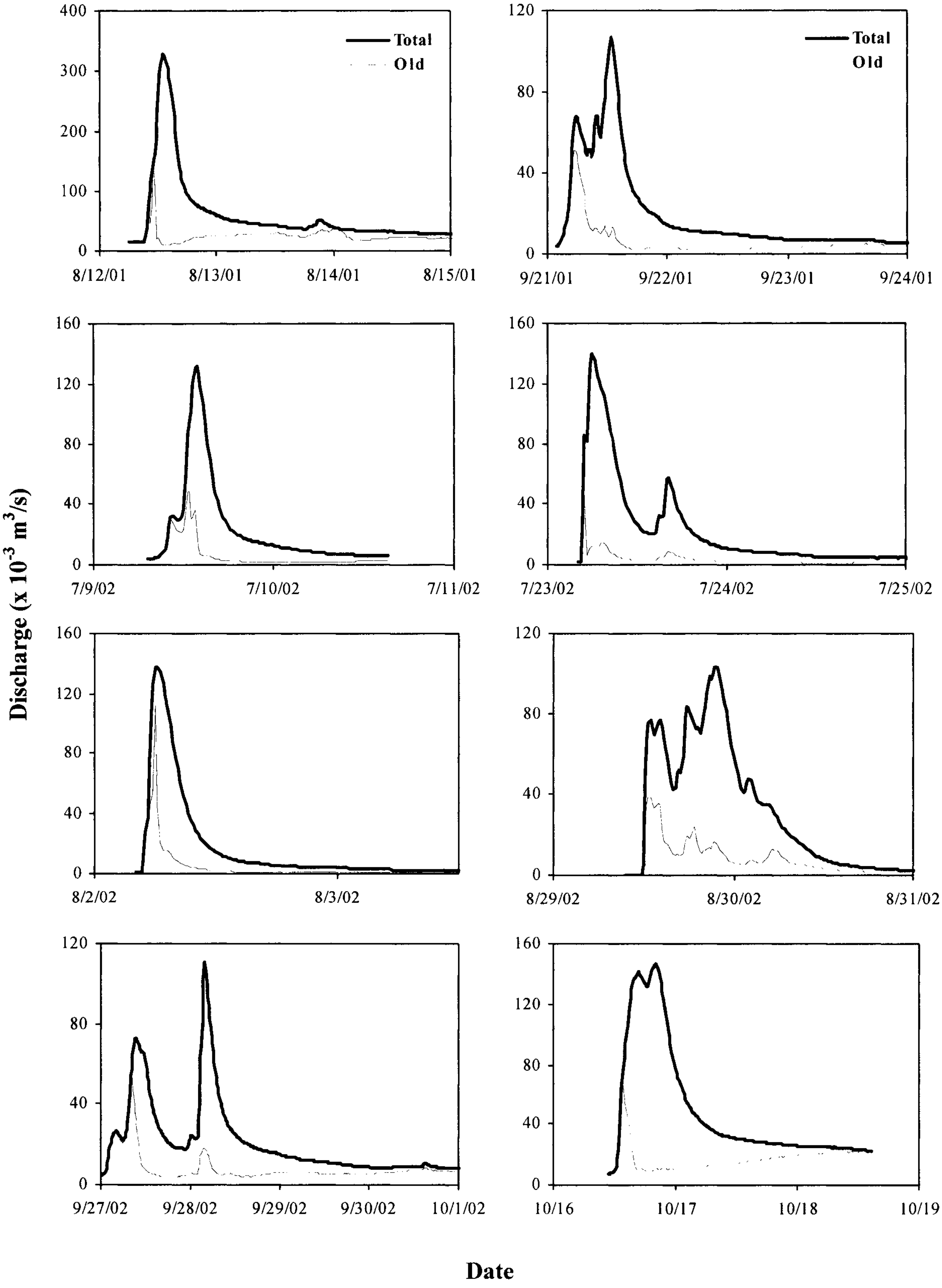


Figure 4. Total discharge and old (pre-event) water discharge for four events with antecedent discharge > 10 x 10^{-3} m^3/s. Only events with EC as a tracer are shown.

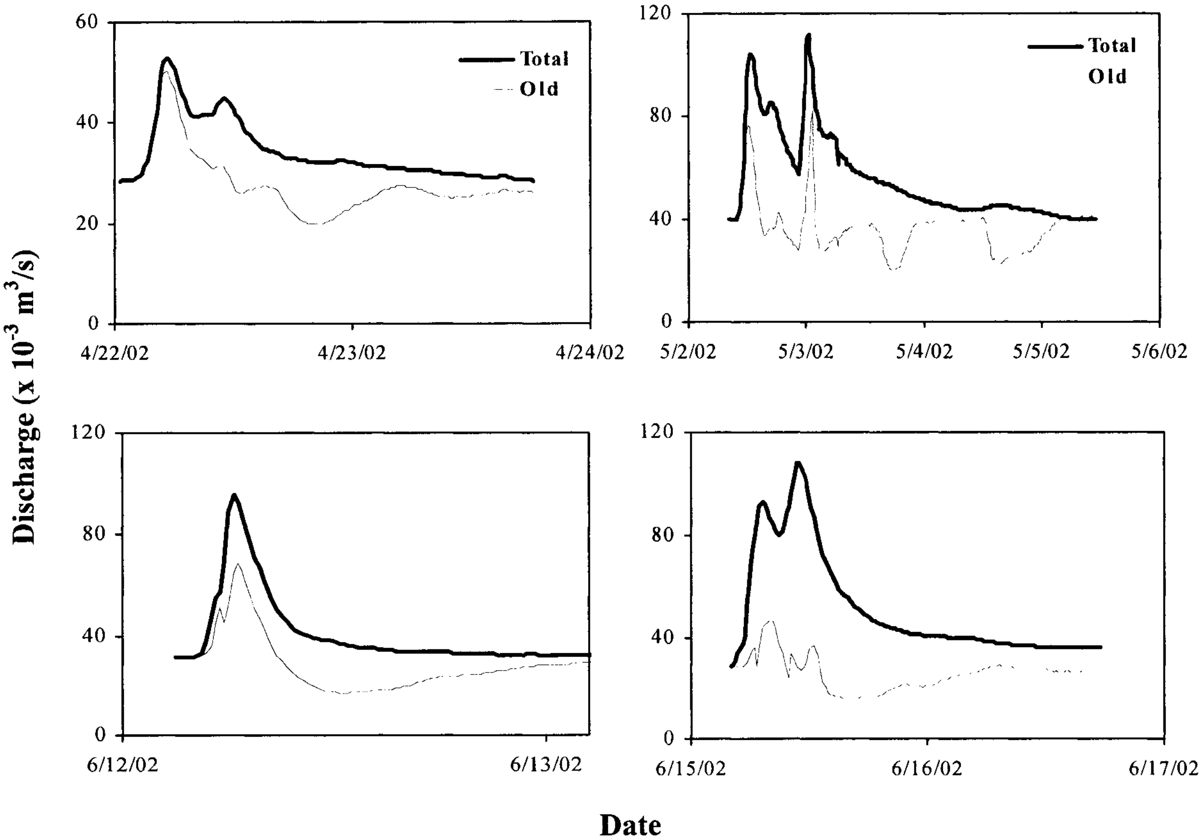


Figure 5. The percentage of new water (based on EC and δD) versus antecedent discharge (x 10^{-3} m^3/s) for the 14 rainfall events in our study. Error bars are uncertainty estimates at the 80^{th} percentile confidence interval.

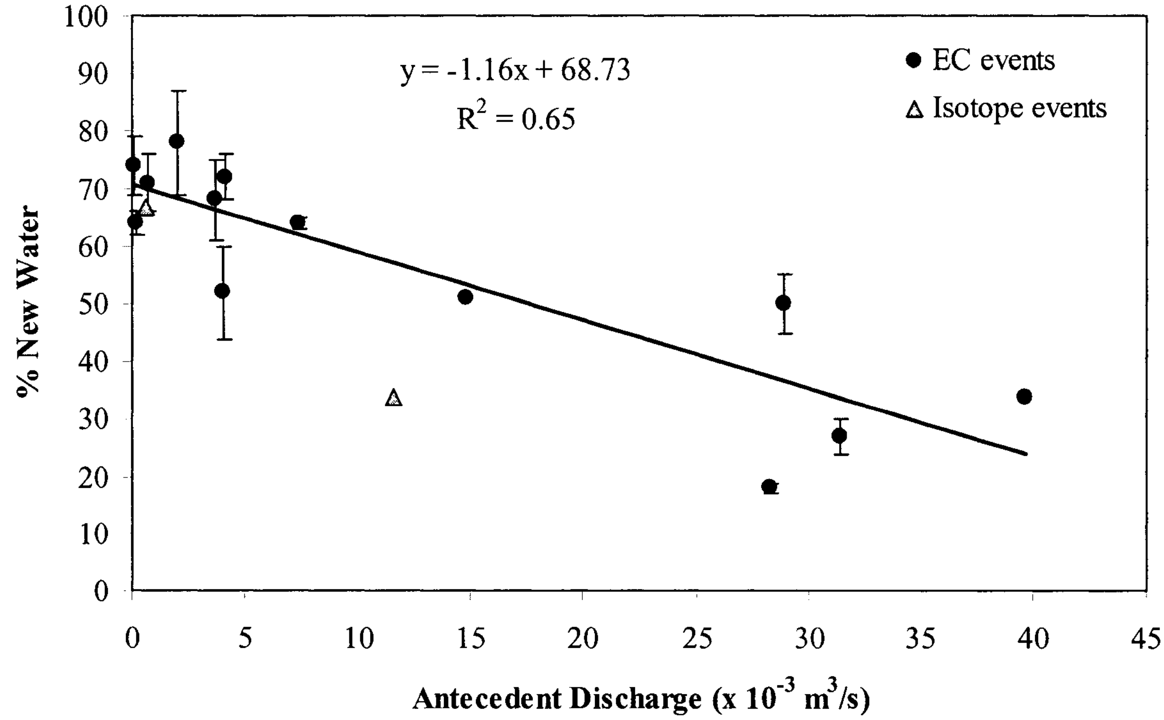


Figure 6. The percentage of new water at peak discharge versus the total precipitation volume (cm) for the 14 events studied. Low antecedent discharge for these events is < 10 x 10^{-3} m^3/s, high antecedent discharge is > 10 x 10^{-3} m^3/s.

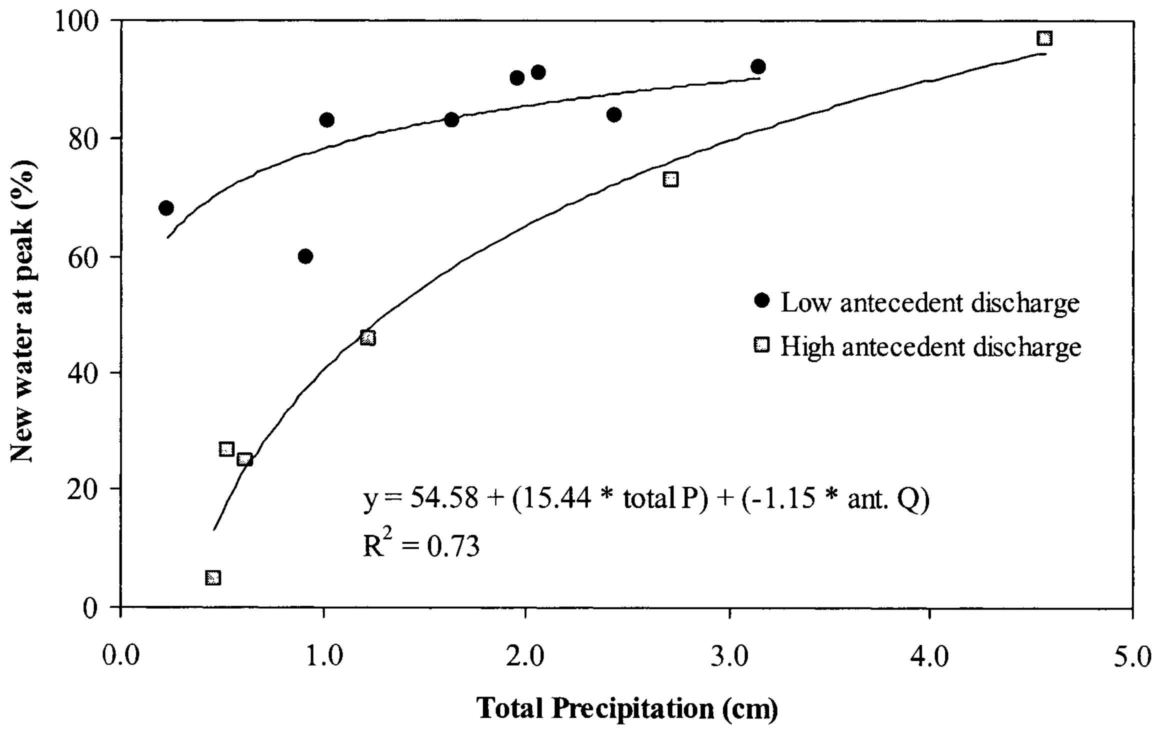
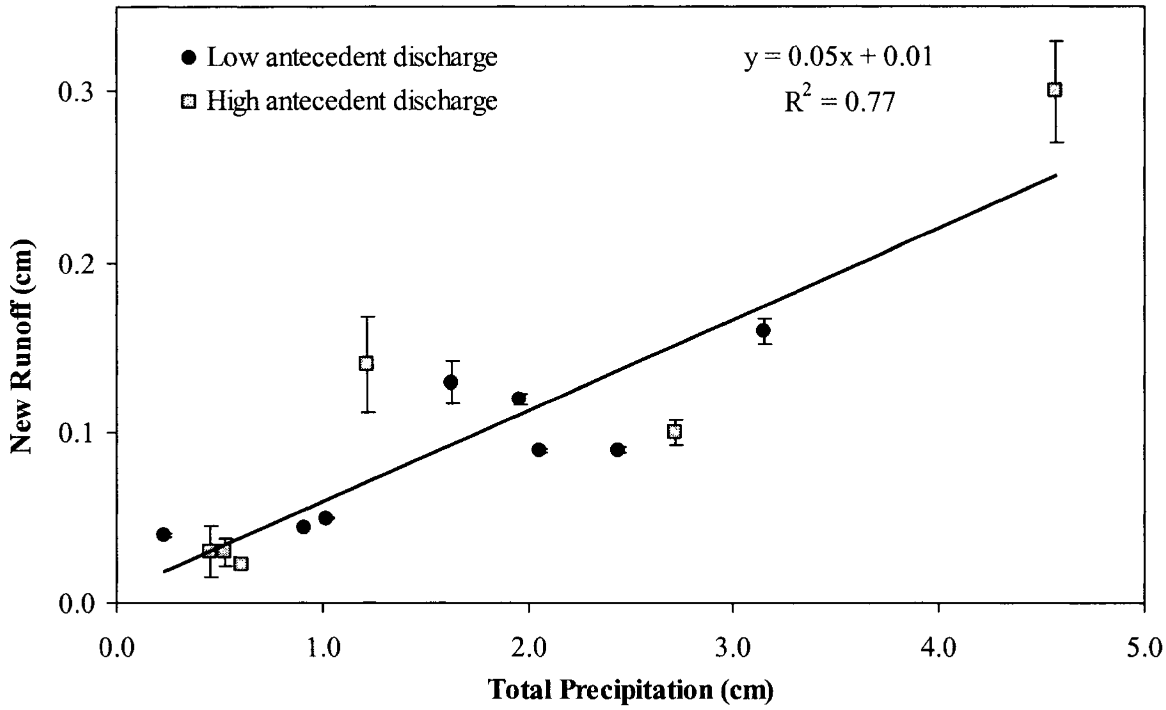


Figure 7. The volume of new water runoff (cm) versus the total precipitation volume (cm) for low (< 10 x 10^{-3} m^3/s) and high (> 10 x 10^{-3} m^3/s) antecedent discharge events.



<u>Uncertainty analysis</u> - The uncertainty associated with hydrograph separation was calculated according to Genereux (1998) for all events using EC as a tracer. Several assumptions were made in the absence of extensive temporal or spatial data and we therefore view the absolute uncertainty values with caution. However, these values represent our best estimates and provide additional detail about the hydrograph separation results. Precipitation EC values ranged from 12-46 μS/cm (mean = 27 μS/cm), 1-2 orders of magnitude lower than antecedent stream baseflow EC values (520 – 1297 uS/cm; Table 1). Estimates of uncertainty at the 80th percentile (approximately 1 SD) ranged from ± 1 to ± 9 %, with greater than 5 % uncertainty in only three high antecedent discharge events (Table 2). Uncertainty estimates in our study are generally not sensitive

to assumptions about temporal variability in precipitation EC values, the number of precipitation samples collected during an event or the assumption that weekly NADP precipitation EC values are representative of individual events (data not shown). Uncertainty estimates are sensitive to the pre-event standard deviation and values greater than 10 % of pre-event EC values would increase the calculated uncertainty for these events.

Assumptions of EC-based two-component hydrograph separation - There are several assumptions inherent in the use of hydrograph separation techniques (Sklash and Farvolden, 1979). Violation of these assumptions has been discussed in the literature (Buttle, 1994) and may affect the interpretation of results. Here we address the following assumptions of EC-based two-component hydrograph separation:

(1) EC values in new and old water differs significantly,

(2) 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).

The acceptable difference in event and pre-event water tracer concentrations is determined by the amount of uncertainty that a researcher is willing to accept in the hydrograph separation (Genereux and Hooper, 1998). The large difference between precipitation EC values (12-46 μS/cm) and pre-event streamwater EC values (520-1297 μS/cm) results in uncertainty estimates in the fraction of new water of ± 1-9 %, with most events in the range of ± 1-5 % (Table 2). As noted by Buttle (1994), an uncertainty of ±

10 % in the relative contribution of end-members is generally not enough error to compromise the essential findings of the hydrograph separation. Our uncertainty estimates therefore suggest that assumption (1) is not violated in our study.

Elevated stream EC values are common in urban watersheds due to non-point source contamination of groundwater, soil water, and streams (Paul and Meyer, 2001). Urban sub-catchments within the Ipswich River watershed typically have baseflow EC values greater than 400 μS/cm (data not shown). In contrast, annual baseflow EC values in a number of forested watersheds in the northeastern U.S. were only 14 – 120 μS/cm (mean = 41 μS/cm, n = 16; USGS Hydrologic Benchmark Network). Studies in other forested watersheds often report differences of < 50 μS/cm between precipitation and stream baseflow EC values (Laudon and Slaymaker, 1997; Matsubayashi et al., 1993; McDonnell et al., 1991), indicating that using EC as a tracer in forested watersheds may result in high uncertainty.

Many studies use the isotopic or geochemical signature of antecedent baseflow to characterize the pre-event water because addressing the spatial and temporal variability (assumption 2) is often not feasible at the watershed scale (Renshaw et a., 2003; Buttle et al., 1995; Nolan and Hill, 1990). This may be particularly appropriate in urban watersheds where (1) groundwater chemistry may be spatially variable due to localized recharge and (2) logistical constraints in establishing and sampling a dense network of groundwater wells may be significant (Buttle et al., 1995). While the measured variability in EC value during 24-hour baseflow periods was typically ≈ 2-4 % of stream baseflow EC values, we assumed a groundwater standard deviation equal to 10 % of stream EC values (52-130 μS/cm) in our analysis and therefore account for some unmeasured variability with our uncertainty estimates.

The use of precipitation chemistry to characterize new water inputs assumes that throughfall-enrichment of rapid runoff water is negligible. In urban catchments, the rapid delivery of throughfall to streams is probably minimal relative to runoff from impervious surfaces (Buttle et al., 1995). Doubling the measured precipitation EC values and increasing the standard deviation to 100 % to account for enrichment results in only modest increases (± 1-3 %) in uncertainty estimates in our study, suggesting that throughfall-enrichment would not significantly change our results.

The "first flush" of solutes from impervious surface runoff also represents a source of variability when using chemical hydrograph tracers in urban watersheds. In our study, the increase in stream EC values from the first flush is generally short-lived (< 1 hour) and typically occurs prior to peak discharge (Figure 2). We removed the first flush effect from the events studied by linearly interpolating between pre- and post-flush EC values. However, leaving in the first flush results in overestimates of pre-event water contributions of 1-6 % for most storms but higher overestimates (11 and 16 %) during the two lowest antecedent discharge events (data not shown). While the "first flush" has little impact on our hydrograph separations for most storms, the rapid deliver of nutrients, metals and sediments from impervious surfaces may be significant for stream biota and long-term water quality (Brabec et al., 2002). The high temporal resolution of EC measurements highlight their potential use in identifying the timing and magnitude of the first flush in urban watersheds, but is not discussed in this paper.

The potential role of soil water in stormflow generation was not specifically evaluated for this catchment (assumption 3), but inferences from EC-discharge hysteresis loops in our study suggest that stormflow is dominated by two components, groundwater and surface runoff (C3 loop as described by Evans and Davies, 1998; Rose, 2003). Since soil water samples had relatively low EC values when sampled (30-120 μS/cm), significant soil water contributions to stormflow would result in an overestimate of new water. The contribution of soil water is unlikely during low-intensity, low-volume precipitation events in drier periods (Nolan and Hill, 1990), an assumption supported by a general lack of soil water in lysimeters during summer months (personal observation). Buttle and Peters (1997) reported that pre-event soil water silica concentrations were spatially and temporally variable in a forested watershed, and others have noted the potential variability in soil water EC values with changes in soil contact time (Matsubayashi et al., 1993; Pilgrim et al., 1979). While variability within the measured range of soil water EC values in our study would not change our results, hydrograph separation during spring events suggests that soil water contributions may result in overestimates of new water contributions (Figure 4). The use of only one tracer precludes us from identifying the contribution of a third end-member to stormflow during spring storm events. However, assuming that ≈ 30 % of elevated discharge was composed of soil water during the highest antecedent discharge event only decreases the new water contribution from 0.14 to 0.10 cm. While this has little impact on the ratio of new water / precipitation (11 vs. 8 %), the role of soil water contributions during high antecedent moisture periods in urban watersheds deserves further attention.

Discussion

Event Water Contributions to Urban Stormflow - Two-component hydrograph separation indicates that elevated discharge is largely composed of new water during the 14 storms studied in our urban catchment (Figures 2 and 3). Since the stream channel occupies about 1 % of the watershed area at our site, new water is presumably delivered via overland flow to streams (Arnold and Gibbons, 1996). Hortonian overland flow is rarely evoked as a significant mechanism of new water delivery to streams in forested watersheds (Burns, 2002; Genereux and Hooper, 1998), with direct channel precipitation (Renshaw et al., 2003) and overland flow from near-stream saturated zones (Shanley et al., 2002; Waddington et al., 1993) typically cited as sources of new water. The importance of macropore flow for new water delivery to streams in forested watersheds is unclear (Renshaw et al., 2003; Buttle, 1994; McDonnell et al., 1990) and we assume it represents a minor contribution to streamflow in our urban catchment during the events studied.

While overland flow from near-stream saturated zones cannot be ruled out as a possible source of new water in our study catchment, evidence suggests that new water runoff is probably generated as Hortonian overland flow from impervious surfaces such as roads and parking lots. First, new water runoff volumes during high and low antecedent discharge periods were similar (Figure 7), whereas higher new water volumes would be expected if saturated pervious surfaces were generating surface runoff (Eshleman et al., 1993) or soil water contributions to stormflow were significant (Buttle, 1994). In addition, EC data indicate a first flush of solutes commonly reported from impervious surfaces runoff in urban watersheds (Sansalone and Buchberger, 1997). Our isotopic and EC-based separation results show that changes in water composition lag behind changes in discharge (Figures 3 and 4), as indicate by increasing discharge composed largely of old water at the beginning of events. Nolan and Hill (1990) attributed this phenomenon to flood waves of pre-event channel water displaced by rapid new water runoff from localized impervious surfaces.

<u>Variability in Event Water Contributions</u> - The role of precipitation characteristics and antecedent moisture on stormflow generation has been difficult to interpret because hydrograph separation studies typically sample only a few events per catchment. The application of EC tracer allows for an assessment of a larger number of events because EC measurements are inexpensive and can be recorded continuously. Our results indicate that the volume of new runoff is largely dependent on the total precipitation depth (Figure 7) with no apparent differences in new water runoff during wet and dry periods. This suggests that precipitation volume is more important than antecedent moisture conditions in our urban watershed, presumably as a result of impervious surfaces diverting a uniform fraction ($\approx$ 5 %) of rainfall directly to streams (Brown, 1988). Therefore, a reduction in the relative importance of this saturation overland flow throughout much of the year (Dunne and Black, 1970; Eshleman et al., 1993) could be a ubiquitous yet seldom articulated feature of many urbanizing catchments.

The percentage of new water percentages (as a fraction of total discharge) for individual storms at our site was largely dependent on the volume of antecedent discharge (Figure 5). During low flow periods, 60-80 % of total discharge and therefore most elevated discharge was composed of new water. This is in contrast to forested watersheds, where pre-event soil and groundwater typically account for about 70 % of the total and peak stream discharge during rainfall events (Genereux and Hooper, 1998; Buttle et al., 1995). While mechanisms describing the delivery of pre-event water to streams in forested watersheds are fairly well understood, the reasons for high pre-event water contributions in some urban hydrograph separation studies are not clear (Gremillion et al., 2000; Sidle and Lee, 1999; Buttle et al., 1995). A physical mechanism of increased hydraulic gradient and displacement of pre-event soil and groundwater similar to that in forested watersheds may be important in urban watersheds with significant pervious area, rapid soil infiltration and a shallow water table (Gremillion et al., 2000; Sidle and Lee, 1999).

In our study, we found that new water accounts for < 50 % of streamflow during some events due to mixing with a large volume of pre-event baseflow (Figure 5) rather than an apparent increase of groundwater discharge as described in forested watersheds. However, the role of pre-event soil water displacement may be important during higher antecedent moisture conditions. In addition, we have not evaluated the presence of flood waves with hydrometric measurements and therefore cannot eliminate rapid displacement of near-stream pre-event water as a source of increased pre-event discharge during the initial stages of the events studied.

Estimating the Effective Impervious Area from Hydrograph Separation - Assuming that new water inputs in the stream are from impervious surface runoff only, our hydrograph separation results indicate that $\approx$ 16 - 44 % of the total impervious area in our study catchment contributes runoff directly to the stream during most storms (Table 2). This highlights the distinction between the total impervious area (TIA) and the hydrologically-connected or *effective* impervious area (EIA) in urban watersheds. Other studies in urban watersheds have found that runoff-contributing areas may be less than the total impervious areas, with total runoff typically between 40 and 75 % of estimated rainfall onto impervious surfaces (Taylor, 1977; Ku et al., 1992; Booth and Jackson, 1997; Brun and Band, 2000). One outlier in our study (19 % new water on August 2-5, 2002) had very low rainfall depths and was therefore particularly sensitive to localized differences in precipitation. However, the ratio of new water runoff / precipitation was generally not sensitive to differences in precipitation volumes, with precipitation from a different rain gage (NCDC, Middleton) resulting in differences of –1 to 2 % in 12 of 14 events studied (data not shown).

Because of difficulty in measuring the EIA, many field and modeling studies use the TIA to estimate impervious surface runoff volumes (Lee and Heaney, 2003; Brabec et al., 2002; Jennings and Jarnagin, 2002). In contrast, some studies have used reported site-specific relationships between the EIA and either TIA or land use categories to estimate the contributing impervious area (Booth and Jackson, 1997; Alley and Veenhuis, 1983). These values provide a better estimate of impervious surface runoff than TIA, but local differences in watershed drainage may preclude their widespread application. For example, Zariello and Reis (2000) found that estimates of EIA calibrated to summer rainfall events were 20-50 % lower than estimates based on published land use relationships.

Quantifying the ultimate fate of rainfall in a complex urban watershed is beyond the scope of this paper. However, our results suggest that about 70 % of rainfall onto impervious surfaces evaporates, runs off to pervious surfaces, and / or enters the storm drainage infrastructure to become groundwater recharge or export from the watershed. High groundwater recharge rates could help reconcile the dominance of pre-event water in urban watersheds by maintaining an elevated water table and enhancing the displacement of pre-event water during precipitation events. In addition, the import of water to urban watersheds and discharge via septic systems could be an important unmeasured source of groundwater recharge (Lerner, 2002). The dominance of new water in stormflow generation at our site does not support a mechanism of high groundwater recharge and elevated pre-event discharge in urban watersheds. Understanding the contribution of impervious surface runoff to stormflow generation and groundwater recharge in urban catchments has potentially significant long-term implications for watershed hydrology and water quality and therefore deserves further attention.

CHAPTER 3

WATERSHED-SCALE ATTRIBUTES INFLUENCING STREAM NUTRIENT CONCENTRATIONS ACROSS A RURAL-TO-URBAN LAND USE GRADIENT

Abstract

Few studies of urbanization evaluate factors influencing stream nitrogen (N) and phosphorus (P) concentrations in watersheds largely influenced by non-point source inputs. Here, we compare aggregate parameters that integrate urban attributes (population density, percent residential), watershed-scale attributes influenced by urbanization (percent wetlands, percent impervious, percent forest, septic and sewer density) and inorganic N and P concentrations in 23 headwater catchments across a rural-to-urban gradient in Massachusetts. Our results indicate that watershed-scale attributes are particularly variable at intermediate levels of urbanization as defined by population density (e.g. 100-620 people / km^2). Mean annual stream P (as PO_4) concentrations are not significantly correlated with population density, while nitrate (NO_3) and ammonium (NH_4) are weakly correlated (r^2 = 0.27 and 0.22) across the gradient. The percentage of residential land describes a significant fraction of NO_3 variability both across the gradient and between suburban watersheds (r^2 = 0.52 and 0.70). However, water quality management requires an understanding of specific mechanisms influencing stream chemistry. A multiple regression using both the percentage of wetlands plus open water and septic density explains 51 and 73 % of the variability in NO_3 concentrations across

the gradient and within suburban watersheds, respectively, and highlights the potential role of septic wastewater and wetlands as mechanisms (N sources and sinks, respectively). Isotopic data ($\delta^{15}N$-NO_3) supports the potential role of wastewater as the dominant source of NO_3 in suburban watersheds, but also suggests wastewater as an important source of N in urban watersheds (> 620 people / km^2). Identifying the non-point sources and sinks in urbanizing watersheds will likely become increasingly important as land use change continues and point source pollutants are more strictly managed.

Introduction

The conversion of natural and agricultural land to suburban and urban landscapes is the major current land cover change in the U.S. (Hasse and Lathrop, 2003; McDonnell et al., 1997). Urbanization results in a number of watershed alterations including changes in wetland abundance (Groffman et al., 2002), point and non-point source wastewater inputs (Howarth et al., 1996; Bowen and Valiela, 2001), urban fertilizer use (Groffman et al., 2004) and increased impervious surface runoff (Taylor et al., 2004). Significant impacts on stream hydrology, geomorphology, aquatic biota and water quality have also been reported as a result of land use change (Paul and Meyer, 2001).

Increased nitrogen (N) and phosphorus (P) flux is of particular concern for coastal eutrophication, which reduces aquatic biodiversity, increases toxic algal blooms, and may lead to fish kills (Carpenter et al., 1998). Several studies have attributed increased N and P fluxes in streams, rivers and estuaries to urbanization (Paul and Meyer, 2001; Roman et al., 2000). The role of urbanization has been difficult to interpret, however, since many studies are in watersheds dominated by agriculture (Jordan et al., 1997; Herlihy et al., 1998; Tufford et al., 1998; Wernick et al., 1998; Miller et al., 1997; Osborne and Wiley, 1988; Omernik et al., 1981). In addition, the role of point source inputs may mask the signal of non-point source urban land use (Castillo et al., 2000). For example, Caraco and Cole (1999) found that direct human wastewater inputs, agricultural fertilizer use, and atmospheric deposition explained a large fraction of the variability in NO_3 flux from large river basins globally. Urbanization results in a number of non-point sources of N and P such as septic systems and lawn fertilizers, but these sources are often difficult to measure and regulate (Carpenter et al., 1998).

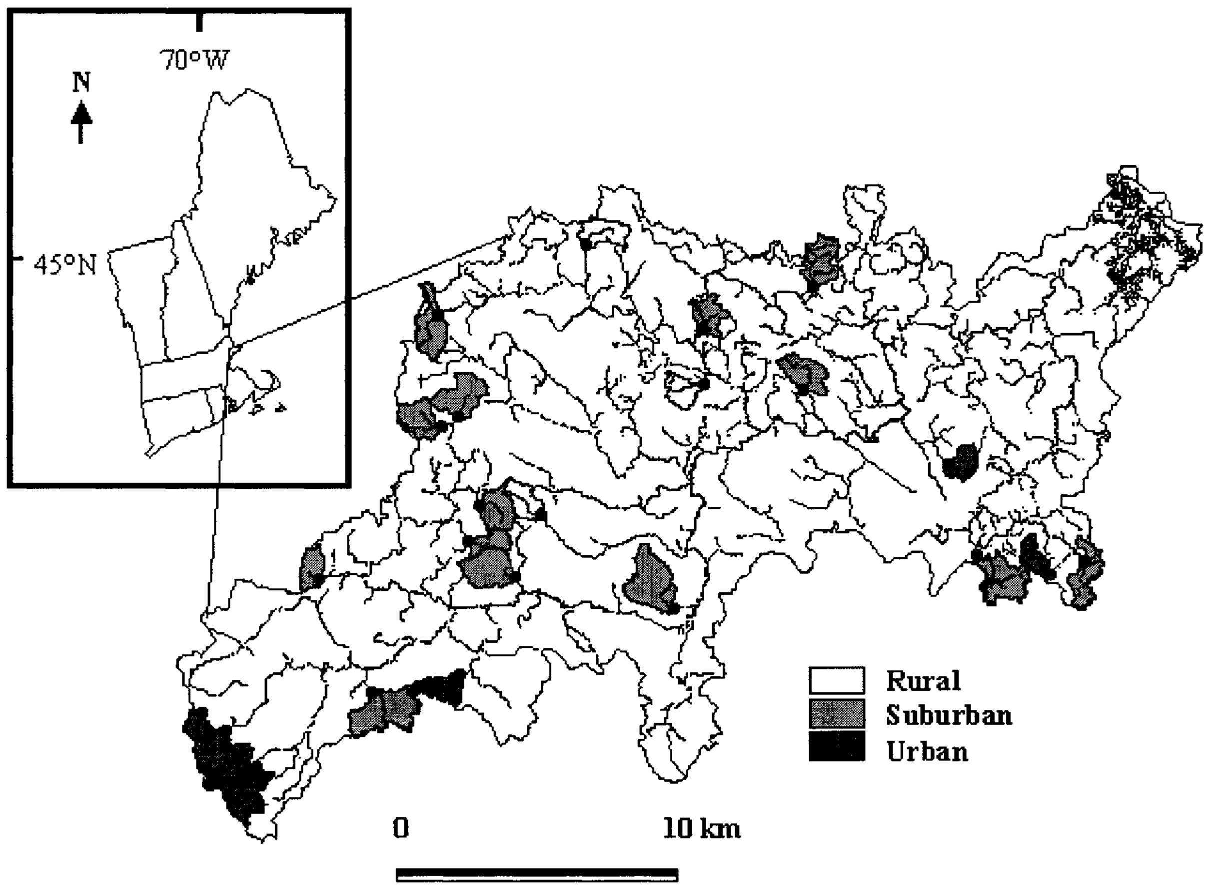
The percentage of urban or residential land use is often used as an integrator of landscape alterations in watersheds influenced by urbanization (Alberti et al., 2003). While this is useful for understanding the role of land use in a broader context, lumped attributes fail to identify mechanisms influencing stream chemistry and hydrology. Several studies have broken down urbanization into rural, suburban and urban areas based on population density, though standard definitions are lacking (Theobald, 2004). Urbanization results in a mix of roads, water infrastructure, lawns and natural areas and variability across the land use gradient needs to be represented (Groffman et al., 2004; Alberti et al., 2003). Watershed-scale attributes of urbanization such as septic density, wetland area and percent impervious may provide data at a scale that is appropriate for land managers concerned with water quality (Groffman et al., 2004; Taylor et al., 2004).

The specific objectives of our study were to: (1) evaluate the distribution of watershed-scale features of urbanization across a rural-to-urban land use gradient, (2) relate lumped and specific watershed-scale attributes to variability in stream water inorganic N and P chemistry both within and between land use categories and (3) validate the sources of N in several urbanizing watersheds with stable nitrogen isotopes ($^{15}N-NO_3$). The role of suburban (e.g. 100 – 620 people / km^2; McDonnell et al., 1997) development in particular has received little attention, yet accounts for a large fraction of current land use change (Hasse and Lathrop, 2003). We study headwater catchments with no point source wastewater inputs and minimal agriculture to identify factors influencing stream chemistry in urbanizing watersheds (Taylor et al., 2004). As agricultural land area declines and point source pollutants are more strictly managed, understanding the non-point source impacts of urbanizing landscapes on stream water chemistry and coastal eutrophication will be of increasing importance.

Methods

Site Description - Stream water samples were collected from sub-catchments of the 404 km^2 Ipswich River watershed in northeastern Massachusetts (Figure 1). The Ipswich River watershed is one of three that drain into the Plum Island Sound estuary and is part of the Plum Island Ecosystem Long Term Ecological Research (LTER) project. The watersheds are in the coastal lowland section of New England and are characterized by low to moderate relief and relatively poor drainage. Maximum elevation is about 150 m and mean watershed slope is 24 m / km. Average annual precipitation is 1180 mm yr^{-1} and is uniformly distributed throughout the year. Mean monthly air temperature ranges from –2 °C in winter to 23 °C in summer. Atmospheric N deposition (inorganic, wet plus dry) is approximately 700-800 kg N km^{-2} yr (Ollinger et al., 1993).

Figure 1. Location of sub-catchments of the Ipswich River watershed sampled for N and P concentrations in this study.



Sub-watersheds sampled as part of this study are headwater catchments (0.6-3.8 km^2) with 1-89 % urban development largely as residential land use (Table 1). Agriculture is mainly pasture and accounts for < 10 % of the land area in most watersheds. Wastewater from developed areas is released to septic systems or exported via municipal sewer systems to a Massachusetts Water Resources Authority (MWRA) treatment facility off the coast of Massachusetts. Bedrock is mainly igneous and sedimentary rock (Paleozoic and Precambrian) and shallow soils are developed largely on surficial till, gravel and sand deposits (Baker et al., 1964). Wetlands account for 2-36 % of the watershed area in the sub-catchments (MassGIS) and are typically located along stream channels and in scattered small upland depressions. The percentage of open water ranges from 0-21 % of the watershed area, but is typically < 1 % for most watersheds. Land use (residential, agricultural, industrial / commercial, forest) and open water were delineated from 1:25000 aerial photography (MassGIS) and were analyzed using GIS software. Wetland data layers (National Wetland Inventory) were from 1:5000 orthophotography and were given precedence over the land use identified in the 1:25000 database.

Watershed-Scale Attributes - Individual features of urbanizing watersheds were quantified at the watershed scale to better describe land use change and stream chemistry. Distributed population density data were based on Census 2000 tabular data and the Topologically Integrated Geographic Encoding and Referencing system (TIGER/line) geographical database which is at the block level. The percent of the population on septic systems was determined from 1990 census survey (SF3 tables, code HO24) at the census tract level. We assume that percentage of people on septic systems is the same as in 1990 since the wastewater survey discontinued in 2000. We believe our catchment-scale estimates of waste treatment are reasonable despite the relatively course scale of census tract data because most variability in waste treatment is at the town level (DEP, 2002) and there are typically several census tracts per town. Impervious surface area was derived from estimates of percent impervious surfaces versus land use type (Arnold and Gibbons, 1996). Watershed attributes were estimated using a 120 m gridded river network developed from 30 m DEM's in ARC/INFO. Spatial datasets were aggregated to 120 m grid cells as percentage grids (land cover) or density grids (population). At the 120 m grid scale, there are 70 grid cells in each km^2.

Standard quantitative definitions to categorize urbanizing watersheds are currently lacking (Theobald, 2004). We therefore use population density values from McDonnell et al. (1997) to determine three classes: rural (< 100 people / km^2), suburban (100-620 people / km^2) and urban (> 620 people / km^2). Exurban (e.g. low density, large lot suburban development; Theobald, 2004) is a further distinction between suburban and rural, but is not evaluated in our study.

<u>Sample Collection and Analysis</u> - Stream water surveys were conducted monthly at approximately 44 sub-watersheds from December 2001 – November 2002. Of these, 23 watersheds were selected for analysis in this study based on the following criteria: (1) agricultural land was < 10 % of the total watershed area and (3) samples were collected during at least 8 of 12 months to characterize mean annual concentrations. In addition, no point source inputs are known for these sub-watersheds. The number of samples

collected from each site is a limitation in our dataset, but one that is often necessary when using spatially extensive sampling to discern broad scale patterns (Pellerin et al., 2004; Perakis and Hedin, 2002; Lovett et al., 2000; Hedin et al., 1995).

Stream water samples for nutrient analysis were collected in 250-ml polyethylene bottles, immediately preserved with 1 ml of sodium azide and stored on ice while transported to the laboratory. Samples were filtered within 48 hours of collection through 25-mm diameter membrane filters (0.45 μm pore size) and were frozen in HDPE bottles until analysis. A subset of samples filtered through pre-combusted 24-mm Whatman GF/F filters (pore size = 0.7 μm) indicated no increase in N or P concentrations as a result of using membrane filters (data not shown). All N and P analyses were run colorimetrically on a Lachat QuikChem 8000 flow injection analyzer. NO_3 was measured using the cadmium reduction method, while NH_4^+ was measured by the indophenol method. $NO_2^-$was also measured colorimetrically, but accounts for a negligible fraction of dissolved inorganic N. Instrument detection limits are 0.1 μM for NO_3, 0.02 μM for NH_4, and 0.05 μM for PO_4.

Table 1. Area, land use, population density, septic density, and mean annual N and P concentrations for 23 sub-catchments of the Ipswich River watershed. For = forest, Wet = wetland, Res = residential, Imp = impervious.

Site	Area (km^2)	Population density (people/km^2)	Septic (%)	Watershed area (%)				Mean concentration (μM)		
				For	Wet	Res	Imp	NO_3^--N	NH_4^+-N	PO_4^+-P
143	1.1	56	92	81	16	1	0	2.7	3.9	0.2
127	1.3	69	91	63	22	10	2	40.8	7.5	0.9
137	1.4	85	92	56	5	14	3	1.5	2.1	0.1
132	1.9	119	23	55	22	16	3	0.9	3.9	0.2
145	1.1	143	100	53	10	33	7	23.0	1.8	0.2
148	1.8	145	91	54	18	23	5	1.2	1.5	0.2
129	1.4	150	77	63	19	14	3	3.0	3.4	0.6
167	1.7	317	22	54	15	22	13	1.7	3.3	na
135	1.8	318	17	28	14	25	29	14.1	7.9	0.4
128	0.9	346	94	52	11	37	7	76.0	10.7	0.2
131	1.6	378	84	30	8	51	14	66.2	4.3	0.4
152	1.5	419	93	33	7	56	12	94.1	12.3	0.2
164	2.5	456	8	42	19	24	12	3.5	3.4	0.2
118	1.9	466	93	37	10	46	10	29.7	5.4	0.2
120	2.5	469	83	28	17	50	15	59.4	5.2	0.3
110	3.0	512	43	16	26	41	23	18.6	8.8	0.2
111	1.1	532	98	17	36	24	27	17.4	4.8	0.3
166	0.8	650	10	27	15	57	15	39.2	8.3	0.2
115	1.4	859	20	23	12	64	18	45.2	5.0	0.4
104	1.4	888	32	12	13	64	20	62.3	8.6	0.2
102	3.8	979	7	13	4	73	25	68.0	7.1	0.2
161	0.9	1056	100	9	17	73	22	52.0	7.0	0.5
103	0.6	1149	9	8	2	89	26	59.1	8.8	0.4

Volume weighted annual mean concentrations were calculated as:

$$VWM = (\Sigma C_i\, Q_i) \,/\, \Sigma Q_i \qquad (1)$$

where C_i is the measured nutrient concentration on sample date i, Q_i is the discharge volume on the day sampled, and ΣQ_i is the sum of the daily discharge on all days sampled. Since stream discharge was not routinely measured for most sub-catchments, the relative fraction of discharge on the sampling dates was estimated from discharge near the mouth of the Ipswich River (USGS station 02102000). Most missed nutrient samples were during the summer months when flow was very low and therefore the impact on flow-weighted concentrations was likely negligible. For example, discharge on the sample days in July-September accounted for only 3 % of the summed daily discharge for the 12 sampling dates at the mouth of the Ipswich River (data not shown).

Samples were also collected from two synoptic surveys (February and August 2003) in conjunction with the Lotic Intersite Nitrogen Experiment (LINX II) for analysis of NO_3^- concentrations and natural abundance of nitrogen isotopes ($^{15}N\text{-}NO_3$) in streamwater. Approximately 1-L of stream water was filtered in the field from 5-8 headwater catchments sampled during our monthly surveys. Samples were stored on ice until transported to the lab and frozen until processed for $^{15}N\text{-}NO_3$ via the alkaline headspace diffusion procedure (Mulholland et al., 2004; Sigman et al., 1997). Dried filter packs were run for $^{15}N\text{-}NO_3$ on a gas source isotope mass spectrometer with a precision of ± 0.1 ‰. All stable isotope ratios are expressed in delta per mil notation (‰):

$$\delta_{sample}\ (‰) = [(R_{sample} - R_{standard}) \,/\, R_{standard}] * 1000 \qquad (2)$$

where R is the ratio of ^{14}N:^{15}N of the sample and standard (air), respectively.

Statistics - Relationships between population density and landscape attributes or NO_3, NH_4 and PO_4 concentrations were assessed via regression analyses. Stepwise multiple regression was used to evaluate relationships between stream water chemistry and (1) population density plus several watershed-scale attributes and (2) watershed-scale attributes without population density. Regressions were developed along both the rural-to-urban gradient and within the suburban category (n = 14), but were not evaluated within rural and urban categories due to a lower n (3 and 6, respectively). All analyses were at the 95 % confidence interval using JMP 4.0.4 (SAS Institute, Inc.)

Results

Landscape Attributes - Population densities for the 23 catchments studied ranged from 56-1149 people / km^2. These sites are generally representative of the range of sub-catchments in our study area, several of which did not meet the criteria for evaluating N and P concentrations (Figure 2). The percentage of forest and percent wetlands were both negatively correlated with population density ($p < 0.01$), while the percentage of residential land, impervious surface percentage, sewer density and septic density were positively correlated with population density ($p < 0.01$; Table 2). The intercept for residential, septic and sewer parameters was set to zero to account for the absence of humans. The percentage of forested land, residential land, impervious area, and sewer were more strongly correlated with population density ($r^2 = 0.56 – 0.64$) than wetland percentage and septic density ($r^2 = 0.16 – 0.18$). Watershed area and the percentages of open water, industrial land use, and agricultural land were not correlated with population density, explaining only < 2 % of the variability in landscape attributes (data not shown).

Based on the population density thresholds, 3 watersheds were classified as rural, 14 as suburban and 6 were classified as urban. One urban watershed is an outlier due to high septic densities (1051 people / km^2) but is included in our analysis. In contrast, suburban watersheds have high variability in all landscape attributes with differences at a given population density as large as 20-30 % of the total land area (Figure 2). In addition, septic densities for a given population density within the suburban category vary by as much as 400 people / km^2 with corresponding differences in the density of individuals on sewer systems.

Stream Nutrient Chemistry - Mean annual stream dissolved inorganic N concentrations ranged from 3-106 μM for individual watersheds, with differences largely attributable to NO_3 concentrations (Table 1). Mean NH_4 concentrations ranged from 2–11 μM, while PO_4 concentrations were 0.1–0.9 μM. Comparison of monthly NO_3 samples with more intensive sampling at one site (site 102) suggests that monthly data was adequate for characterizing mean annual concentrations and drawing inferences on the role of landscape attributes (Figure 3).

Figure 2. Relationship between population density and landscape attributes in the Ipswich River sub-catchments. Lines distinguish between rural (< 100 people / km^2), suburban (100-620 / km^2), and urban (> 620 / km^2) catchments. Solid circles were sub-catchments with N and P data in this study, while open circles are sites that did not meet the sampling criteria.

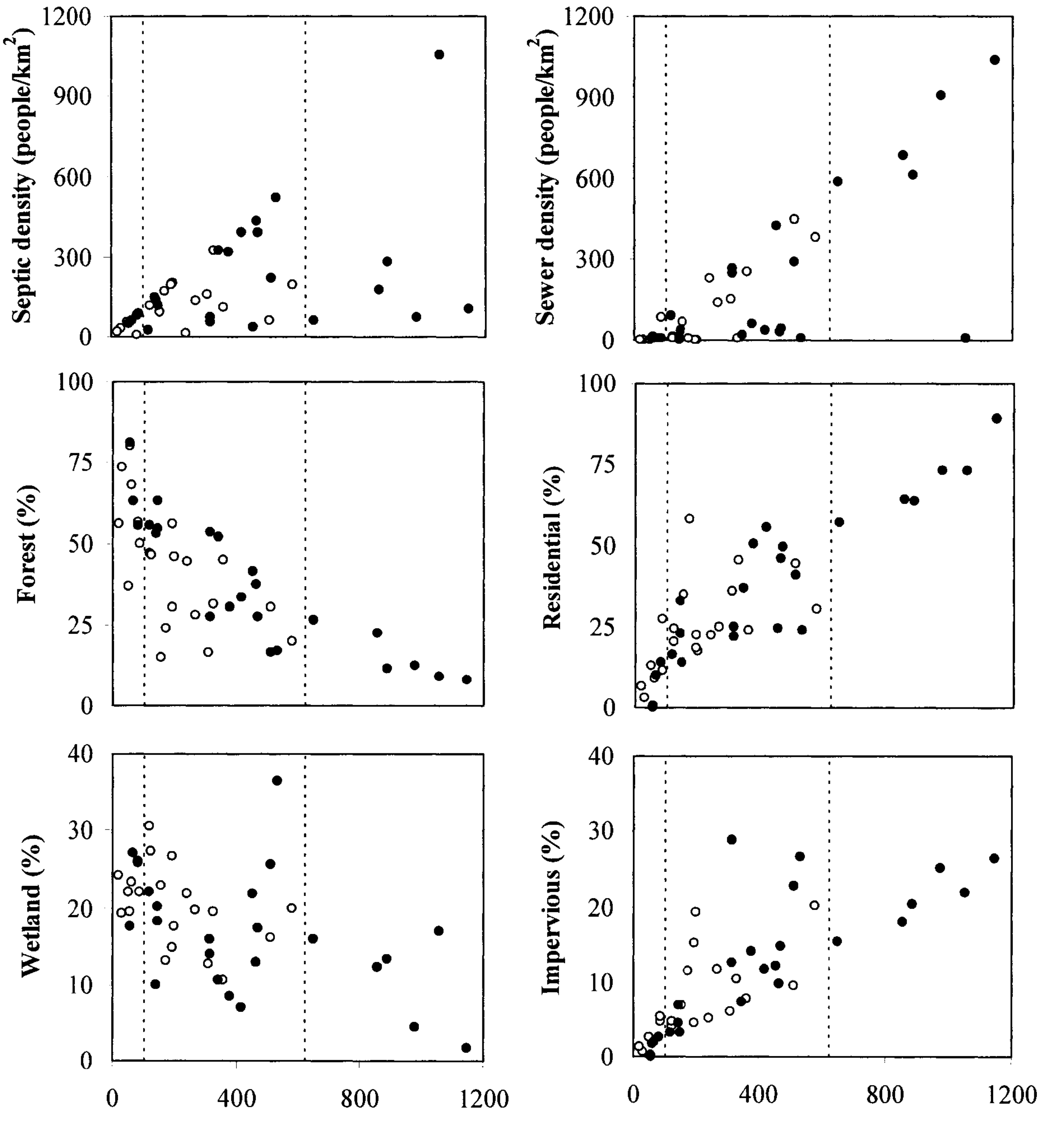


Table 2. Relationship between population density and landscape attributes across the rural-to-urban gradient for all Ipswich River sub-watersheds (n = 44). Only significant relationships are shown. [†]Intercept was set to 0.

Landscape Attribute	r^2	p	Slope	Intercept
Forest (%)	0.56	<.01	-0.05	56.88
Wetland (%)	0.16	<.01	-0.01	20.17
Impervious (%)	0.62	<.01	0.02	3.13
Residential (%)	0.64	<.01	0.08	0[†]
Sewer density (people/km^2)	0.57	<.01	0.57	0[†]
Septic density (people /km^2)	0.18	<.01	0.24	0[†]

Mean annual NO_3 and NH_4 concentrations were weakly correlated with watershed population density (Figure 4). Mean annual PO_4 concentrations were not correlated with population density (Figure 4) and data are therefore not discussed relative to the rural-to-urban gradient. Rural watersheds had mean NO_3 and NH_4 concentrations of 15 and 5 μM, respectively, with variability largely due to high N concentrations from one catchment (site 127, Table 1). Mean annual N concentrations in suburban watersheds were highly variable, ranging from 1 – 94 μM for NO_3 (mean = 29 μM) and 2 – 12 μM for NH_4 (mean = 6 μM). Urban watersheds had the highest mean annual NO_3 (54 μM) and NH_4 concentrations (8 μM) for a land use category, and were less variable than suburban watersheds. No clear temporal patterns in N and P concentrations were evident within land use categories, although NH_4 and PO_4 were elevated during low flow periods (July-September) at some sites (data not shown). In addition, some sites had low NO_3 concentrations during autumn litterfall (Figure 3) presumably due to immobalization or denitrification within the stream channel. Changes in N or P concentrations during the summer and fall typically had little impact on annual flow-weighted concentrations as a result of low flows.

Population density explained 27 % of the variability in NO_3 concentrations and 22 % of NH_4 concentrations across the range of sites (Table 3). The best single predictor was the percentage of residential land use for both NO_3 and NH_4 ($r^2 = 0.52$ and 0.24). Watershed-scale attributes of urbanization were evaluated separately and in multiple regressions to identify drivers of stream inorganic N chemistry. The use of wetland plus open water percent and septic density explains nearly as much variability in NO_3 as residential land use (Table 3), with wetlands plus open water alone explaining more variability than population density ($r^2 = 0.34$, $p < 0.01$). Septic density and the percentage of wetlands plus open water are not correlated in this dataset ($r^2 = -0.05$) indicating that the two parameters are independent variables. The percent forest and wetland plus open water percentage was the best multiple regression for NH_4, but explained only 22 % of the variability ($p < 0.05$).

Figure 3. Comparison of NO_3^- from monthly and intensive sampling at a sub-catchment of the Ipswich River watershed (site 102).

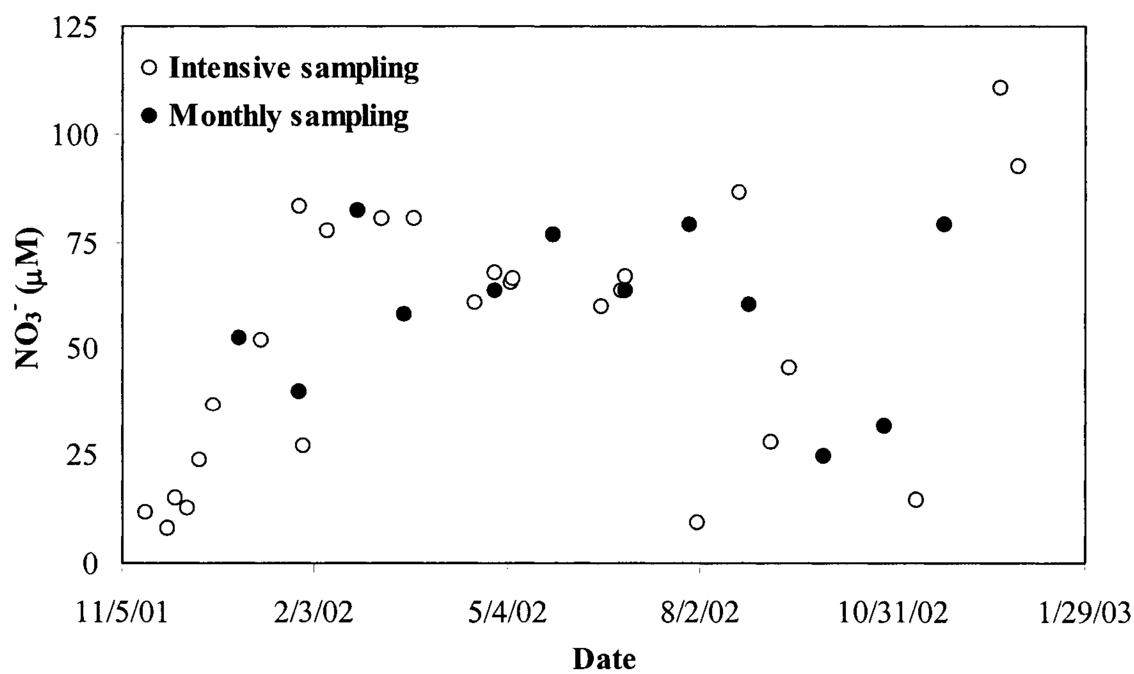
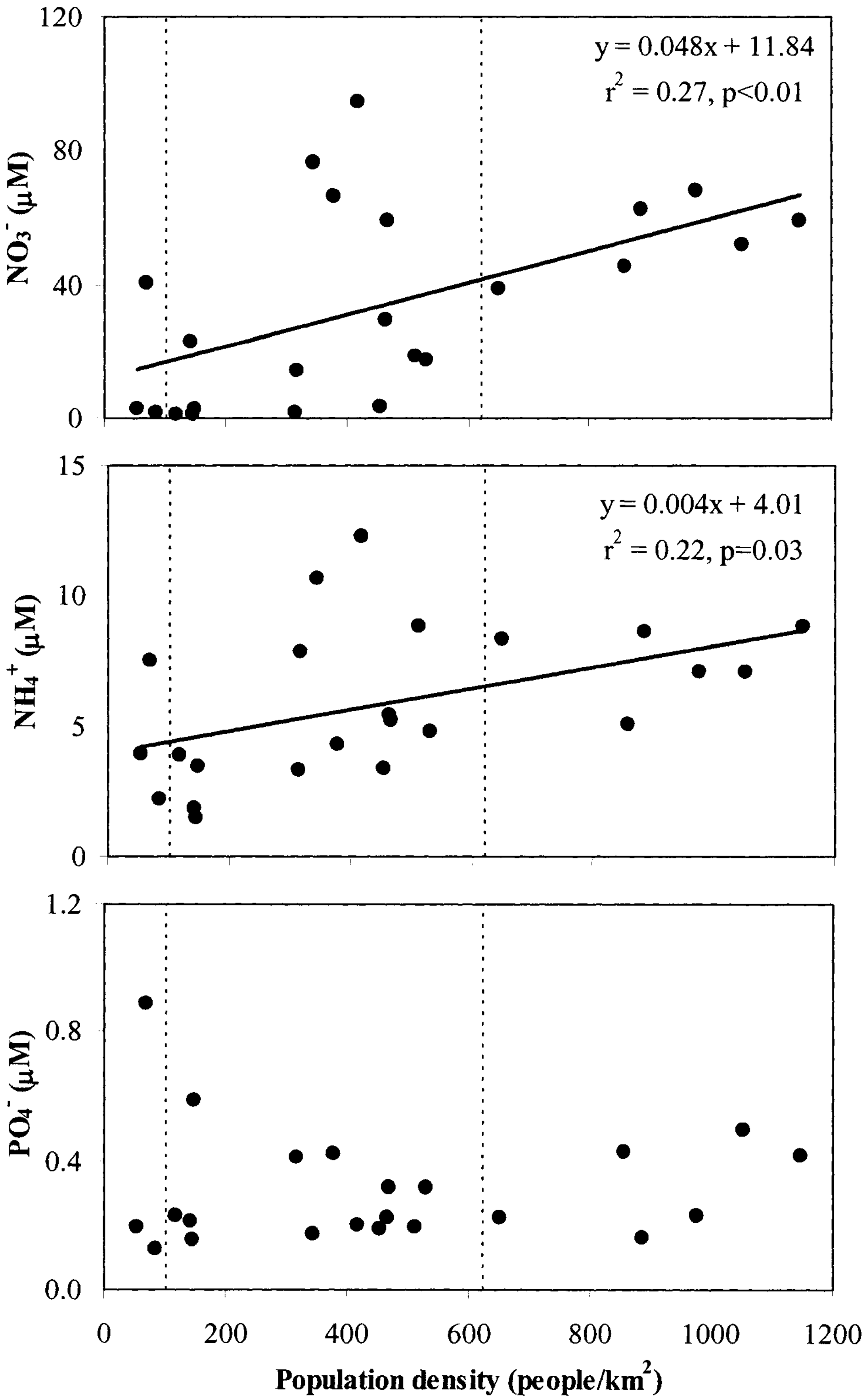


Figure 4. Relationship between population density and mean stream N and P concentrations for sub-catchments of the Ipswich River watershed. Dashed lines distinguish between rural, suburban and urban watersheds.



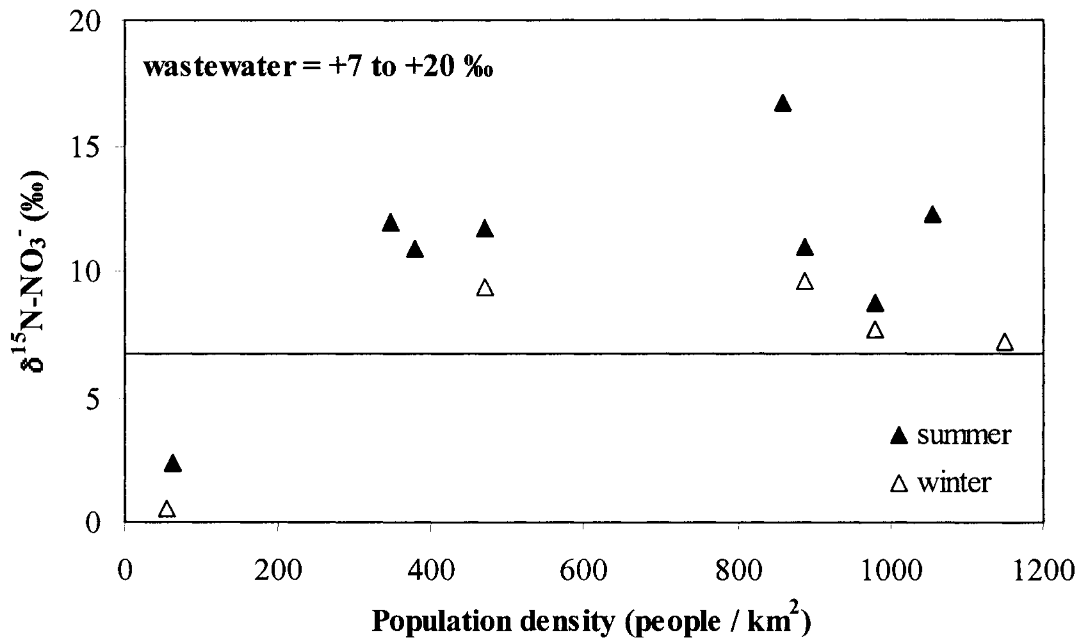
A multiple regression of the percent wetlands plus open water and septic density explains 73 % of the variability in mean NO_3 concentrations within the highly variable suburban category (Table 3), slightly better than residential land use alone ($r^2 = 0.70$). NO_3^- concentrations were highest in low wetland, high septic density sites (e.g. 30-94 μM) and lowest (1-4 μM) in high wetland, low septic density sites (Table 1). Only 22 % ($p = 0.10$) of the variability in mean NH_4 concentrations was explained in the suburban category using the percent forest and wetlands plus open water percentage. Multiple regressions were not developed for rural or urban watersheds because *n* was low (3-6 watersheds) and variability in inorganic N concentrations were typically less than in suburban watersheds.

Table 3. Linear and multiple regression (adjusted r^2) and *p* values for predictors of mean NO_3^- and NH_4^+ concentrations for all watershed and within the suburban land use category.

Attribute	NO_3^-	*p*	NH_4^+	*p*
<u>All wastersheds (*n* = 23)</u>				
Residential (%)	0.52	< 0.01	0.24	< 0.05
Population density (people/km^2)	0.27	< 0.01	0.18	< 0.05
Multiple regression†	0.51	< 0.01	0.22	< 0.05
<u>Suburban only (*n* = 14)</u>				
Residential (%)	0.70	< 0.01	0.23	< 0.05
Population density (people/km^2)	0.07	ns	0.15	ns
Multiple regression‡	0.73	< 0.01	0.22	ns

† NO_3^- = 58.95 – (2.26 * wetland+open water %)+(0.05 * septic density)
NH_4^+ = 9.48 – (0.06 * forest %) – (0.09 * wetland+open water %)
‡ NO_3^- = 41.90 – (2.41* wetland+open water %) + (0.13 * septic density)
NH_4^+ = 13.18 – (0.12 * forest %) – (0.17 * wetland+open water %)

Figure 5. Population density and $^{15}N\text{-}NO_3^-$ (‰) during summer (solid triangles; $n = 8$) and winter 2003 (open triangles; $n = 5$) for Ipswich River sub-catchments. Values above the solid line are characteristic wastewater ^{15}N values.



Samples from the $^{15}N\text{-}NO_3$ synoptic sampling during August 2003 ranged from 2.4 – 16.7 ‰ ($n = 8$), while February 2003 values ranged from 0.6 – 9.6 ‰ ($n = 4$). Isotope values were lowest at the site with low population densities (Figure 5), but greater than 7.2 - 8.7 ‰ in all other catchments. Stream water NO_3^- concentrations were correlated with $\delta^{15}N$ ($r^2 = 0.39$ in summer; data not shown) although the relationship was not statistically significant ($p = 0.06$). Winter ^{15}N values were approximately 1.0 – 2.3 ‰ lower than the summer for the 3 watersheds where samples were collected during both synoptic surveys (Figure 5) and may reflect mixing our water from different sources or fractionation due to denitrification during the summer.

Discussion

Relationships Between Stream Water Chemistry and Land Use – Contrary to the results in other studies of stream PO_4 concentrations (Osborne and Wiley, 1988; Paul and Meyer, 2001; Taylor et al., 2004), there was no relationship between PO_4 concentrations and population density in our study (Figure 4). The direct discharge of wastewater to rivers and streams is a dominant factor in determining P concentrations and fluxes (Castillo et al., 2000) and accounts for up to 90 % of the total P load to urban northeastern U.S. estuaries (Roman et al., 2000). While the long-term P retention capacity of mineral soils is not well known (Bennett et al., 2001), subsurface soil retention of septic P-loads may explain the lack of correlation between stream water PO_4 concentrations and septic density in our study catchments (Robertson and Cherry, 1992). A small number of sample run for both PO_4 and total P indicate that PO_4 was 6-49 % of TP (mean = 19 %; n = 10) at the mouth of the Ipswich River and 8-46 % (mean = 17 %; n = 16) in an urban sub-catchment (unpublished data). Data to evaluate the role of urbanization on the delivery of P to streams via suspended sediments are not available but may be important in urban areas with high soil erosion (Bennett et al., 2001; Carpenter et al., 1998).

Stream NO_3 and NH_4 concentrations are both correlated with population density (Figure 4), but population density only explains a small fraction (22-27 %) of the variability in N concentrations. Population density has been shown to be good predictor of NO_3 exports from large rivers globally (Peierls et al., 1991) presumably due to a correlation between population density, ecosystem N loads and the abundance of N sinks such as riparian wetlands (Caraco et al., 2003). However, population density explains little variability in NO_3 export from small (e.g. < 100 km^2) watersheds (Caraco et al., 2003). Studies have also found that population density explained a significant fraction of NH_4 variability and attributed this to higher municipal waste discharge in more urbanized watersheds (Miller et al., 1997). Septic wastewater NH_4 in our study catchments might be retained in mineral soils via adsorption or converted to NO_3 via nitrification (Robertson and Cherry, 1992), with significant fluxes of anthropogenic NH_4 likely limited to flushing during storm events (unpublished data).

Our results indicate that the percentage of wetlands plus open water and the density of septic systems explain about 51 % of the variability in mean NO_3 concentrations across the rural-to-urban gradient. While the single best predictor of NO_3 concentrations in our study is the percentage of residential land use (Table 3), this parameter integrates all land use attributes and provides limited information about important landscape features in urbanizing watersheds. An evaluation of watershed-scale attributes such as septic density and wetlands provides additional detail about nutrient sources and sinks at a scale that is appropriate for water quality managers (Groffman et al., 2004; Taylor et al., 2004). The spatial distribution of septic systems (Wernick et al., 1998) and wetlands (Pinay et al., 2002) within watersheds may be an additional source of variability in stream water N concentrations both temporally and across the rural-to-urban gradient, but was not explicitly evaluated here.

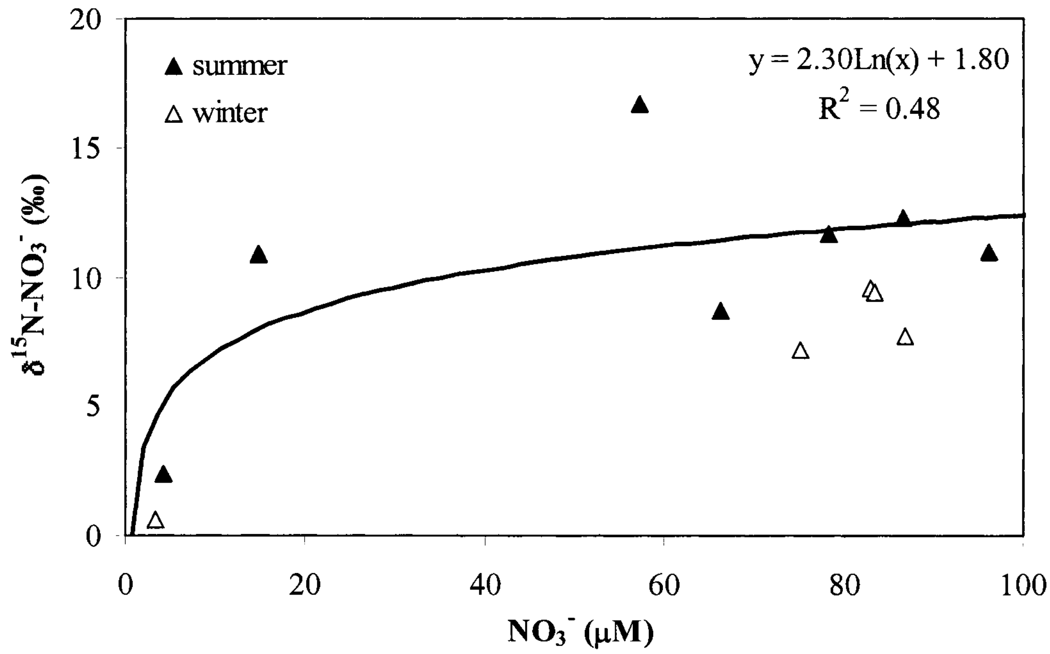
Variability in septic densities, wetland percentages and other landscape attributes is particularly high within the suburban category (Figure 2) and results in some of the highest estimates of watershed N loading (Wollheim et al., submitted) and stream N concentrations in our study. Taylor et al. (2004) also reported high septic tank densities and stream N concentrations in watersheds with intermediate urban density in Australia. Suburban watersheds account for the largest number of sites in our study and likely play a disproportionate role in determining relationships between attributes and N concentrations across the rural-to-urban gradient. For example, 73 % of the 10-fold variability in NO_3 concentrations in suburban watersheds is explained by the percentage of wetlands plus open water and septic density.

Nitrogen isotope data in our study supports the conclusions of the regression model that wastewater is the dominant source of NO_3 in a subset of suburban study catchments, but also indicates wastewater as the likely source of elevated NO_3 urban watersheds (Figure 5). Most studies report $\delta^{15}N$-NO_3 values in the range of +7 to +20 ‰ for wastewater, while other N sources (e.g. precipitation, NO_3^- fertilizer, and soil N) are typically in the range of −10 to +8 ‰ (Bedard-Haughn et al., 2003; Mayer et al., 2002; Kendall, 1998). Fractionation during denitrification increases $\delta^{15}N$ values in the residual NO_3 pool (Kendall, 1998) and therefore may contribute to elevated ^{15}N in our study catchments. However, evidence suggests that wastewater inputs are the dominant mechanism of elevated ^{15}N-NO_3 values in our study. First, the differences between $\delta^{15}N$-NO_3 values was only 1.0-2.3 ‰ for three watersheds sampled during both the winter (e.g. low biotic activity) and summer (e.g. high biotic activity) sampling (Figure 5). Second, a comparison of $\delta^{15}N$ and NO_3 suggests a positive correlation in our study catchments (Figure 6), whereas denitrification would typically result in a negative correlation between $\delta^{15}N$ concentrations and stream NO_3 concentrations as N is lost to the atmosphere as N_2O and N_2 gas (Mayer et al., 2002). Finally, $\delta^{15}N$ concentrations in urban watersheds remain high despite relatively low wetland percentages (Figure 5), suggesting that either septic wastewater or leaking sewer lines are important sources of elevated N to urban streams. Additional isotopic investigations to validate the sources, transformations and variability in $\delta^{15}N$ in urbanizing watersheds are clearly needed, but are beyond the scope of this paper.

<u>The Influence of Septic Systems and Wetlands on Stream N Concentrations</u> - While it is tempting to draw inferences on the relative role of septic wastewater and wetlands as N sources and sinks, our results highlight the importance of considering both simultaneously in urbanizing watersheds. Septic system leaching to the vadose zone and groundwater bypasses N uptake in the biologically-active rooting zone and likely increases the importance of NO_3^- retention in riparian wetlands (Hanson et al., 1994). While the relative importance of wetland N retention mechanisms is not known for these sites, recent studies suggest that denitrification (Filoso et al., in press) and the loss as organic N (Pellerin et al., 2004) may be important. Therefore wetlands likely play a key role in determining the ratio of inorganic to organic N in watershed exports. Storage of N in lake and riverine sediments may also occur, but open water typically accounts for < 5 % of the wetland area in our study catchments.

Impervious surfaces such as roads, parking lots, and driveways may also influence riparian N retention in urbanizing watersheds by increasing surface runoff to streams and reducing groundwater recharge (Groffman et al., 2002; Gremillion et al., 2000). Changes in hydrologic flow paths could therefore limit interactions between carbon-rich shallow soils and anoxic zones as the groundwater table declines, reducing denitrification in urban riparian zones (Groffman et al., 2002). Discharge from septic systems may compensate by providing some groundwater recharge (Lerner, 2002), but will typically result in elevated subsurface NO_3^- inputs. Isotopic ($\delta^{15}N$-NO_3^-) evidence supports that conclusion that wastewater is the dominant source of high NO_3^- concentrations in suburban watersheds, highlighting the importance of septic systems and wetlands for management at the watershed scale.

Figure 6. Stream NO_3^- concentrations and ^{15}N-NO_3^- (‰) during summer (solid triangles; n = 8) and winter 2003 (open triangles; n = 5) for Ipswich River sub-catchments. Regression line is for summer data only.



The effect of wetlands on stream water N concentration has been difficult to establish at the watershed-scale since most wetland and riparian N retention studies have been conducted at the plot-scale (Chestnut and McDowell, 2000). Also, previous studies evaluating land use – N concentration relationships often have low wetland abundance in their study sites (Herlihy et al., 1998; Jordan et al., 1997). We do not know if low wetland abundance is due to recent or historical land use or is a natural feature of some suburban and urban catchments in our study. Although urbanization is historically associated with wetland loss, coastal lowland sections of New England are typically characterized by low to moderate relief, relatively poor drainage, and high population densities. For example, Roman et al. (2000) reported that 16 % of the U.S. population reside in a narrow fringe of northeastern coastal counties. Therefore, wetlands are likely a key watershed-scale attribute in urbanizing watersheds and additional research on the interactions between nutrient sources, catchment hydrology and wetland abundance and function is clearly warranted (Wollheim et al., *submitted*; Groffman et al., 2004, 2002). As forests and agricultural land continue to be modified for human development, the use of watershed-scale attributes may be a simple method for understanding and managing future non-point source urban impacts on stream water quality.

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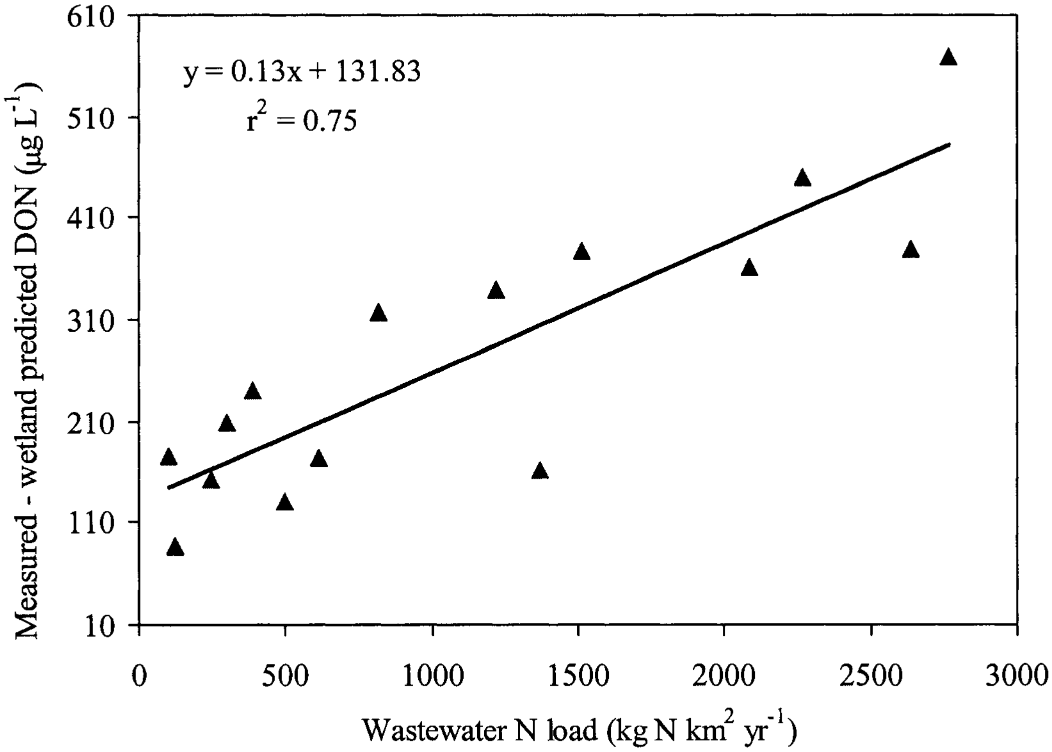
APPENDIX A

SUPPORTING DATA FOR CHAPTER 1

Monthly DON concentrations from Ipswich River sub-watersheds used in study.

Site	Monthly DON concentration (ug/L)					Number of samples	Mean DON (μg/L)
	2/1/99	4/1/99	11/1/99	4/1/00	9/1/00		
IS_102	395	na	96	241	165	4	224
IS_103	358	na	86	466	187	4	274
IS_104	361	na	169	368	65	4	241
IS_107	241	na	42	173	226	4	170
IS_110	585	na	692	441	370	4	522
IS_115	419	na	585	333	562	4	475
IS_118	389	na	375	307	474	4	386
IS_120	606	na	476	452	387	4	480
IS_124	296	na	711	279	942	4	557
IS_128	368	na	321	380	31	4	275
IS_129	304	na	549	386	324	4	391
IS_131	288	na	379	415	695	4	444
IS_132	412	na	880	384	1306	4	745
IS_135	252	417	480	373	na	4	381
IS_136	453	513	845	430	1251	5	698
IS_137	266	224	245	202	267	5	241
IS_138	513	512	846	395	1177	5	689
IS_140	657	806	1374	464	na	4	825
IS_141	363	379	652	277	557	5	445
IS_142	225	384	644	347	na	4	400
IS_143	445	403	431	256	na	4	384
IS_145	190	240	252	169	133	5	197
IS_147	496	392	381	290	517	5	415
IS_150	337	328	318	243	na	4	307
IS_152	440	410	123	436	244	5	331
IS_154	405	536	1051	329	na	4	580
IS_155	192	287	491	287	454	5	342
IS_160	694	737	916	506	1229	5	816
IS_161	679	497	708	411	639	5	587
IS_162	617	848	731	478	na	4	669
IS_163	286	na	476	306	368	4	359
IS_164	383	292	307	160	638	5	356
IS_166	202	230	302	221	495	5	290
IS_167	224	260	712	301	1513	5	602
IS_169	395	293	450	199	370	5	341
IS_172	763	437	616	651	594	5	612
IS_173	352	na	761	346	731	4	548
IS_175	312	240	240	292	292	5	275

Relationship between wastewater N load and measured minus wetland predicted DON concentrations for the sites with direct N inputs (SCOPE watershed - Boyer et al., 2002)



Comparison of regular and reduced frequency sampling on DON concentrations near the mouth of the Ipswich River (IP-24). Regular samples are volume-weighted means, while reduced frequency is an arithmetic mean of five sampling dates. Reduced frequency was estimated base on the months of subwatershed sampling. For example, 1999-2000 is based on samples during Feb, April and Nov. 1999 and April and Sept. 2000).

Sampling Regime	**Year**	***n***	**DON ($\mu g\ l^{-1}$)**	**DON flux (kg/d)**
Regular Frequency	1998-1999	18	397.7	127.0
	1999-2000	21	452.3	219.5
	2000-2001	12	362.4	194.4
	2001-2002	11	333.9	57.4
Reduced Frequency	1998-1999	5	510.0	240.5
	1999-2000	5	476.8	330.4
	2000-2001	5	384.5	373.1
	2001-2002	5	318.0	137.0

Northeastern U.S. watersheds in regional DON dataset.

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Aberjona River	MA	4	68	70	2459	310	2149	na	13	4
Accotink C Near Annandale	VA	na	98	98	1686	795	890	826	47	8
Androscoggin River	ME	3	1	6	645	370	275	180	57	1
Arbutus Lake Watershed	NY	4	0	0	506	182	324	266	36	11
Blackstone River	MA	7	18	26	2105	544	1561	680	26	1
Bound Bk At Middlesex	NJ	na	69	70	1463	612	852	772	42	8
Cedar Run At Eberlys Mill	PA	na	78	99	3760	279	3481	3433	7	8
Charles River	MA	7	22	31	1150	592	558	540	51	1
Cone Pond	NH	3	0	0	132	105	26	6	80	2,3
Connecticut River	CT	5	4	13	839	349	490	310	42	1
Deer Creek Near Dorseyville	PA	na	20	63	1219	365	854	830	30	8
Delaware River	MD	3	3	20	1407	436	971	870	31	1
Esopus Creek	NY	na	na	6	350	80	270	250	23	5
Fall Kill At Poughkeepsie	NY	na	29	57	547	122	425	400	22	8
Georges Gorge	NH	0	0	0	104	69	35	30	66	7
Gibbs Brook	NH	4	0	0	147	82	65	67	56	7
Glen Boulder	NH	0	0	0	209	69	140	135	33	7
Great Egg Harbor R Nr Sicklerville	NJ	na	33	44	771	381	390	365	49	8
Hockanum R Nr East Hartford	CT	na	51	62	3412	515	2896	2466	15	8
Holiday Creek	VA	na	<20	<20	208	149	59	36	72	5
Hubbard Brook 6	NH	0	0	0	148	100	47	38	68	2,3
Hubbard Brook 7	NH	0	0	0	162	88	75	75	54	2,3
Hubbard Brook 8	NH	0	0	0	210	126	84	77	60	2,3

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Hubbard Brook 9	NH	4	0	0	227	182	45	37	80	2,3
Hudson River	NY	3	3	13	929	227	702	360	24	1
Ipswich River	MA	16	35	42	616	406	209	214	66	12
IS_102	MA	5	78	83	974	224	750	663	23	12
IS_103	MA	1	90	92	1039	274	765	685	26	12
IS_104	MA	13	69	74	1082	241	841	736	22	12
IS_107	MA	6	47	52	912	170	742	635	19	12
IS_110	MA	27	55	56	1093	522	571	426	48	12
IS_115	MA	13	63	63	1138	475	663	617	42	12
IS_118	MA	10	47	51	1014	386	627	582	38	12
IS_120	MA	18	49	54	1251	480	770	726	38	12
IS_124	MA	20	3	6	584	557	27	15	95	12
IS_128	MA	10	35	36	1589	275	1314	1233	17	12
IS_129	MA	19	18	19	486	391	96	67	80	12
IS_131	MA	10	50	58	1076	444	632	526	41	12
IS_132	MA	23	15	21	767	745	21	12	97	12
IS_135	MA	15	56	59	657	381	277	165	58	12
IS_136	MA	23	21	31	819	698	121	77	85	12
IS_137	MA	5	15	19	296	241	55	41	81	12
IS_138	MA	19	26	27	875	689	187	29	79	12
IS_140	MA	31	21	23	857	825	32	15	96	12
IS_141	MA	23	9	9	501	445	56	32	89	12
IS_142	MA	20	0	0	416	400	16	10	96	12

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
IS_143	MA	16	0	0	433	384	49	22	89	12
IS_145	MA	9	35	38	452	197	255	240	44	12
IS_147	MA	22	25	27	454	415	39	18	91	12
IS_150	MA	17	37	39	482	307	175	151	64	12
IS_152	MA	6	57	61	1490	331	1160	1046	22	12
IS_154	MA	16	25	31	681	580	101	82	85	12
IS_155	MA	18	48	50	488	342	146	123	70	12
IS_160	MA	24	6	19	1060	816	243	65	77	12
IS_161	MA	17	73	74	1486	587	899	825	40	12
IS_162	MA	32	25	38	775	669	106	91	86	12
IS_163	MA	15	43	58	867	359	508	425	41	12
IS_164	MA	21	31	33	611	356	255	114	58	12
IS_166	MA	15	56	56	956	290	666	589	30	12
IS_167	MA	16	27	27	790	602	188	18	76	12
IS_169	MA	14	60	60	1061	341	719	669	32	12
IS_172	MA	21	35	63	1350	612	738	663	45	12
IS_173	MA	19	32	52	700	548	153	52	78	12
IS_175	MA	11	23	43	972	275	697	668	28	12
Kennebec River	ME	4	1	7	530	331	199	150	62	1
Lafayette Brook	NH	0	0	0	296	89	207	205	30	7
Lamprey 1	NH	6	21	30	893	172	721	820	19	6
Lamprey 10	NH	7	1	2	195	146	49	39	75	6
Lamprey 11	NH	6	11	15	249	145	104	66	58	6

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Lamprey 2	NH	12	5	6	275	219	56	41	80	6
Lamprey 3	NH	11	5	8	290	219	71	61	76	6
Lamprey 4	NH	9	8	10	355	202	153	139	57	6
Lamprey 5	NH	9	7	9	325	196	129	128	60	6
Lamprey 6	NH	8	5	7	271	177	94	92	65	6
Lamprey 7	NH	8	5	6	262	201	61	46	77	6
Lamprey 8	NH	7	5	7	252	164	88	95	65	6
Lamprey 9	NH	11	2	7	291	246	45	19	85	6
Lamprey mainstem	NH	11	7	10	362	242	120	108	67	6
Lisha Kill Northwest Of Niskayuna	NY	na	77	83	784	300	483	421	38	8
Little Wildcat	NH	0	0	0	85	57	28	19	67	2,3
Lost Pond	NH	0	0	0	141	96	45	35	68	2,3
Lovett 2	NY	0	0	0	419	78	340	339	19	10
Lovett 10	NY	0	0	0	364	43	321	316	12	10
Lovett 11	NY	0	0	0	557	69	489	503	12	10
Lovett 12	NY	0	0	0	571	41	531	503	7	10
Lovett 13	NY	0	0	0	392	81	311	314	21	10
Lovett 14	NY	0	0	0	361	56	305	311	16	10
Lovett 15	NY	0	0	0	332	45	287	295	14	10
Lovett 17	NY	0	0	0	326	55	272	287	17	10
Lovett 18	NY	0	0	0	430	80	350	349	19	10
Lovett 19	NY	0	0	0	568	87	482	463	15	10
Lovett 20	NY	0	0	0	371	53	318	328	14	10

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Lovett 21	NY	0	0	0	234	83	151	143	35	10
Lovett 22	NY	0	0	0	354	92	262	260	26	10
Lovett 23	NY	0	0	0	379	95	284	273	25	10
Lovett 24	NY	0	0	0	447	63	384	392	14	10
Lovett 25	NY	0	0	0	349	55	294	301	16	10
Lovett 26	NY	0	0	0	431	108	323	316	25	10
Lovett 28	NY	0	0	0	336	94	242	241	28	10
Lovett 3	NY	0	0	0	424	69	356	356	16	10
Lovett 30	NY	0	0	0	153	80	73	53	52	10
Lovett 31	NY	0	0	0	386	87	300	293	22	10
Lovett 32	NY	0	0	0	116	78	38	29	67	10
Lovett 33	NY	0	0	0	147	99	48	42	68	10
Lovett 35	NY	0	0	0	566	55	511	505	10	10
Lovett 36	NY	0	0	0	398	81	316	314	20	10
Lovett 37	NY	0	0	0	504	39	465	482	8	10
Lovett 38	NY	0	0	0	528	77	451	445	15	10
Lovett 39	NY	0	0	0	354	50	304	302	14	10
Lovett 4	NY	0	0	0	462	62	400	416	13	10
Lovett 40	NY	0	0	0	510	62	448	451	12	10
Lovett 41	NY	0	0	0	298	64	234	227	22	10
Lovett 42	NY	0	0	0	319	45	274	277	14	10
Lovett 43	NY	0	0	0	312	50	262	244	16	10
Lovett 44	NY	0	0	0	420	66	354	377	16	10

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Lovett 5	NY	0	0	0	396	85	311	309	22	10
Lovett 6	NY	0	0	0	246	80	167	183	32	10
Lovett 7	NY	0	0	0	431	42	389	385	10	10
Lovett 8	NY	0	0	0	459	66	393	393	14	10
Lovett 9	NY	0	0	0	519	76	444	437	15	10
Lye Brook 1	VT	na	0	0	532	370	162	150	70	2,3
Lye Brook 2	VT	na	0	0	499	410	89	70	82	2,3
Lye Brook 3	VT	na	0	0	515	410	105	80	80	2,3
Lye Brook 4	VT	na	0	0	340	170	170	160	50	2,3
Lye Brook 5	VT	na	0	0	458	240	218	210	52	2,3
Lye Brook 6	VT	na	0	0	467	200	267	260	43	2,3
Lye Brook 7	VT	na	0	0	538	230	308	300	43	2,3
Lye Brook 8	VT	na	0	0	446	330	116	100	74	2,3
Lye Brook 9	VT	na	0	0	496	370	126	110	75	2,3
MacDonalds Branch	NJ	na	0	0	190	142	48	25	75	5
Merrimack River	MA	3	9	17	822	401	421	210	49	1
Mohawk River	NY	3	5	33	1056	249	807	620	24	1
Neponset River	MA	10	30	36	694	289	405	na	42	4
Norwalk River At Winnipauk	CT	na	50	55	742	173	569	539	23	8
Parker River	MA	12	25	38	33	25	8	9	75	12
Passaic R At Two Bridges	NJ	na	42	45	1777	462	1315	1223	26	8
Peaboldy Trib	NH	0	0	0	136	95	41	30	70	7
Penobscot River	ME	5	0	2	498	351	147	110	70	1

Northeastern U.S. watersheds in regional DON dataset (cont'd)

Site	State	Wetland (%)	Urban (%)	Urban + Ag (%)	TDN (ug/L)	DON (ug/L)	DIN (ug/L)	NO3 (ug/L)	DON/TDN (%)	Source
Pequabuck R At Forestville	CT	na	43	49	3898	537	3361	2907	14	8
Potomac River	MD	1	3	37	1814	452	1362	1070	25	1
Quashnet R.	MA	na	0	0	280	168	112		60	13
Rappahannock River	VA	0	1	37	911	316	595	490	35	1
Rocky Branch	NH	0	0	0	62	50	12	9	81	7
Rooster River At Fairfield	CT	na	98	98	2030	213	1818	1741	10	8
Saco River	NH	4	1	3	408	268	140	120	66	1
Saddle R At Ridgewood	NJ	na	83	86	1519	227	1292	1267	15	8
Saugus River	MA	9	56	60	950	323	627	na	34	4
Saw Mill River At Yonkers	NY	na	86	86	1335	328	1008	931	25	8
Schuylkill River	PA	1	10	49	3866	712	3154	2570	18	1
Sleepers River	VT	5	0	0	327	79	249	229	24	2,3
Slide Brook	NH	0	0	0	114	58	56	49	51	7
Stillwater River	MA	8	4	14	365	167	198	na	46	4
Susquehanna River	VA	1	2	31	1684	284	1400	1100	17	1
Wading River	MA	9	18	25	539	288	251	na	53	4
Waquoit R.	MA	1	51	53	1960	560	1400		29	9
Wild River	ME	na	0	0	120	76	44	29	63	5
Young Womans Creek	PA	na	0	0	503	151	352	335	30	5
Zealand Valley	NH	0	0	0	126	43	83	76	34	7

Sources for northeastern U.S. watershed data in regional DON dataset

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APPENDIX B

SUPPORTING DATA FOR CHAPTER 2

Isotopic data for hydrograph separation of January 29-31, 2002 storm event at the Saw Mill Brook sub-catchment.

ID	Date	Time	Cumulative precip (in)	Discharge (cfs)	δ^2H (per mil)	Old water (%)
baseflow	1/27/02	12:00				
baseflow	1/29/02	13:30	0	0.44	-52.13	100
S-1	1/30/02	6:54	0.21	0.75	-45.95	82
S-2	1/30/02	7:14	0.22	1.13	-49.79	93
S-3	1/30/02	7:34	0.22	1.88	-39.14	61
S-4	1/30/02	8:04	0.23	2.87	-44.79	78
S-5	1/30/02	8:34	0.23	2.86	-43.63	75
S-6	1/30/02	9:04	0.23	2.55	-36.12	52
S-8	1/30/02	10:34	0.24	1.69	-31.29	38
S-9	1/30/02	12:34	0.24	1.16	-36.65	54
S-10	1/30/02	14:34	0.24	0.87	-36.97	55
S-11	1/30/02	16:34	0.24	0.76	-41.41	68
S-12	1/30/02	18:34	0.24	0.67	-38.65	60
S-13	1/30/02	20:34	0.24	0.63	-40.18	64
S-14	1/30/02	22:34	0.24	0.60	-48.35	89
S-15	1/31/02	0:34	0.24	0.59	-45.75	81
S-16	1/31/02	2:34	0.24	0.56	-46.70	84
S-17	1/31/02	4:34	0.24	0.54	-47.24	85
S-18	1/31/02	6:34	0.24	0.53	-48.51	89
S-19	1/31/02	8:34	0.24	0.52	-49.60	92
S-20	1/31/02	10:34	0.24	0.51	-47.03	85
S-21	1/31/02	12:34	0.24	0.50	-49.15	91
post-event	2/10/02	12:00			-50.93	
pipe	1/29/02	12:00			-55.77	
pipe	2/1/02	12:00			-32.04	
rain	2/1/02				-18.64	

Isotopic data for hydrograph separation of September 15-21, 2002 storm event at the Saw Mill Brook sub-catchment.

ID	Date	Time	Cumulative precip (in)	Discharge (cfs)	$\delta\,^2H$ (per mil)	Old water (%)
S-1	9/15/02	21:03	0.08	0.01	-40.42	100
S-2	9/15/02	21:23	0.1	0.01	-40.77	99
S-3	9/15/02	21:43	0.13	0.01	-40.44	100
S-4	9/15/02	22:13	0.15	0.01	na	na
S-5	9/15/02	22:43	0.15	0.01	-40.62	99
S-6	9/15/02	23:13	0.16	0.01	-41.35	97
S-7	9/16/02	0:13	0.16	0.01	-40.63	99
S-8	9/16/02	1:13	0.16	0.55	-45.93	80
S-9	9/16/02	2:13	0.17	0.52	-42.97	91
S-10	9/16/02	3:13	0.19	0.40	-43.01	91
S-11	9/16/02	4:13	0.28	0.31	-45.12	83
S-12	9/16/02	6:13	0.33	3.51	-49.05	69
S-13	9/16/02	8:13	0.33	1.95	-66.69	6
stream	9/16/02	10:00	0.33	1.03	-67.86	2
S-14	9/16/02	15:25	0.36	0.24	-62.29	22
S-15	9/16/02	20:25	0.36	0.63	-60.90	27
S-16	9/17/02	1:25	0.36	0.14	-63.36	18
S-17	9/17/02	6:25	0.36	0.09	-66.50	7
S-18	9/17/02	11:25	0.36	0.07	-69.23	0
S-19	9/17/02	16:25	0.36	0.06	-66.90	6
S-20	9/17/02	21:25	0.36	0.05	-67.06	5
stream	9/18/02	12:00	0.36	0.05	-63.84	16
stream	9/21/02	12:00	0.36	0.01	-55.95	45
precipitation	9/16/02			0.01	-68.46	

APPENDIX C

SUPPORTING DATA FOR CHAPTER 3

Watershed area, population density and land use for Ipswich River sub-catchments (see chapter 3).

Name	Area (km^2)	Pop density (#/km^2)	Ag (%)	Forest (%)	Human (%)	Imperv (%)	Indust (%)	Open water (%)	Wetlands (%)
IS_160	1.9	20.1	13.2	55.9	6.6	1.3	0.2	0.1	24.0
IS_124	2.4	31.5	4.2	73.5	3.1	0.6	0.0	0.1	19.2
IS_170	4.2	53.0	28.2	37.0	12.8	2.6	0.0	0.2	21.7
IS_143	1.1	55.9	0.8	80.9	0.7	0.1	0.0	1.9	15.7
IS_142	1.4	56.4	0.1	80.2	0.1	0.0	0.0	0.0	19.5
IS_141	2.2	63.3	0.0	67.8	9.0	1.8	0.0	0.7	22.6
IS_127	1.3	69.4	0.0	63.2	9.8	2.0	0.0	5.1	21.8
IS_137	1.4	84.8	4.3	55.7	13.8	2.5	0.5	20.7	5.0
IS_133	2.2	86.2	1.6	56.7	11.4	4.7	4.2	0.2	25.9
IS_138	1.6	89.9	0.2	50.2	27.5	5.4	0.0	3.5	18.6
IS_132	1.9	119.5	6.2	55.4	16.3	3.2	0.0	0.1	22.0
IS_140	1.5	124.1	2.1	46.9	20.5	4.0	0.0	0.5	30.0
IS_147	1.6	126.6	1.5	46.4	24.6	4.8	0.0	7.4	20.0
IS_145	1.1	143.2	3.2	53.1	32.8	6.9	0.9	0.4	9.6
IS_148	1.8	145.4	4.5	54.4	22.9	4.6	0.0	0.0	18.1
IS_129	1.4	149.9	1.6	63.1	14.1	3.2	1.1	0.6	19.5
IS_172	1.4	157.4	27.3	15.1	34.8	6.9	0.0	0.8	22.0
IS_169	0.6	174.8	1.0	24.1	58.0	11.5	0.0	0.4	12.8
IS_162	0.8	194.8	13.4	30.5	18.5	15.1	9.1	1.0	25.6
IS_154	1.0	195.4	6.6	56.2	22.4	4.6	0.1	0.1	14.6
IS_150	1.1	201.5	2.3	46.1	17.4	19.2	16.8	0.0	17.5
IS_136	2.5	240.7	10.0	44.7	22.7	5.2	0.0	0.0	21.8
IS_173	2.1	270.7	22.0	27.8	25.0	11.8	5.6	0.5	19.1
IS_122	1.4	309.3	32.2	16.6	35.9	6.0	1.6	0.0	12.7
IS_167	1.7	317.2	0.0	53.7	21.9	12.6	6.5	0.6	15.3
IS_135	1.8	317.7	3.2	27.6	24.8	28.7	29.0	0.0	13.9
IS_155	1.5	328.7	1.8	31.6	45.6	10.5	1.6	0.1	19.3
IS_128	0.9	346.1	0.4	51.9	37.1	7.3	0.0	0.0	10.5
IS_175	2.2	361.9	19.9	44.9	23.8	7.8	0.9	0.2	10.3
IS_131	1.6	378.3	7.8	30.3	50.6	14.2	1.2	0.2	8.4
IS_152	1.5	418.7	3.7	33.4	55.6	11.7	0.4	0.1	6.8
IS_164	2.5	455.5	2.3	41.7	24.5	12.1	6.4	3.2	18.7

Watershed area, population density and land use for Ipswich River sub-catchments (cont'd).

Name	Area (km^2)	Pop density ($\#/km^2$)	Ag (%)	Forest (%)	Human (%)	Imperv (%)	Indust (%)	Open water (%)	Wetlands (%)
IS_118	1.9	466.0	3.8	37.4	45.8	9.7	0.0	3.1	9.8
IS_120	2.5	469.2	4.7	27.5	49.7	14.8	0.8	0.5	16.8
IS_107	2.8	510.7	5.7	30.4	44.3	9.5	1.1	10.5	5.6
IS_110	3.0	512.2	1.1	16.4	40.8	22.6	14.0	0.1	25.6
IS_111	1.1	531.5	0.7	17.2	23.8	26.6	20.3	0.3	36.0
IS_163	3.5	579.2	15.1	20.2	30.3	20.1	13.2	4.5	15.5
IS_166	0.8	650.3	0.2	26.5	56.9	15.4	0.0	0.4	15.4
IS_115	1.4	858.8	0.0	22.6	64.1	17.9	0.0	0.0	12.2
IS_104	1.4	887.5	5.9	11.7	63.6	20.4	2.5	0.0	13.3
IS_102	3.8	979.2	4.4	12.6	72.9	25.2	4.8	0.0	4.4
IS_161	0.9	1055.6	1.1	9.2	72.8	21.9	0.0	0.0	16.9
IS_103	0.6	1149.2	1.5	7.8	89.0	26.4	0.0	0.0	1.7

Watershed area, population density, percent on septic systems, percent on public water and surficial geology in Ipswich River sub-catchments (see chapter 3).

Name	Area (km^2)	Pop density ($\#/km^2$)	Pop on septic (%)	Pop on public water (%)	Alluvium (%)	Sand (%)	Till (%)
IS_160	1.9	20.1	100	98	0.0	67.1	32.5
IS_124	2.4	31.5	93	8	0.0	0.0	100.0
IS_170	4.2	53.0	100	100	12.0	52.1	32.7
IS_143	1.1	55.9	92	9	0.0	0.1	99.9
IS_142	1.4	56.4	92	9	0.0	4.3	95.6
IS_141	2.2	63.3	85	16	0.0	1.1	98.9
IS_127	1.3	69.4	91	97	0.0	3.7	96.2
IS_137	1.4	84.8	92	9	0.5	0.5	98.9
IS_133	2.2	86.2	4	99	0.0	14.5	85.3
IS_138	1.6	89.9	92	9	0.5	20.5	78.8
IS_132	1.9	119.5	23	98	0.0	0.0	100.0
IS_140	1.5	124.1	92	9	0.0	34.5	65.2
IS_147	1.6	126.6	94	9	13.7	51.3	34.5
IS_145	1.1	143.2	100	3	0.0	76.7	22.8
IS_148	1.8	145.4	91	59	0.0	75.4	24.2
IS_129	1.4	149.9	77	95	0.0	10.9	88.9
IS_172	1.4	157.4	58	96	0.0	69.9	0.5
IS_169	0.6	174.8	97	91	0.0	55.0	38.7
IS_162	0.8	194.8	99	98	0.0	48.6	48.6
IS_154	1.0	195.4	99	79	1.6	16.2	81.9
IS_150	1.1	201.5	100	0	0.0	60.4	39.1
IS_136	2.5	240.7	6	96	0.0	0.5	98.6
IS_173	2.1	270.7	49	96	5.6	64.1	30.1
IS_122	1.4	309.3	50	94	0.0	66.8	31.1
IS_167	1.7	317.2	22	98	4.8	30.8	53.4
IS_135	1.8	317.7	17	97	0.0	0.0	98.2
IS_155	1.5	328.7	98	83	0.0	69.7	30.1
IS_128	0.9	346.1	94	95	9.5	17.8	72.2
IS_175	2.2	361.9	30	96	0.0	36.6	62.9
IS_131	1.6	378.3	84	92	0.0	0.0	98.1
IS_152	1.5	418.7	93	96	0.0	49.4	50.2
IS_164	2.5	455.5	8	99	0.0	64.8	23.2

Watershed area, population density, percent on septic systems, percent on public water and surficial geology in Ipswich River sub-catchments (cont'd).

Name	Area (km^2)	Pop density ($\#/km^2$)	Ag (%)	Forest (%)	Human (%)	Imperv (%)	Indust (%)
IS_118	1.9	466.0	93	97	0.6	14.6	69.0
IS_120	2.5	469.2	83	74	0.0	40.2	59.4
IS_107	2.8	510.7	13	98	0.0	22.5	72.9
IS_110	3.0	512.2	43	100	33.0	49.1	13.7
IS_111	1.1	531.5	98	99	0.0	94.2	4.0
IS_163	3.5	579.2	34	91	0.0	28.9	69.1
IS_166	0.8	650.3	10	99	0.0	31.3	67.4
IS_115	1.4	858.8	20	98	0.0	21.0	76.4
IS_104	1.4	887.5	32	99	0.0	42.1	53.9
IS_102	3.8	979.2	7	97	6.3	15.5	76.6
IS_161	0.9	1055.6	100	91	0.0	92.6	7.3
IS_103	0.6	1149.2	9	100	0.0	0.6	99.4

Isotopic values ($^{15}N-NO_3$) and NO_3 concentrations in streams during summer (August 2003) and winter (February 2003) in sub-catchments of the Ipswich River watershed.

	$\delta^{15}N-NO_3$ (per mil)		NO_3 (µM)	
Site	**Summer**	**Winter**	**Summer**	**Winter**
IS-102	8.7	7.7	66.32	86.70
IS-104	11.0	9.6	96.16	83.08
IS-115	16.7	na	57.19	
IS-120	11.7	9.4	78.20	83.36
IS-128	11.9	na	181.39	na
IS-131	10.9	na	14.81	na
IS-141	2.4	na	4.14	na
IS-161	12.3	na	86.54	na
IS-172	na	0.6	na	3.34

Monthly NO_3 concentrations from sub-catchments of the Ipswich River watershed.

Site	Pop density (#/km^2)	NO$_3$ concentration (µM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_160	20	21.7	16.2	8.5	9.5	5.7	9.5	5.7	0.0	na	13.3	56.7	10.6
IS_170	53	na	17.6	20.5	16.7	13.1	8.1	18.4	84.4	na	48.0	4.6	15.0
IS_143	56	2.0	6.7	3.6	2.7	na	1.3	2.5	na	na	na	0.1	4.0
IS_127	69	11.8	31.6	50.1	37.0	35.1	61.3	8.0	na	na	na	25.2	40.4
IS_137	85	3.6	4.7	1.2	na	na	0.2	0.8	2.0	2.1	na	5.2	1.4
IS_132	119	7.8	1.7	1.4	0.5	0.0	0.4	2.0	0.5	0.4	0.5	0.5	0.5
IS_145	143	na	7.1	30.5	na	na	19.5	37.7	43.6	na	10.7	18.3	24.0
IS_148	145	2.1	7.2	3.2	2.8	0.2	0.7		na	na	2.8	0.1	na
IS_129	150	8.9	6.8	7.0	1.8	0.6	1.1	1.0	na	61.5	na	13.7	1.8
IS_162	195	1.8	18.6	7.5	3.8	5.0	4.2	5.2	na	na	2.7	8.8	4.8
IS_136	241	5.1	16.2	7.5	4.1	2.1	4.3	2.2	na	na	na	4.7	2.3
IS_167	317	2.7	5.1	3.2	2.4	0.5	0.3	0.4	na	na	na	4.2	2.4
IS_135	318	41.2	30.7	31.7	15.7	14.3	9.3	16.0	na	24.3	2.6	12.8	6.5
IS_128	346	96.0	73.3	80.2	65.4	64.3	79.6	137.8	na	na	na	45.1	63.4
IS_131	378	83.9	117.1	111.0	78.6	48.3	46.9	22.0	9.5	na	25.1	38.4	94.3
IS_152	419	93.3	112.0	120.3	99.1	na	na	89.2	76.9	104.3	74.1	63.3	92.4
IS_164	456	3.4	3.7	3.1	3.4	2.3	1.9	1.1	23.1	na	na	4.2	5.4
IS_118	466	44.5	40.8	38.9	33.9	21.8	25.1	20.0	54.6	na	12.1	23.3	34.7
IS_120	469	80.7	54.1	74.2	62.2	52.0	na	101.9	na	61.8	53.5	16.8	52.2
IS_110	512	28.1	25.7	26.6	22.8	36.0	14.1	4.7	na	48.1	80.3	20.3	8.3

Monthly NO_3 concentrations from sub-catchments of the Ipswich River watershed (cont'd)

Site	Pop density (#/km^2)	NO_3 concentration (μM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_111	532	55.8	10.7	11.3	12.9	6.4	9.9	9.2	na	na	na	127.2	8.8
IS_163	579	32.2	28.6	32.0	24.3	31.3	28.6	8.4	19.0	27.3	5.1	15.1	25.6
IS_166	650	41.7	43.4	46.1	35.8	20.6	38.5	55.6	80.9	125.3	49.3	25.0	41.3
IS_115	859	75.1	50.1	45.7		30.5	38.4	49.5	24.2	na	45.1	143.7	33.6
IS_104	888	96.8	77.8	75.8	55.8	49.5	68.3	61.2	93.6	27.5	61.3	59.2	50.7
IS_102	979	52.6	40.0	82.3	58.3	63.7	76.6	63.6	79.2	60.5	24.8	31.8	79.2
IS_161	1056	59.3	27.3	57.9	44.6	48.6	73.3	19.5	194.7	na	26.5	6.0	47.6
IS_103	1149	48.4	70.0	77.7	57.1	58.4	65.9	42.4	21.3	32.2	16.1	51.0	59.3

Monthly NH_4 concentrations from sub-catchments of the Ipswich River watershed.

Site	Pop density (#/km^2)	NH$_4$ concentration (μM) on sampling date											
		12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_160	20	7.3	2.6	2.2	2.6	4.6	10.2	15.1	37.2	na	5.6	7.6	2.0
IS_170	53	na	2.8	1.6	1.6	2.7	3.8	9.7	9.8	na	4.0	2.5	2.2
IS_143	56	1.4	4.9	2.2	1.2	na	2.3	5.0	na	na	na	1.6	7.2
IS_127	69	6.8	4.7	4.2	4.3	4.4	6.5	35.2	na	na	na	8.1	3.2
IS_137	85	2.8	2.5	1.0	na	na	1.0	2.7	35.9	2.4	na	2.8	1.0
IS_132	119	3.7	2.4	2.1	1.7	2.4	3.2	10.0	10.0	9.7	6.2	5.5	3.9
IS_145	143	na	2.0	1.2	na	na	1.8	4.0	3.1	na	2.2	2.5	1.0
IS_148	145	1.4	1.4	1.4	1.3	2.1	2.5	na	na	na	1.1	1.9	na
IS_129	150	3.8	3.0	2.9	1.7	1.7	2.5	12.6	na	7.1	na	3.9	2.8
IS_162	195	2.7	3.2	2.0	1.8	3.9	5.3	16.4	na	na	5.1	5.0	2.8
IS_136	241	2.8	2.3	2.0	1.5	2.1	5.6	13.4	na	na	na	5.7	2.2
IS_167	317	4.8	1.6	1.8	1.9	1.8	2.1	14.1	na	na	na	6.2	2.1
IS_135	318	9.9	15.6	13.3	3.1	3.3	4.4	16.1	na	10.4	18.8	2.4	9.5
IS_128	346	16.3	11.5	11.6	8.3	10.2	10.2	16.2	na	na	na	5.5	10.0
IS_131	378	5.3	6.3	2.5	2.6	3.6	4.1	10.5	3.5	na	3.5	2.4	3.6
IS_152	419	20.6	13.8	12.4	11.6	na	na	15.4	23.9	53.1	40.4	9.2	7.8
IS_164	456	2.1	4.3	1.6	2.6	2.2	3.0	3.8	16.2	na	na	0.9	4.5
IS_118	466	4.4	5.5	3.3	3.4	2.7	5.5	25.4	3.6	na	1.7	2.4	2.4
IS_120	469	4.1	5.3	6.0	5.7	4.0	na	5.2	na	6.3	4.7	3.6	6.0
IS_110	512	23.0	12.8	7.8	4.9	3.7	9.3	21.6	na	29.8	4.2	6.5	5.6

Monthly NH_4 concentrations from sub-catchments of the Ipswich River watershed (cont'd).

Site	Pop density (#/km^2)	NH$_4$ concentration (µM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_111	532	3.5	3.2	3.0	1.7	2.0	3.6	19.0	na	na	na	12.9	2.9
IS_163	579	5.4	3.1	2.8	2.0	19.8	4.6	6.3	0.9	7.9	3.6	2.8	1.8
IS_166	650	10.8	9.7	4.7	3.9	4.9	11.4	23.9	6.6	19.1	9.4	3.9	4.0
IS_115	859	9.4	2.5	2.3	na	4.2	5.2	15.1	2.7	na	9.2	5.3	2.4
IS_104	888	10.8	9.3	8.1	5.6	8.7	10.5	16.5	11.8	16.0	16.3	3.1	4.8
IS_102	979	na	6.2	10.0	5.0	5.2	8.8	7.6	6.1	13.0	6.9	3.0	7.0
IS_161	1056	8.4	4.8	6.1	5.5	10.8	8.7	9.8	11.4	na	7.1	4.8	3.5
IS_103	1149	7.1	7.4	8.5	4.9	10.9	10.4	19.0	7.0	9.7	3.7	4.3	5.7

Monthly PO_4 concentrations from sub-catchments of the Ipswich River watershed.

Site	Pop density (#/km^2)	PO$_4$ concentration (μM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_160	20	0.25	0.18	0.24	0.18	0.53	0.76	1.00	2.38	na	0.91	0.48	0.14
IS_170	53	na	0.46	0.19	0.14	0.40	0.33	0.48	0.85	na	0.14	0.39	0.29
IS_143	56	0.03	0.31	0.18	0.13	na	0.25	0.28	na	na	na	0.23	0.12
IS_127	69	0.32	0.26	0.31	0.26	0.71	0.97	4.21	na	na	na	0.90	0.32
IS_137	85	0.07	0.18	0.05	na	na	0.06	0.15	1.42	0.09	na	0.13	0.11
IS_132	119	0.21	0.15	0.13	0.11	0.20	0.19	0.60	1.02	0.40	0.37	0.24	0.18
IS_145	143	na	0.39	0.17	na	na	0.25	0.17	0.45	na	0.06	0.21	0.15
IS_148	145	0.16	0.26	0.28	0.21	0.27	0.17		na	na	0.29	0.13	na
IS_129	150	0.32	0.33	0.58	0.28	0.57	0.66	1.25	na	0.18	na	0.88	0.40
IS_162	195	0.18	0.13	0.12	0.12	0.47	0.38	0.51	na	na	0.73	0.33	0.18
IS_136	241	0.27	0.13	0.09	0.05	0.42	0.58	0.97	na	na	na	0.29	0.13
IS_167	317	na	na	na	na	na	na	na	na	na	na	na	na
IS_135	318	0.09	0.12	0.23	0.11	0.29	0.50	0.72	na	0.50	1.51	0.46	0.42
IS_128	346	0.23	0.30	0.33	0.09	0.32	0.05	0.29	na	na		0.22	0.12
IS_131	378	0.43	0.30	0.25	0.27	0.41	0.26	0.61	0.46	na	0.47	1.82	0.35
IS_152	419	0.20	0.33	0.27	0.34	na	na	0.07	0.34	0.03	0.07	0.14	0.17
IS_164	456	0.14	0.02	0.20	0.13	0.11	0.28	0.17	0.54	na	na	0.15	0.16
IS_118	466	0.19	0.32	0.21	0.15	0.23	0.20	0.31	0.56	na	0.35	0.40	0.14
IS_120	469	0.17	0.37	0.36	0.39	0.40	na	0.49	na	0.96	0.51	na	0.19
IS_110	512	0.39	0.30	0.15	0.15	0.17	0.25	0.23	na	1.21	0.07	0.22	0.09

Monthly PO_4 concentrations from sub-catchments of the Ipswich River watershed (cont'd)

Site	Pop density (#/km^2)	PO$_4$ concentration (µM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_111	532	0.51	0.51	0.21	0.17	0.31	0.25	0.79	na	na	na	0.73	0.15
IS_163	579	0.18	0.20	0.29	0.15	0.47	0.37	0.34	0.42	0.41	0.23	0.32	0.16
IS_166	650	0.10	0.34	0.22	0.16	0.14	0.20	0.44	0.40	0.17	0.49	0.19	0.20
IS_115	**859**	0.26	0.33	0.26	na	0.50	0.28	0.69	0.38	na	0.49	1.68	0.28
IS_104	**888**	0.09	0.30	0.25	0.11	0.40	0.03	0.22	0.34	0.21	0.12	0.14	0.11
IS_102	**979**	na	0.10	0.36	0.10	0.45	0.27	0.05	0.05	0.34	0.36	0.28	0.16
IS_161	**1056**	0.18	0.12	0.25	0.27	0.80	0.63	0.77	0.51	na	0.48	0.36	0.38
IS_103	**1149**	0.32	0.45	0.99	0.32	0.79	0.25	0.26	1.37	2.43	1.10	0.23	0.25

Monthly SiO_2 concentrations from sub-catchments of the Ipswich River watershed.

Site	Pop density (#/km^2)	SiO_2 concentration (μM) on sampling date 12/30/01	1/27/02	2/24/02	3/17/02	4/28/02	5/26/02	6/28/02	7/28/02	8/25/02	9/29/02	10/27/02	11/24/02
IS_160	20	na	175.80	161.60	152.41	150.04	77.31	122.75	178.68	na	268.01	156.29	116.81
IS_170	53	na	167.19	131.36	133.22	151.10	69.64	119.13	251.55	na	262.73	88.98	110.75
IS_143	56	na	152.37	156.69	na	na	125.76	143.87	143.09	na	119.60	136.95	163.32
IS_127	69	162.64	113.96	118.59	114.12	113.48	55.13	101.22	na	na	na	137.03	73.29
IS_137	85	52.23	41.83	12.63	na	na	13.43	3.43	62.77	16.23	na	29.42	16.36
IS_132	119	79.82	127.11	93.79	41.32	72.06	13.00	13.22	12.22	15.16	21.80	58.65	122.88
IS_145	143	102.59	160.70	134.95	102.42	106.92	90.68		na	na	252.71	136.56	na
IS_148	145	na	157.62	148.55	na	na	98.06	133.87	na	na	na	98.50	126.18
IS_129	150	41.8	184.58	114.29	125.83	122.12	43.54	51.22	na	209.35	na	151.45	80.40
IS_162	195	na	113.71	100.99	101.50	69.40	31.93	52.23	na	na	53.99	147.97	55.40
IS_136	241	289.69	204.31	143.73	90.60	70.00	30.08	73.71	na	na	na	194.37	51.88
IS_167	317	na	103.86	147.51	128.63	81.78	11.61	50.74	na	na	na	150.15	86.92
IS_135	318	48.94	129.40	170.76	115.95	172.14	126.10	120.28	na	28.77	106.40	80.62	95.84
IS_128	346	na	204.77	186.72	163.70	159.99	128.24	196.55	na	na	na	148.87	180.58
IS_131	378	159.83	194.37	168.59	147.83	160.46	144.99	153.63	74.58	na	315.77	176.50	159.43
IS_152	419	na	194.31	200.60	187.72	na	na	70.29	182.96	190.88	259.23	161.44	199.23
IS_164	456	na	14.42	30.09	29.97	16.16	19.83	66.94	93.83	na	na	47.28	15.30
IS_118	466	146.68	143.48	135.54	133.46	72.39	79.98	119.05	95.53	na	na	126.63	170.16
IS_120	469	155.36	197.73	199.32	181.72	175.33	na	221.36	na	61.47	155.61	na	176.23
IS_110	512	na	188.32	160.54	146.41	71.35	105.70	112.80	na	24.15	191.62	152.29	147.76

Monthly SiO_2 concentrations from sub-catchments of the Ipswich River watershed (cont'd)

Site	**Pop density (#/km^2)**	**SiO_2 concentration (μM) on sampling date**											
		12/30/01	**1/27/02**	**2/24/02**	**3/17/02**	**4/28/02**	**5/26/02**	**6/28/02**	**7/28/02**	**8/25/02**	**9/29/02**	**10/27/02**	**11/24/02**
IS_111	532	221.96	101.18	88.05	130.90	118.45	7.02	30.66	na	na	na	221.56	41.80
IS_163	579	na	138.54	169.23	148.51	84.92	123.52	134.78	226.00	24.07	247.32	127.41	na
IS_166	650	na	185.54	175.10	143.72	24.88	102.25	25.33	176.50	162.54	287.12	157.60	137.70
IS_115	859	195.37	179.41	165.88	95.84	170.98	156.74	171.10	93.18	na	137.06	na	149.56
IS_104	888	na	183.85	199.36	186.40	178.60	171.25	158.04	220.88	146.00	202.14	109.39	168.84
IS_102	979	na	93.12	202.80	161.35	198.55	190.22	228.05	194.10	21.31	162.67	165.41	227.14
IS_161	1056	na	176.24	179.37	166.29	132.54	122.98	119.95	260.18	na	181.91	109.32	175.82
IS_103	1149	na	197.04	na	197.39	169.97	170.49	155.54	91.99	8.11	138.72	32.83	200.65