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The effects of land use on stream nitrate dynamics

Cara J. Poor [a,*], Jeffrey J. McDonnell [b]

[a] *Department of Civil and Environmental Engineering, Washington State University, 118 Sloan Hall, Pullman, WA 99164-2910, United States*
[b] *Department of Forest Engineering, Oregon State University, 204 Peavy Hall, Corvallis, OR 97331-5706, United States*

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Summary The effects of land use and land use change on stream nitrate are poorly understood. While case studies have been presented, most process work has been done in areas with one land use (minimally disturbed or agricultural) and areas with substantial atmospheric deposition. In this paper we present results from three neighboring headwater catchments in western Oregon with similar (low) atmospheric deposition, size, and geology but with different, spatially consistent land use expressions: forest, agriculture, and residential. The climate in western Oregon has a distinct pattern of a three-month rainless period in the summer, a wetting up with many storms in the fall and winter, and a decrease of storms in the spring. We investigate how human activity alters the export of nitrate, whether the input of nitrate changes throughout the year which may affect storm response (i.e., depletion of soil water nitrate, addition of fertilizer, etc.), and how the changing contribution of source waters throughout the year affects streamflow concentrations. Our results showed marked differences in export rates between the three catchments. The forested catchment showed minimal export for three monitored storms (fall, winter, spring) through the seasonal wetting up of the catchments, and the residential catchment showed high export for all three storms. While the agricultural catchment displayed elevated export in the fall (similar to the residential catchment), exports decreased progressively throughout the rainy period (following late summer manure and green bean application). Overall, our results of storm event nitrate concentrations suggest that varying nitrate inputs have a large affect on nitrate dynamics. While within-storm nitrate concentration response patterns in the residential catchment were the same as the patterns in the reference forested catchment (a ''concentration'' pattern throughout the year), a ''dilution'' pattern was observed in the fall and winter and a ''concentration'' pattern was observed in the spring in the agricultural catchment.
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* Corresponding author. Tel.: +1 509 335 4547.
E-mail address: cpoor@wsu.edu (C.J. Poor).

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Introduction

Increases in nitrogen inputs in the last 50 years have caused great concern for the health of stream ecosystems (Pimentel, 1993; Howarth et al., 2002). Nitrogen inputs from human activity have doubled in the United States from 1961 to 1997 (Howarth et al., 2002). In general, approximately one-third of nitrogen inputs to catchments are exported, with the majority exported to surface waters (Howarth et al., 2002). This increase in export to surface waters has been shown to cause algal blooms, which in turn cause hypoxia and ''dead'' zones for fish (National Science and Technology Council, 2000; Rabalais et al., 2002; National Research Council, 2000). Episodic acidification of streams has also resulted from increased nitrate levels (Wigington et al., 1996a,b; Wellington and Driscoll, 2004).

Not surprisingly, land use has been found to have a large effect on the amount of nitrogen exported to the stream (Salvia-Castellvi et al., 2005; Schilling, 2002; Jordan et al., 1997; Owens et al., 1991; Howarth et al., 2002; Jordan and Weller, 1996; Johnson et al., 1997; Herlihy et al., 1998; Wernick et al., 1998; Arheimer and Liden, 2000; Jones et al., 2001; Wayland et al., 2003; Donner et al., 2004; Woli et al., 2004; Buck et al., 2004; Lattin et al., 2004; Little et al., 2003). Since a significant portion of nitrogen export from catchments is due to non-point source fertilizer runoff, the proportion of agricultural land in a catchment is often correlated to stream nitrate export (Howarth et al., 2002). Nitrogen export is generally greater in rivers draining more densely populated catchments (Jordan and Weller, 1996). This may be due to sewage inputs or deposition and subsequent runoff of NO_x emissions. The majority of the work on land use effects has focused on baseflow or a small number of sampling events correlating land use and nitrate (Johnson et al., 1997; Herlihy et al., 1998; Wernick et al., 1998; Arheimer and Liden, 2000; Jones et al., 2001; Wayland et al., 2003; Donner et al., 2004; Woli et al., 2004; Buck et al., 2004; Lattin et al., 2004; Little et al., 2003; Schilling, 2002). While it is clear that land use affects the magnitude of nitrate and other nutrients exported from catchments, it is not clear how it affects nutrient dynamics or the nutrient concentration pattern during storm events.

A few studies have been conducted in catchments with mixed land use during storm events; however, much of the work has been concerned with monthly exports, and little is shown of nitrate concentrations varying with discharge dynamics (Jordan et al., 1997; Owens et al., 1991; Bolstad and Swank, 1997; Salvia-Castellvi et al., 2005). Results are shown as a baseflow index or monthly averages (Jordan et al., 1997; Owens et al., 1991; Salvia-Castellvi et al., 2005). Alternatively, one event or the ''typical'' response for a catchment is shown (Salvia-Castellvi et al., 2005; Bolstad and Swank, 1997). These studies, in addition to studies conducted in forested or agricultural catchments, either show a ''concentration'' pattern, where nitrate concentrations increase with increasing flow rates and essentially mimic the storm hydrograph, or a ''dilution'' pattern, where nitrate concentrations decrease with increasing flow rates as a mirror image of the hydrograph (Salvia-Castellvi et al., 2005; Bolstad and Swank, 1997; Webb and Walling, 1985; Petry et al., 2002; Vanni et al., 2001; Inamdar et al., 2004; McHale et al., 2002; Burns et al., 1998). During storm events, nitrate may be quickly mobilized to the stream (Creed et al., 1996; Creed and Band, 1998; McHale et al., 2002). The magnitude of nitrate concentrations undoubtedly vary throughout the year due to the ''wetting-up'' and ''drying-down'' of the catchment, but how do these storm patterns change with season? While the strong links between hydrology and nitrate are well established, most studies to date have been conducted predominantly in either minimally disturbed environments or agricultural areas.

We argue that further investigation of the seasonality of nitrate dynamics during storm events should occur in catchments with varying land uses. In order to understand the behavior of solutes during storm events, studies need to be conducted in areas with major disturbances (Burns, 2005). Here, we present a study that examines the seasonality of nitrate dynamics in three catchments with similar physical characteristics (area, geographic proximity, geology, soils, topography, elevation) but different land uses. Storm events were monitored in this Mediterranean climate from the end of a 3-month rainless period through a clear progression of wet-up and potential flushing events. We explore how human activity alters the export of nitrate. In addition, we determine whether or not the input of nitrate changes throughout the year, which may affect storm response (i.e., depletion of soil water nitrate, addition of fertilizer, etc.), and how the changing contribution of source waters throughout the year affects streamflow concentrations.

Site description

The three study catchments are each on the order of 50 ha and are sub-basins of the 33 km^2 Oak Creek Watershed, located near Corvallis, Oregon, USA (Fig. 1). This area is located in the Pacific Northwest of the United States in a region virtually devoid of atmospheric nitrogen deposition (annual rate of approximately 1.52 kg/ha/year, http://nadp.sws.uiuc.edu/nadpdata/annualReq.asp?site=OR97). The climate in the Pacific Northwest is relatively mild and often described as a mediterranean climate, with dry summers and wet winters. Average temperature in the Oak Creek Watershed is 11.5 °C, and mean annual precipitation is approximately 111 cm/year (Oregon Climate Service, www.ocs.oregonstate.edu). The majority of the precipitation falls during the rainy season (November–June). Minimal snowfall occurs in the catchment, with snowmelt occurring 1–2 days after the event. The Oak Creek Watershed has clear and well-defined land uses expressed within its subcatchments. The upper portion of the watershed is a minimally disturbed, second growth Douglas Fir forest. The mid-portion of the watershed is primarily agricultural (sheep and cattle grazing, growth of clover, wheat, and fescue) with small inholdings of residential areas. Land use in the lower portion of the watershed consists of urban residential and the Oregon State University campus. Each study catchment has a clean expression of land use (forested, agricultural, residential) and shares approximately the same headwater divide.

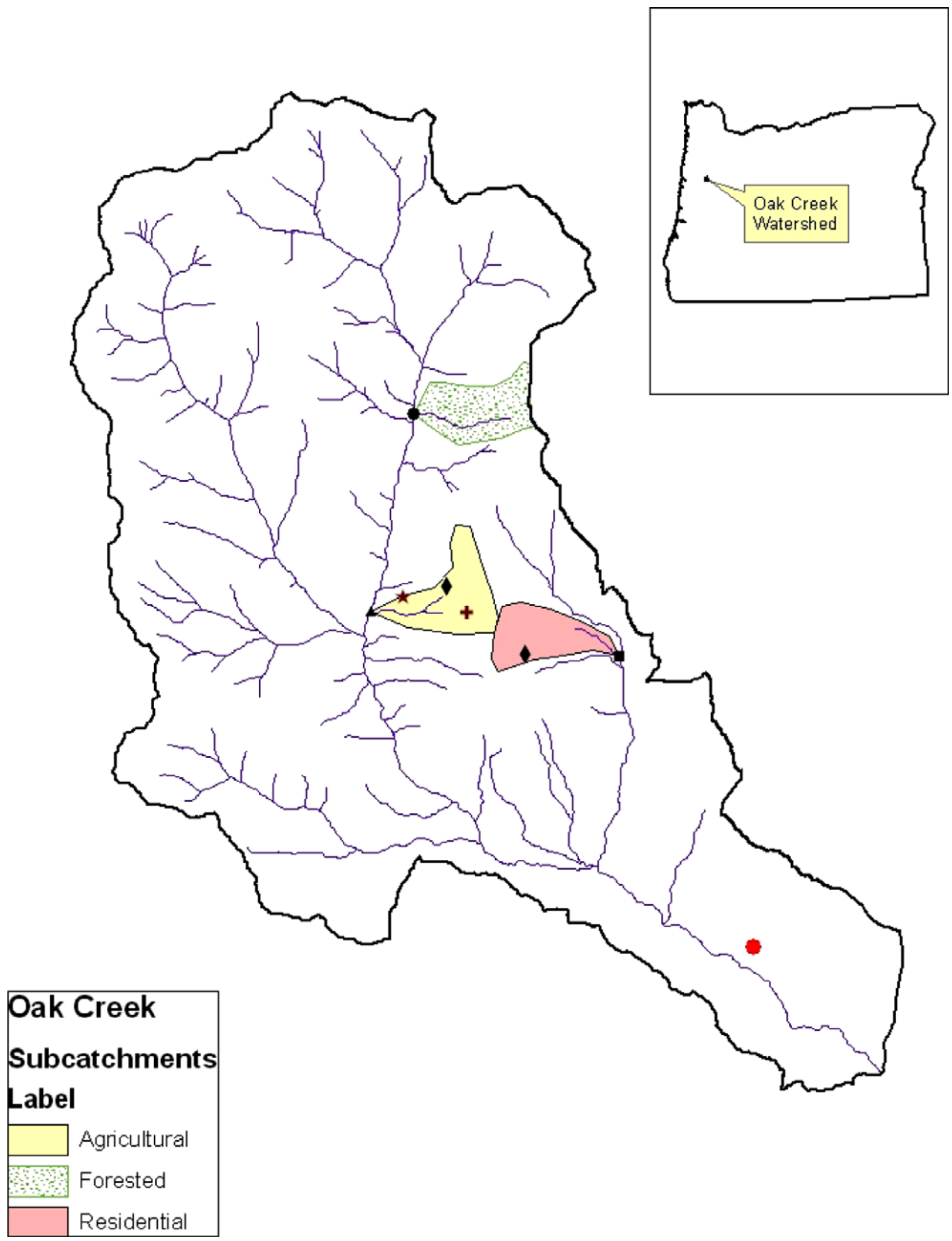

Figure 1 Oak Creek Watershed and study catchments. Rain gage location = ●, well locations in agricultural and residential catchments = ⧫, groundwater seep = ★, soil pipe = ✚, sampling point in the forested catchment = ●, sampling point in the agricultural catchment = ▲, and sampling point in the residential catchment = ■.

Forested catchment

The 49.5-ha forested catchment is minimally disturbed (Fig. 1) and is drained by a first-order stream. Land use is entirely forested with approximately 1750 m of abandoned gravel roads. Elevation ranges from 152 to 450 m. Additional physical features of the forested catchment are listed in Table 1. Vegetation consists mainly of Douglas Fir, alder, ash, sword ferns, blackberry, and various weed species. The soil in the catchment is classified as the Dixonville–Philomath association, which is moderately deep (approximately 1 m of weathered basalt bedrock), well-drained silty clay loams and shallow, well-drained silty clays (Soil Conservation Service, 1975). The ~30 cm-thick surface layer consists of silty clay loam and silty clay, and the ~60 cm-thick subsurface layer consists of silty clay and clay. Underlying geology is mafic volcanic.

Agricultural catchment

The 52.2-ha agricultural catchment is located within the Wilson Sheep Farm, where 325 sheep are rotated through the catchment and neighboring 100 ha of pasture land. The sheep are confined in a building for several weeks when the ewes are lambing, and graze in the catchment the rest of the year, rotating weekly to biweekly amongst the fields. The manure generated during the lambing period is kept under roof throughout the winter and applied to the fields in

Table 1 Physical features of study catchments

	Site		
	Forested[a]	Agricultural[a]	Residential[b]
Watershed area (ha)	49.5	52.2	42.9
Tree cover (%)	98.1	52.8	83.1
Mean slope (%)	22.7	12.4	15.1
Mean TI	6.42	6.84	6.56
Elevation density (ft)	298	158	84
Drainage density (km/km^2)	1.95	1.78	1.20
Road density (km/km^2)	3.55	1.20	5.64

[a] All roads are unpaved.
[b] All roads are paved.

the summer when conditions are dry. Green bean waste is also applied to fields in the summer. The sampling site for the agricultural catchment is shown in Fig. 1. This catchment is drained by a second-order ephemeral tributary to Oak Creek that flows through grass fields. Land use is entirely agricultural with approximately 625 m of gravel road leading to the main sheep barn and one outbuilding. The catchment varies in elevation from 116 to 274 m. Additional physical features of the agricultural catchment are listed in Table 1. Approximately 62 kg N/ha of manure and green beans are spread in the summer onto fields. Grazing animals input approximately 0.25 kg N/ha/day as manure to the catchment throughout the year (except in February and March during the lambing period), based on data supplied to us by the Oregon State University sheep farm manager (Tom Nichols, personal communication, 2004) and published numbers for average manure production per sheep and quantity of nitrogen per kg of manure (American Society of Agricultural Engineers, 2003). This large input of nitrogen will likely affect streamflow quality during the grazing period and when stored manure is applied. Unlike the perennial flow in the forested catchment, stream flows in the agricultural catchment are continuous during the rainy season but discontinuous in the summer months. The main vegetation consists of blackberry adjacent to the stream and grass fields interspersed with oak and ash throughout the catchment. Soil type is classified as the Waldo–Bashaw association, which include poorly drained silty clay loams and clays (Soil Conservation Service, 1975). Approximate depth to bedrock is 2 m, and the underlying geology is mafic volcanic.

Residential catchment

The 42.9-ha residential catchment shares a portion of the agricultural catchment's drainage divide, and is heavily wooded. Land use is entirely residential, including a park with woodlands and marshes in the lower portion of the catchment. Some sections of the catchment are hardened (i.e., runoff or rainfall cannot infiltrate into the soil in these areas) by paved streets, concrete lining of the stream, and storm drains that empty directly into the stream channel. Impervious areas cover approximately 15% of the catchment. Housing density (2.7 houses/ha) is relatively low compared to most residential neighborhoods, with houses on 0.1-ha lots and approximately 3950 m of sanitary sewer lines in the upper portion of the catchment. Although much of the catchment is wooded and some natural features have remained, land use in the catchment is significantly different from the forested catchment due to the paved streets, concrete lining of the stream, storm drains, and houses. Elevation varies from 116 to 200 m. Additional physical features of the residential catchment are listed in Table 1. The main vegetation consists of Douglas Fir, alder, ash, sword ferns, and blackberry mixed with lawns and ornamental shrubs. In the lower portion of the catchment, the stream flows through a park, which contains a marshy area, baseball fields, and lawns. Soil type is classified as the Waldo–Bashaw association, which are poorly drained silty clay loams and clays (Soil Conservation Service, 1975). Approximate depth to bedrock is 2 m, and the underlying geology is mafic volcanic. The only known anthropogenic input of nitrogen is sporadic fertilization of lawns and bushes by homeowners in the upper portion of the catchment.

Methods

Stream chemistry was sampled at the outlets of the three catchments during one of the first fall storms (12/9/2003), following a 3-month summer drought. We refer to this as the ''wetting up'' period (i.e., the beginning of the 2003–2004 water year). A winter storm on 2/23/2004 was sampled at each catchment outlet when water tables at each of the sites were close to the surface. A spring storm on 4/13/2004, when each catchment was beginning to dry out, was also sampled. Three ISCO Model 1672 autosamplers were used at sampling locations for hourly sampling on the rising limb of the hydrograph and a bi-hourly sampling on the falling limb. Biweekly grab samples were taken at each site during the 2003–2004 field season (and when the agricultural stream was flowing – from November 2003 to June 2004).

Biweekly soil water samples were also taken at each site during the 2003–2004 field season from porous-cup tension lysimeters. Lysimeters for each site were located <2 m laterally and <10 m longitudinally from the stream sampling point, and were approximately 53, 76, and 48 cm deep in the forested, agricultural, and residential catchments, respectively. Groundwater samples were taken on 2/19/2004 from an existing shallow well ~24 m deep in the agricultural catchment (Tom Nichols, personal communication, 2004), and on 7/20/2003 and 7/23/2004 from a deeper residential well in the residential catchment (see Fig. 1 for locations). The exact depth of the residential well is unknown; however, several other wells in the area are ~60 m deep. Additional samples were taken from a groundwater seep and soil pipe in the agricultural catchment on 2/19/2004.

Flow was gauged at stream sections with good natural flow control. We used TRUTRACK Inc. capacitance rods to measure stage height at 10-min intervals throughout the year. We used the salt-dilution technique of Gordon et al. (1992) to establish rating curves for each gauging position. From these relationships, flow rates were determined for the sampling period. There is some uncertainty in flow rates due to uncertainties in the rating curves from the natural flow control sections and due also to the estimates of watershed area based on a 30-m DEM. Uncertainty was quantified from the difference in flow measurement data and the approximated rating curve, and was ±14.87%, ±6.87%, and ±4.48% for the forested, agricultural, and residential hydrographs, respectively. Uncertainties are shown as a percentage due to the nature of stream flow gauging; fewer measurements were made at the higher flows and therefore there is more uncertainty. This uncertainty is shown in the hydrographs as a band of upper and lower flow rates. Precipitation data were obtained from a Met One model 385 tipping bucket rain gauge located within the Oak Creek Watershed at the point shown in Fig. 1. We computed 7-day and 30-day API using the method of Mosley (1979). Biweekly precipitation chemistry data were obtained from the NADP Hyslop Farm site (latitude 44.6347, longitude 123.19), which is approximately 10 km northeast of the Oak Creek Watershed (http://nadp.sws.uiuc.edu/nadpdata/annualReq.asp?site=OR97).

Samples were preserved and collected according to Standard Methods for the Examination of Water and Wastewater (Clesceri et al., 1998). Sample bottles were rinsed with hydrochloric acid and deionized water before use. When the autosamplers were used, the bottles filled automatically through a rinsed tube. Samples were taken from the middle of the channel at mid-depth in fast-moving water to ensure adequate mixing. When grab samples were taken, the bottle was rinsed three times with stream water, and then filled beneath the water surface. Conductivity, pH, and temperature were measured during sampling. All collected samples were analyzed for nitrate, DOC, and major anions and cations. Samples were filtered with Whatman 0.7 μm glass fiber syringe filters within 24 h of collection. Dissolved organic carbon was measured using a Dohrmann DC-190 Total Organic Carbon Analyzer. Nitrate, sulfate, chloride, and fluoride were measured using a Dionex Model DX 500 Ion Chromatograph. A Varian Liberty 150 ICP Atomic Emission Spectrophotometer was used to determine potassium, calcium, sodium, magnesium, and silica concentrations. All samples were measured in duplicate to determine the reliability of methods, and uncertainty was quantified from the standard deviation. Due to the accuracy of the instruments, uncertainty was very small and thus not decipherable in the resulting plots.

Results

Hydrologic response to storm events

Characteristics of storm 1 (from 12/9/2003 to 12/12/2003), storm 2 (from 2/23/2004 to 2/25/2004), and storm 3 (from 4/13/2004 to 4/16/2004) are shown in Table 2. Rainfall duration and total rainfall ranged from 15 to 24 h and 17–26 mm, respectively. Ranges for the 7-day and 30-day API were 0–18 and 0.5–31 mm, respectively. The 7-day API for storm 3 was zero, indicating that no precipitation occurred 7 days before the rain event. Storm 1 had the lowest intensity (22.9 mm in 24 h) and highest API (7-day API of 18.3), whereas storm 3 had the highest intensity (25.5 mm in 17 h) and lowest API (7-day API of 0.0). Although the API is higher during storm 1 (fall) than storm 2 (winter), the total seasonal precipitation is higher in the winter (Table 3). The wetter conditions in the winter are also re-

Table 2 Characteristics of storms 1 (from 12/9/2003 to 12/12/2003), 2 (from 2/23/2004 to 2/25/2004) and 3 (from 4/13/2004 to 4/16/2004)

Storm	Total rainfall (mm)	Rain duration (h)	7-Day API (mm)	30-Day API (mm)
1	22.9	24	18.3	30.6
2	16.7	15	3.7	13.6
3	25.5	17	0.0	0.6

Table 3 Seasonal precipitation and baseflow for the catchments

	Season		
	Fall	Winter	Spring
Total precipitation (mm)	415	521	153
Average baseflow (mm/h)			
Forested	0.019	0.061	0.039
Agricultural	0.002	0.064	0.018
Residential	0.075	0.130	0.86

Table 4 Catchment response to storms

	Site		
	Forested	Agricultural	Residential
Nitrate export rate (kg/ha/storm)			
Storm 1	0.012	0.121	0.131
Storm 2	0.005	0.040	0.108
Storm 3	0.010	0.021	0.131
Runoff ratio			
Storm 1	0.105	0.094	0.326
Storm 2	0.092	0.168	0.319
Storm 3	0.056	0.145	0.229
Peak discharge (mm/h)			
Storm 1	0.173	0.208	0.256
Storm 2	0.142	0.497	0.422
Storm 3	0.077	0.216	0.289
Baseflow (mm/h)			
Storm 1	0.062	0.007	0.071
Storm 2	0.067	0.084	0.110
Storm 3	0.040	0.017	0.141
Hydrograph response time (h)			
Storm 1	3.7	1.0	1.3
Storm 2	7.2	0.0	2.3
Storm 3	2.7	2.0	0.0
Time to peak (h)			
Storm 1	15.0	11.3	19.3
Storm 2	7.0	13.7	15.3
Storm 3	25.0	22.3	35.2

Spring storm produced two peaks. Time to peak and peak flow is shown for the second peak in the hydrograph.

flected in the higher baseflows. Higher winter baseflows are due to the fall wet-up; after the 3-month dry period fall storms wet-up the catchment. A significant response to these fall storms is delayed until the winter, when additional rainfall creates saturated conditions.

Catchment response to each storm was variable (Table 4). Runoff ratios increased with increasing development, with the highest ratios in the residential catchment (0.23–0.33) and the lowest ratios in the forested catchment (0.05–0.10). One exception was the runoff ratio in the agricultural catchment during storm 1 (0.09), which was about the same as the runoff ratio in the forested catchment (0.10). Runoff ratio in the agricultural catchment ranged from 0.09 to 0.17. Runoff ratios were still highest in the residential catchment during storm 1 (0.33). Baseflow was highest in the residential catchment during all storms (0.071–0.141 mm/h), and increased through the rainy period as the catchment became more hydrologically connected. Baseflow in the forested catchment stayed relatively constant, ranging from 0.040 to 0.067 mm/h. With the exception of storm 2, the agricultural catchment had the lowest baseflow (0.007–0.084 mm/h). Baseflow increased to 0.084 mm/h in the winter then decreased, which reflects the ephemeral nature of the stream. Peak discharge also generally increased with increasing development, except for storm 2, where peak flows in the agricultural catchment (0.50 mm/h) were higher than peak flows in the residential catchment (0.42 mm/h). Peak discharge ranged from 0.08 to 0.17 mm/h in the forested catchment, 0.21–0.50 mm/h in the agricultural catchment, and 0.26–0.42 mm/h in the residential catchment.

Time to peak (defined as the time from the start of the rising limb of the hydrograph to the peak) ranged from 7 to 25 h in the forested catchment, 11–22 h in the agricultural catchment, and 15–35 h in the residential catchment. Time to peak was longer for the forested catchment than the agricultural catchment during storms 1 and 3, but increased with increasing development for storm 2. Time to peak was the longest in the residential catchment during all storms. Hydrograph response time was the longest for the forested catchment during all storms (2.7–7.2 h). Hydrograph response time (defined as the time from the onset of rainfall to the start of the rising limb of the hydrograph) varied between 0.0–2.0 and 0.0–2.3 h in the agricultural and residential catchments, respectively. Although it appears that time to peak increased with increasing development during storm 2, the hydrograph from the agricultural catchment peaks first when taking hydrograph response time into account (Figs. 2–4). During all storms, the agricultural hydrograph peaks first, followed by the forested hydrograph, then the residential hydrograph. Only the agricultural hydrograph is shown for clarity, with arrows showing the peaks of the forested and residential hydrograph.

Nitrate response to storm events

Export rates of nitrate in all catchments were highest during storm 1. Rates in the forested, agricultural, and residential catchments were 0.012, 0.121, and 0.131 kg/ha/storm, respectively. Fig. 5 shows export rates for each catchment during the three storms, with uncertainty bars that have been carried through from the hydrograph uncertainty.

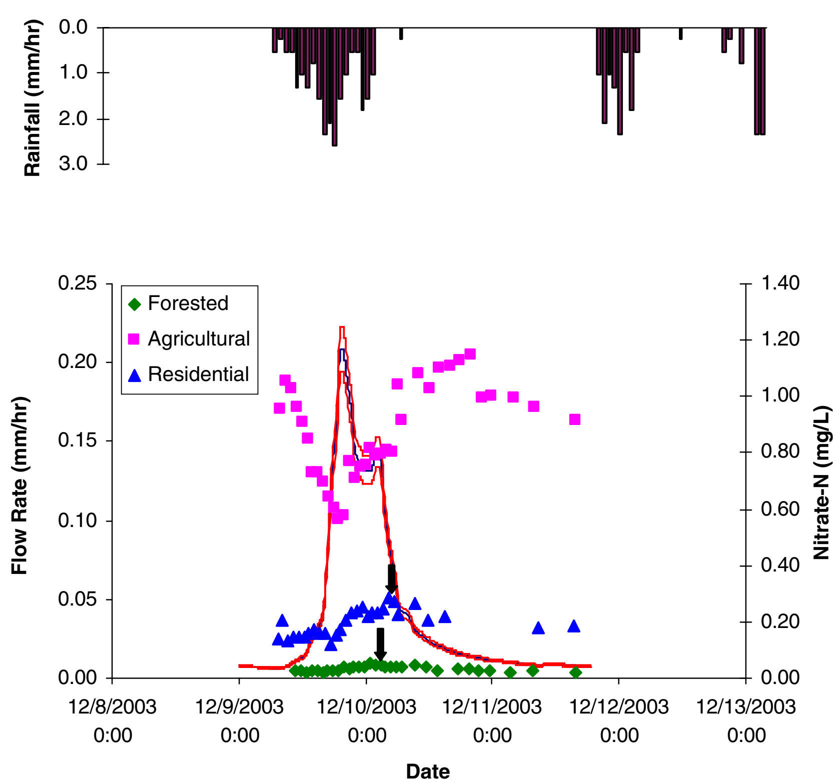

Figure 2 Nitrate response to storm 1 in the three study catchments. Only the agricultural hydrograph is shown for clarity. Arrows indicate the hydrograph peak for the forested and residential catchments.

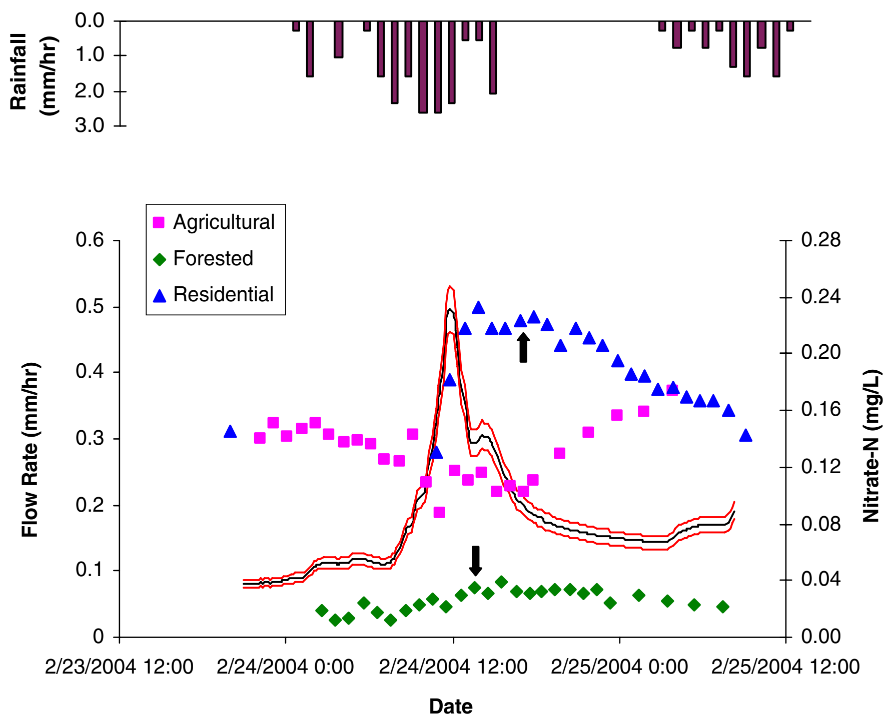

Figure 3 Nitrate response to storm 2 in the three study catchments. Only the agricultural hydrograph is shown for clarity. Arrows indicate the hydrograph peak for the forested and residential catchments.

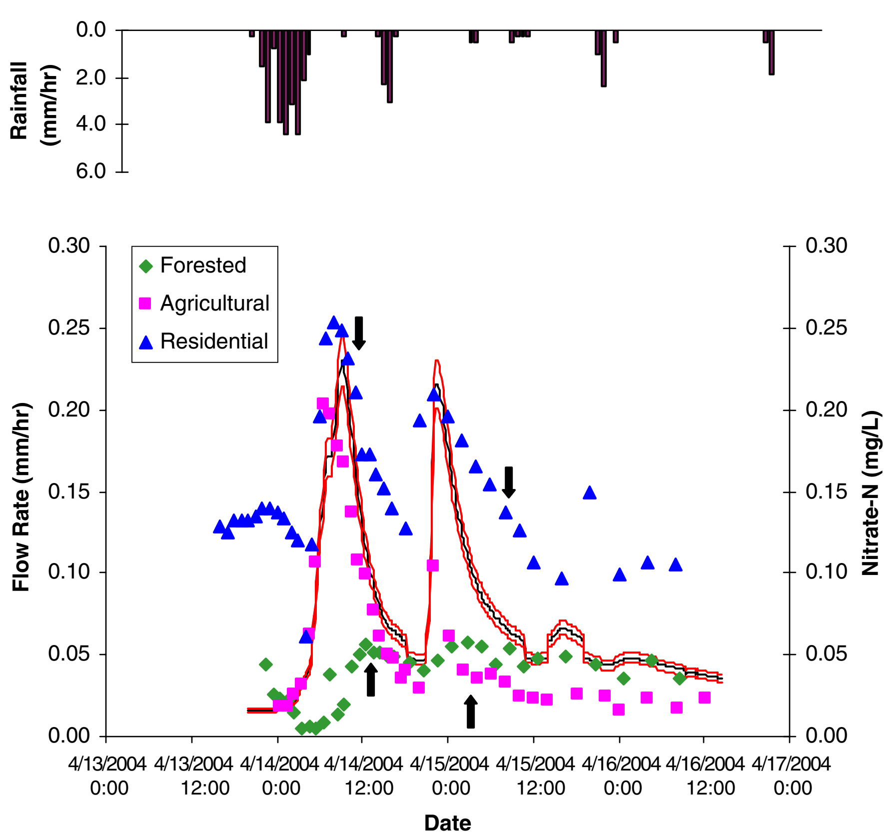

Figure 4 Nitrate response to storm 3 in the three study catchments. Only the agricultural hydrograph is shown for clarity. Arrows indicate the hydrograph peak for the forested and residential catchments.

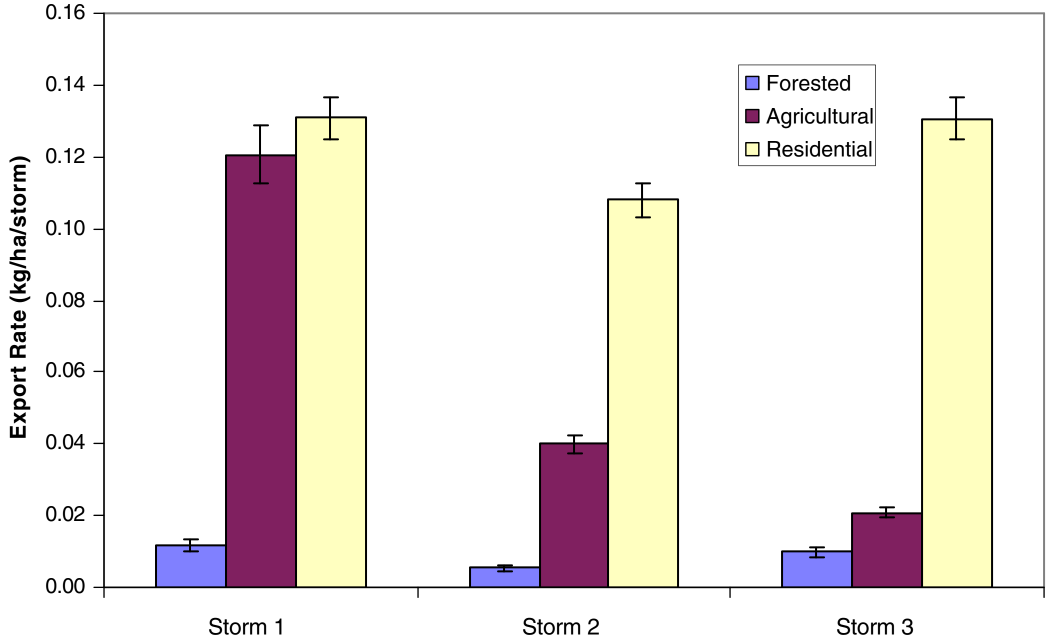

Figure 5 Nitrate export rates in the three study catchments during storms 1, 2, and 3.

Uncertainty due to analytic methods was also included, but the quantified uncertainty is so small it is insignificant (on the order of 1E − 7 kg/ha). The highest nitrate concentrations in the agricultural catchment were in the fall, due to the summer buildup of nitrogen (62 kg N/ha applied). Bi-weekly samples, storm event samples, and export rates revealed a progressive decrease of nitrate concentrations throughout the year. Export rates in the agricultural catchment were 0.121, 0.040, and 0.021 kg/ha/storm for storms 1, 2, and 3, respectively. Nitrate export rates in the forested and residential catchment were relatively constant. The highest export rates occurred in the residential catchment during all three events (0.108–0.131 kg/ha/storm), and the lowest export rates occurred in the forested catchment (0.005–0.012 kg/ha/storm). The high export rates in the residential catchment are likely due to the high baseflow observed in the residential catchment throughout the year and not high nitrate concentrations, which is evident from the baseflow (Tables 3 and 4) and concentration plots (Figs. 2–4).

The nitrate response to the storm events in each catchment are shown in Figs. 2–4. In the forested and residential catchments, nitrate increased with increasing flow rates during storms 1, 2, and 3. A ''concentration'' pattern was observed during all storm events. Concentrations ranged from 0.005–0.06 mg/L as N and 0.06–0.29 mg/L as N in the forested and residential catchments, respectively. In the agricultural catchment, nitrate concentrations decreased with increasing flow rates during storms 1 and 2, and increased with increasing flow rates during storm 3. A ''dilution'' pattern was observed during storms 1 and 2, and a ''concentration'' pattern was observed during storm 3. Nitrate concentrations progressively decreased through the rainy period, from 0.6–1.1 mg/L as N in the fall, 0.09–0.17 mg/L as N in the winter, to 0.02–0.20 mg/L as N in the spring. Nitrate concentrations were lowest in the forested catchment during all storms. During storm 1, nitrate concentrations were highest in the agricultural catchment. Baseflow concentrations were about the same in the agricultural and residential catchments prior to storm 2 (∼0.15 mg/L as N). Peak nitrate concentrations are therefore higher in the residential catchment during storm 2, since baseflow concentrations are about the same and nitrate concentrations exhibit a ''concentration'' pattern in the residential catchment and a ''dilution'' pattern in the agricultural catchment. Nitrate concentrations were highest in the residential catchment during storm 3. Baseflow nitrate concentrations in the agricultural catchment were much lower than the residential catchment during storm 3 (∼0.017 mg/L as N in the agricultural catchment and ∼0.14 mg/L as N in the residential catchment), although the peak nitrate concentration in the agricultural catchment is on the order of the peak nitrate concentration in the residential catchment (0.20 and 0.25 mg/L as N in the agricultural and residential catchments, respectively).

Discussion

The effect of land use change on stream nitrate is poorly understood despite the increasing concerns for stream ecosystem health (Howarth et al., 2002). The majority of the work on land use effects has focused on baseflow or a small number of sampling events correlating land use and nitrate (e.g., Schilling, 2002). While it is clear that land use affects the magnitude of nitrate and other nutrients exported from catchments, it is not clear how it affects nutrient dynamics or the nutrient concentration pattern during storm events. The few studies that have been conducted in catchments with mixed land use during storm events have reported mainly monthly exports, with little analysis of nitrate concentrations under varying discharge dynamics. Those studies that have analyzed concentration–discharge responses and coupled hydrobiogeochemical processes have been focused on exclusively forested or agricultural catchments. Our work in this paper presents results from three neighboring headwater catchments in western Oregon with similar (low) atmospheric deposition, size, and geology but with different, consistent land use expressions: forest, agriculture and residential. This follows work that we have presented in other parts of the USA (see Burns et al., 2005) where land use change effects on hydrological and biogeochemical processes have been quantified.

Seasonal trends

Nitrate concentrations and export rates are always low in the forested catchment. This is likely due to the lack of anthropogenic inputs in this region. Inputs of nitrate in the forested catchment include atmospheric deposition and nitrogen fixation/microbial processing in the soil. Both of these inputs are relatively low locally (Sylvia et al., 1998), resulting in low stream concentrations. In addition, baseflow in the forested catchment is lower than baseflow in the agricultural catchment during storm 2 and lower than baseflow in the residential catchment during all storms. Peak flow in the forested catchment is lower than peak flows in the agricultural and residential catchments during all storms as well. The lower flow rates and nitrate concentrations produce low export rates.

In the agricultural catchment, nitrate concentrations and export rates are high in fall, medium in the winter, and low in the spring. This is likely due to the activities occurring in the agricultural catchment that are absent in the other two catchments. During the summer months, when the streambed is dry, approximately 62 kg N/ha are applied to fields within the catchment (Tom Nichols, personal communication, 2004). We would expect that this nitrogen is incorporated into the soil before the catchment ''wets up''. An estimated 56 kg N/ha of this applied source is taken up by grass growth, transformed to gas via volatilization and denitrification, and binds to soil particles as organic nitrogen based on averages for the area (Moore and Gamroth, 1993). Excess nitrogen at the end of the growing season is estimated to be approximately 6 kg/ha. Peak flows also occur much more quickly in the agricultural catchment, and are higher during storms 1 and 3. A quicker time to peak may be due to less throughfall occurring in the catchment; only 52.8% of the catchment is covered with trees compared to 83.1% and 98.1% in the residential and forested catchments, respectively. Less interception will occur in the agricultural catchment, causing a more rapid input of rainfall to the catchment (other things being equal). The higher peaks in the agricultural catchment in the fall and spring (storms 1 and 3) may be due to smaller subsurface storage zones in this catchment as evidenced through lower baseflow generally, and flow disappearance in the summer months. We estimated the agricultural catchment storage using the recession curve analysis of Vitvar et al. (2002). Hydrographs of the three catchments were plotted in log space, and the recession limbs of four storm events were used to determine the recession coefficient. Recession coefficients were 0.119, 0.141, and 0.087 d^{-1} for the forested, agricultural, and residential catchments, respectively. We then used the recession coefficient, baseflow, and peak flow to derive mean hydraulic conductivity, storage coefficient, and subsequently estimate storage volume. Vitvar et al. (2002) showed that this method provides similar results to the more rigorous convolution integral approach relating rainfall $\delta^{18}O$ to streamflow $\delta^{18}O$. Calculations using this approach suggest that storage volume in the agricultural catchment is approximately 64% and 88% less than that of the forested and residential catchments, respectively. These faster, higher peak flows in the agricultural catchment likely deliver nitrate to the stream more quickly, eventually depleting the applied fertilizer source.

Nitrate export rates are consistently high due to high flow rates in the residential catchment. Baseflow is consistently higher than in the other two catchments, although it is lower before storm 1 than before storms 2 and 3. Increasing baseflow throughout the year can be attributed to the ''wetting up'' of the catchment; source waters are replenished as the rainy period progresses. Baseflow concentrations prior to each storm stay relatively constant (0.15, 0.15, and 0.13 mg/L as N prior to storms 1, 2, and 3, respectively), and peak concentrations are similar (0.27, 0.23, and 0.25 mg/L as N for storms 1, 2, and 3, respectively) which controls the relatively constant export rates throughout the year. The main source of nitrogen in the residential catchment is fertilizer application to lawns and ornamental shrubs. Although it appears that a large amount of nitrate is applied and exported to the stream, the high export in the fall is largely due to relatively high flow rates and not high nitrate concentrations. One surprising result of this study is the time to peak of the three catchments; the time to peak was the longest in the residential catchment for all storms. We would expect the time to peak to be shorter in the residential catchment compared to the forested catchment because of the impervious area, storm drains, lined portions of the stream, and the lower proportion of forest cover. We suspect that the marshy area, which is approximately 20 m upstream of the outlet of the catchment and downstream of the housing development, delays peak flows. The stream channel becomes split into many channels in the marshy area, and many pools are formed. This increase in complexity likely delays the time to peak observed at the outlet of the catchment.

Export rates increased with increasing development, which is in general agreement with other land use studies (Salvia-Castellvi et al., 2005; Schilling, 2002; Jordan et al., 1997; Owens et al., 1991). Maximum nitrate concentrations were found in the watershed with the highest proportion of agriculture in a study conducted in Luxembourg with watersheds having various proportions of land use (Salvia-Castellvi et al., 2005). In a paired agricultural and restored prairie watershed study, more nitrate and chloride was exported in the agricultural than the restored watershed (Schilling, 2002). Nitrate concentrations increased as the proportion of cropland increased in a study of 27 watersheds with varying proportions of cropland and forested land uses (Jordan et al., 1997). In a study of four mixed agricultural watersheds, nitrate export generally increased with increasing watershed development (Owens et al., 1991). Typical seasonal trends in nitrate were found to correspond with streamflow; high export rates occurred during wet periods and periods of high flow and low export rates occurred during dry periods (Salvia-Castellvi et al., 2005; Schilling, 2002; Owens et al., 1991). However, none of these studies show the marked difference in export rates between the agricultural catchment, which progressively decreases throughout the rainy period, and the relatively constant export rates of the residential and forested catchments. The decrease in nitrate export in the agricultural catchment further indicates that varying nitrate inputs have a large affect on nitrate dynamics.

Sources of streamflow

To determine whether differences in nitrate dynamics were due to differences in hydrology and flowpaths, sources of streamflow need to be identified. Mixing diagrams were used to determine sources of streamflow in the forested, agricultural, and residential catchments (Figs. 6–8). Biweekly streamflow, storms 1, 2, and 3 streamflow, soil water, groundwater, and rainfall sulfate and chloride concentrations are presented. Sulfate and chloride are considered quasi-conservative chemicals within these catchments, especially during the short duration of the storm events. Although sulfate can undergo transformations in the soil and chloride has been found to sorb to some types of soil, some useful trends are still revealed with these plots. Other studies have also used sulfate in EMMA analyses (Hooper et al., 1990; Christophersen and Hooper, 1992). The groundwater shown in Figs. 6 and 8 refers to the samples taken in the residential catchment. In Fig. 7, shallow groundwater refers to the sample taken in the agricultural catchment and groundwater refers to the samples taken in the residential catchment. Since the well in the residential catchment is relatively deep and the other catchments are in close proximity, we assume that

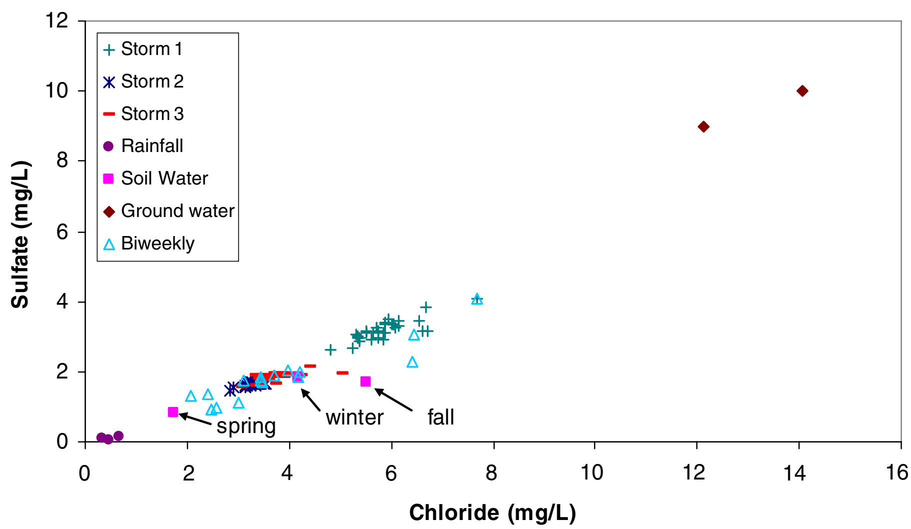

Figure 6 Mixing diagram for the forested catchment.

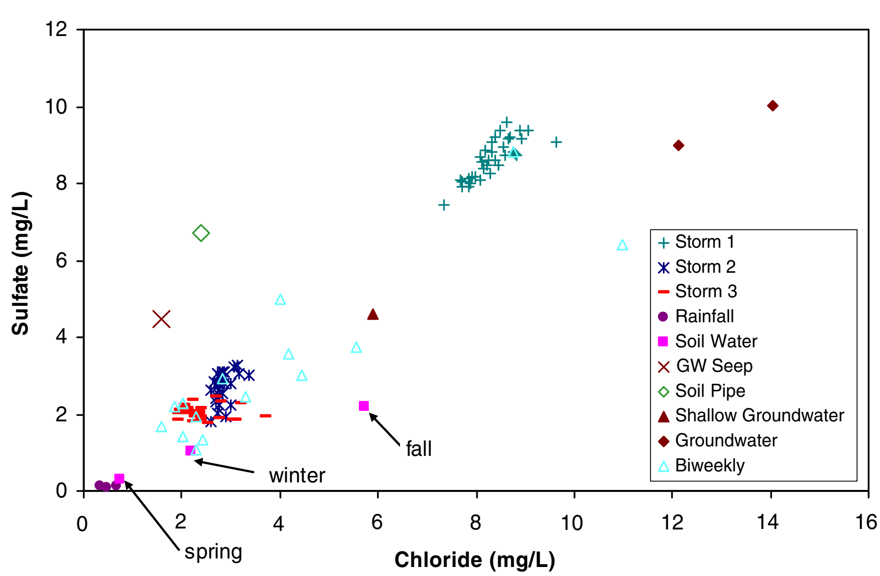

Figure 7 Mixing diagram for the agricultural catchment.

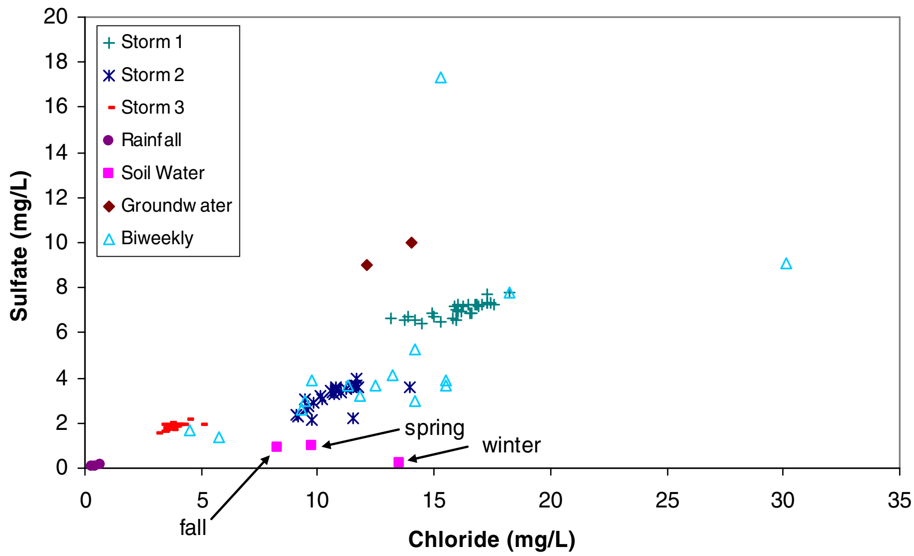

Figure 8 Mixing diagram for the residential catchment.

this sample is representative of the groundwater for the entire area.

Although streamflow is not entirely bound by end members, some inferences can still be made from the mixing diagrams. In the forested catchment, the mixing diagram is strongly linear, suggesting two sources of streamflow: groundwater and rainfall (Fig. 6). Soil water is essentially the same as stream water. The source of streamflow migrates towards rainfall from fall to spring, suggesting that rainfall becomes a more dominant source as the rainy period progresses. During the dry periods, groundwater is the main source of streamflow. Rainfall becomes a larger source as the catchment wets up, which is evident from the progression of storm and biweekly samples towards rainfall concentrations. Soil water also shows this shift from groundwater to rainfall throughout the year. This is likely due to dilution from rainfall, and shows that soil water cannot be considered a constant source.

In the residential catchment, storms 2, 3, and winter and spring biweekly streamflow is bound by groundwater, soil water, and rainfall (Fig. 8). The linear progression of storm and biweekly streamflow (similar to the progression in the forested catchment) suggests that streamflow is shifting from groundwater-dominated in the fall to rainfall-dominated in the spring. Soil water also shifts toward rainfall from winter to spring. The fall soil water is closer to the rainfall source, but this may be an anomaly; the general trend throughout the year for soil water is towards decreasing chloride concentrations (data not shown). Storm 1 and fall biweekly streamflow exhibit higher chloride concentrations than soil and groundwater, thus placing them outside of the bounds formed by the end members. Although further sampling is needed to validate end members, we surmise that there is another source of groundwater (perhaps shallower/deeper?) in the catchment with higher chloride and sulfate concentrations.

The mixing diagram for the agricultural catchment indicates that additional sources contribute to streamflow besides groundwater, rainfall, and soil water (Fig. 7). The soil pipe and groundwater seep samples (see Fig. 1 for locations) have a different chemical makeup than the other sources, and contribute to streamflow as well. Although it is not clear whether one or both are sources for streamflow, it is evident that the streamflow from the agricultural catchment has a different source apportionment. Storm 1 and the fall biweekly samples are dominated by groundwater and the soil pipe/groundwater seep, which is significantly different from the rainfall dominance during storms 2, 3, and the remaining biweekly samples. The difference between nitrate concentrations in fall streamflow and winter and spring streamflow may be due to a shift in sources from groundwater to rainfall dominated (similar to the behavior in the forested and residential catchments), or it may be due to a depletion of nitrogen in the soil. It is likely that both mechanisms are occurring. Although the seasonal progression of streamflow and soil water is similar to the progression in the forested and residential catchments, the difference in nitrate concentrations in storm 1 and fall biweekly samples and storms 2, 3, and the remaining biweekly samples is much larger in the agricultural catchment than the other two catchments.

Hydrology vs. land use

It is evident from the analysis above that in addition to differences in land use, there are differences in hydrology between the three catchments. Study catchments are three previously ungauged catchments that have common headwaters, similar geology and soil type, atmospheric deposition, and are in close proximity. However, these catchments have slight differences that are reflected in the hydrology; the agricultural stream is ephemeral, the residential catchment has higher baseflows and a slower time to peak, and the forested catchment has steeper slopes. The distribution of TI also shows the slight difference in the three catchments (Fig. 9). Although distributions are similar, the forested catchment has more areas with low TI (which indicates steep slopes and a small upslope contributing area), and the agricultural and residential catchments have more areas with high TI (areas with flatter slopes and a

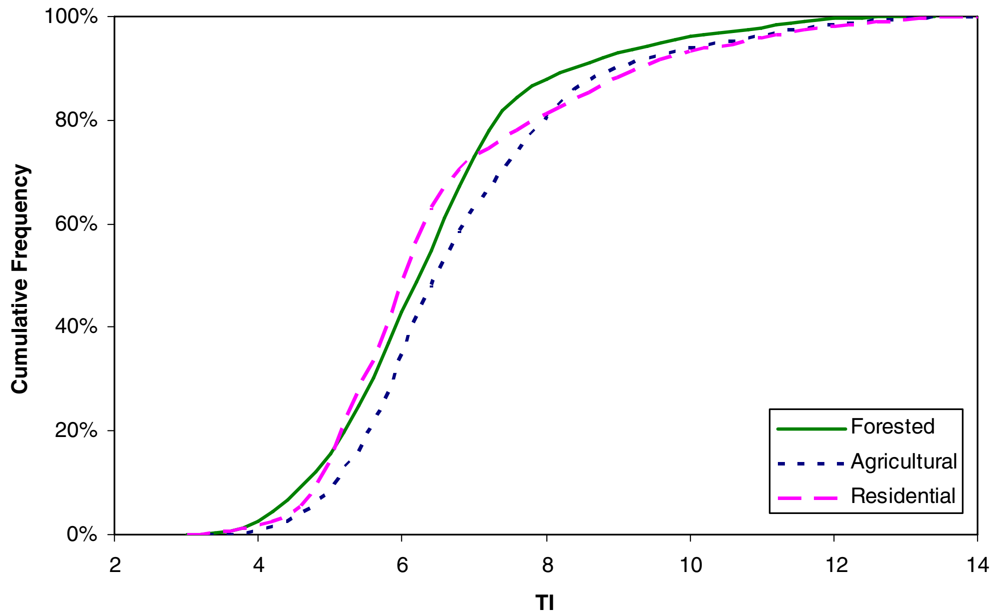

Figure 9 Cumulative frequency distribution of TI for the three study catchments.

large upslope contributing area). The residential catchment has more areas with low TI than the agricultural catchment, which likely reflects the steep upper portion of the residential catchment. The skewness of the TI distribution was also smaller for the forested catchment (1.11) compared to the agricultural and residential catchments (1.22 and 1.39 for the agricultural and residential catchments, respectively).

We believe that these differences, in addition to the other sources of streamflow (soil pipe/groundwater seep) and lower storage volume in the agricultural catchment, contribute somewhat to the differences in nitrate dynamics. Different sources will contribute different amounts of nitrate to the stream, and flowrates will be different (i.e., groundwater flowrates are expected to be much smaller than overland flowrates). However, a similar shift in stream water sources in the three catchments, shifting from groundwater dominated in the fall to rainfall dominated in the spring, indicates that the hydrology is somewhat similar and that land use is also affecting nitrate dynamics. In the agricultural catchment, nitrogen builds up in the soil from the significant summer application of manure and green bean waste. This buildup is depleted from the soil by the end of the year. In contrast, a significant buildup of nitrogen in the soil does not occur in the forested and residential catchments. Separating the effects of hydrology and land use on stream nitrate dynamics or patterns is difficult, since hydrology and land use are linked (in terms of impervious areas, storm drains, compaction of the soil, and/or removal of riparian vegetation). Land use changes can alter both nitrate inputs and the hydrology of a catchment. We argue that in this study, the difference between nitrate patterns in the three catchments during the three storm events is attributed more to land use than background hydrological differences.

Flushing of nitrate

In the forested and residential catchments, a ''concentration'' response occurred during storms 1, 2, and 3, which is indicative of accumulated soil nitrate being flushed to the stream. This ''concentration'' response is similar to the results of other studies conducted in undisturbed catchments (Inamdar et al., 2004; McHale et al., 2002; Burns et al., 1998). The mechanism behind this response has been described as the flushing hypothesis, where the N-enriched upper soil layer is flushed after a period of low demand, often during spring snowmelt and fall storms, when the water table rises to previously unsaturated portions of the N-enriched soil layer (Creed et al., 1996; Creed and Band, 1998). Flushing would thus be expected during the first few fall storms in our catchments.

No seasonal variation in nitrate behavior during storm events was observed in the forested and residential catchments. The mixing diagram for the forested catchment shows streamflow shifting from groundwater-dominated to rainfall-dominated, and soil water is not a significant source (Fig. 6). Flow rates in the Pacific Northwestern United States are characterized by a long and pronounced rain-free low flow period followed by a defined wetting-up period in the fall and then constantly fluctuating flow from multiple rain events (with little seasonal increase following wetup). These hydro-period differences result in mechanisms for labile nutrient mobilization that are different to those described by Creed et al. (1996) for the Northeastern areas of the United States. Their flushing hypothesis is predicated upon microbial activity and slow plant uptake over a quasidormant period (winter, sub-snow), which allows nitrate buildup. Nitrate is then flushed out as the catchment wets up during spring melt and storm events. Other draining mechanisms described by Burns et al. (1998) and McHale et al. (2002) for the Northeastern United States also do not appear to occur in our catchments.

A marked difference in nitrate patterns occurred in the agricultural catchment, with a seasonal shift from a ''dilution'' storm pattern in the fall and winter to a ''concentration'' pattern in the spring. Webb and Walling (1985) observed the same seasonal response of a ''dilution'' response during the winter period and a ''concentration'' response in the spring and summer months in a grassland (agricultural) catchment. They found that seasonal change in nitrate behavior during storm events could be explained by the influence of soil throughflow. Soil moisture increased and saturated areas expanded in their catchment, which resulted in higher contributions of storm water to the stream, diluting nitrate concentrations. As their variable source saturated areas decreased and the catchment drained in the spring and summer, rainfall was more likely to enter the soil profile and displace stored water with higher nitrate concentrations that then became the more dominant source of streamflow. These processes likely operate in our agricultural study catchment, since saturated areas, groundwater seeps, and soil pipes were observed throughout the catchment during the winter months. However, at our agricultural site nitrate concentrations also decrease throughout the year, indicating that soil nitrate pools become depleted. Although the shift from a ''dilution'' pattern to a ''concentration'' pattern indicates more water is coming into contact with soil nitrate pools before reaching the stream, these same pools are also exhausted as the rainy season progresses.

Implications for watershed development

Human activity has altered the movement of nitrate in the agricultural catchment to a larger degree than the residential catchment. Nitrate concentrations are higher in the agricultural catchment in the fall, which is a clear result of manure and green bean application and quick delivery to the stream. Nitrate concentrations in the agricultural catchment are high until the source is depleted, which is in contrast to the consistent nitrate concentrations in the residential catchment. Results from the residential catchment are not as easy to deconstruct; we were unable to locate one of the sources of streamflow during this study. This source may be anthropogenic or may be natural. Export rates were also highest compared to the other two catchments, but this is largely due to high flow rates and not high nitrate concentrations. Nonetheless, compared to our forested reference site, the nitrate dynamics or patterns are not significantly altered in the residential catchment. The residential catchment, with its low density housing and well-wooded yards (and no septic inputs), may be a model for minimal impact on nutrient dynamics within a watershed. Tree cover has been retained (83.1% compared to 52.8% in the agricultural catchment), and the lower portion of the catchment is used as a park. Portions of the park are well developed, with baseball fields and lawns, but other portions are relatively natural, with marshy areas and significant riparian woods acting as control measures. It is these control measures that prevent nitrate patterns from being affected by the development; residential areas with a higher housing density but similar spatial layout may have higher nitrate export rates but the patterns during storm events would likely stay the same. The marshy areas and riparian woods delay runoff response and may retain some of the exported nitrogen from the upper portion of the catchment. We could imagine a scenario, however, where there is so much alteration of the catchment from development that these control measures could be ''swamped'' out and no longer useful. More work would be needed to determine the ideal housing density and spatial layout of control measures.

Conclusions

Most process work to date that deals with nitrate dynamics has been done in areas with one land use (minimally disturbed or agricultural) and areas with substantial atmospheric deposition. Our analysis of three neighboring headwater catchments in western Oregon with similar (low) atmospheric deposition, size, and geology but with different, consistent land use expressions revealed the following:

1. Human activity altered the patterns of stream nitrate concentrations during storm events in the agricultural catchment to a larger extent compared to the residential catchment. Nitrate response patterns in the residential catchment were the same as the patterns in the reference forested catchment (a ''concentration'' pattern throughout the year), whereas a ''dilution'' pattern was observed in the fall and winter and a ''concentration'' pattern was observed in the spring in the agricultural catchment.
2. Manure and green bean application in the agricultural catchment significantly increased nitrate concentrations and exports in the fall, which decreased throughout the year as the source became depleted. This is in contrast to the relatively constant export rates in the forested and residential catchments, which likely had a more constant source of nitrate (i.e., no large source inputs).
3. Streamflow in the forested, agricultural, and residential catchments moved from groundwater-dominated to rainfall-dominated as the rainy period progressed. Additional streamflow sources were identified in the agricultural catchment, which may include a groundwater seep and soil pipe.

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