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Transport of water, solutes and nutrients from a pasture hillslope, southwestern Brazilian Amazon

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Abstract:

A conceptual model of water and solute transport pathways was developed and applied to a pasture hillslope in the southwestern Brazilian Amazon basin using select field measurements. Infiltration-excess or Horton overland flow (HOF), saturation overland flow (SOF), and groundwater in both the near-stream zone and upslope were sampled on a hillslope draining a 3·9 hectare pasture for a total of ten storms during the first half of the rainy season (October–November) in 2002. A Soil Conservation Service SCS curve number model of HOF and an annual water balance of both upslope and near-stream zones were used to calculate the contribution of each flowpath to solute export. HOF occurred in rainstorms greater than 5 mm and accounted for ~8% of annual rainfall. Flow generated in the near-stream zone was ~8% of annual rainfall. Sub-surface flow from upslope groundwater dominated annual runoff (~19–30% of annual rainfall). Solutes fell into three categories according to flowpath. HOF from upslope positions dominated the export of total phosphorus (TP) and total dissolved phosphorus (TDP, 51–72% of total annual export). The near-stream zones controlled the export of K (58–65%), total dissolved nitrogen (TDN, 76–80%), and total nitrogen (TN, ~75%) owing to relatively high solute concentrations and the large volume of water that flowed through the near-stream zone. Na and Si export was via groundwater from upslope (50–67% of annual export). The flux calculations were based on a small number of storms and are preliminary estimates designed to identify broad patterns in solute export via different hydrologic pathways. Additional processes, especially N removal at the groundwater-stream interface and in the stream channel, may affect actual export rates at the watershed scale. Whereas HOF production is negligible in Amazon forests, it represents a significant pathway for additional loss of elements, especially phosphorus, from mature pasture systems. The evidence presented here shows that biogeochemical perturbations and enhanced solute fluxes continue for decades following deforestation for pasture. Copyright © 2006 John Wiley & Sons, Ltd.

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INTRODUCTION

Agriculture in Brazil often involves the establishment of cattle pastures (Browder, 1994). In the Amazon basin, deforestation followed by pasture establishment is the most common land use (Pedlowski *et al*., 1997), and pasture plays a central role in the regional land use pattern of colonization projects (Hecht, 1982; Walker *et al*., 2000). Deforestation for agriculture and pasture in the humid tropics, including the Amazon, has long been described as a dynamic slash-and-burn system with high rates of abandonment and regrowth, where a decline in soil fertility and weed invasion force colonists to abandon old pastures and deforest new areas (Nye and Greenland, 1960). Investigations of the effects of deforestation on soil and stream biogeochemistry have likewise focused on changes observed in soil and stream chemistry

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during forest clearing and regrowth (Hölscher *et al*., 1997; Williams and Melack, 1997), often modelled on small watershed studies such as the classic experiments at Hubbard Brook (Bormann and Likens, 1979). However, time series of deforestation and regrowth based on satellite imagery show that ∼85% of the cleared areas in the State of Rondônia in the southwestern Brazilian Amazon basin remain as pasture up to 25 years after clearing (Roberts *et al*., 2002), and some cleared areas continue as pasture beyond 80 years (Moraes *et al*., 1996). Deforestation, at least in some parts of the Brazilian Amazon, is more accurately understood as a long-term transition from forest to pasture, rather than as a dynamic, patchy mosaic of temporary transitions with significant regrowth. Understanding the effects of regional deforestation on ecosystem functioning and biogeochemistry requires the investigation of these persistent pasture systems.

Regional surveys of stream biogeochemistry in forested and pasture areas of the Amazon basin show that streams draining pastures have higher concentrations and fluxes of Na, Cl, and K than streams draining forests in both wet and dry seasons (Biggs *et al*., 2002), and increased concentrations of nitrogen and phosphorus in the dry season (Biggs *et al*., 2004; Neill *et al*., 2001). The hydrologic and biogeochemical mechanisms responsible for these changes in stream biogeochemistry in persistent pasture systems are not well understood.

Deforestation and pasture establishment, whether in tropical or temperate climates, alter the hydrologic balance of watersheds by decreasing evapotranspiration (Hodnett *et al*., 1996b; Williams and Melack, 1997) and increasing the probability of infiltration-excess or Horton overland flow (HOF) (Elsenbeer *et al*., 1999). The introduction of cattle increases the bulk density and reduces the porosity of the upper soil horizons, reduces infiltration capacity, and increases HOF volumes (Alderfer and Robinson, 1947; Elsenbeer *et al*., 1999; Gifford and Hawkins, 1978; Greenwood and McKenzie, 2001). The increased volumes of overland flow caused by soil compaction, together with ‘churning’ of the soil surface from hoof action may result in increased sediment and nutrient delivery into streams (Petry *et al*., 2002; Warren *et al*., 1986). In the Amazon basin, storm flows in recently deforested and burned catchments show elevated concentrations of nutrients and solutes (Williams and Melack, 1997), though detailed sampling of overland flow has not been performed in long-established pastures of the Amazon basin.

In addition to upslope trampled areas, the near-stream saturated zone contributes to stream water and solute fluxes, particularly in humid climates (Dunne, 1978; Govindaraju, 1996). Near-stream zones are both biogeochemically active and have high throughputs of water, making them important landscape elements for nutrient export (Hedin *et al*., 1998). Near-stream zones differ from upslope areas in rates and types of nitrogen transformations (Cey *et al*., 1999; Cirmo and McDonnell, 1997; Hill *et al*., 2000) and phosphorus mobility (Carlyle and Hill, 2001; deMello *et al*., 1998; Villapando and Graetz, 2001). Processes operating in the near-stream zone may dominate the export of nutrients from a watershed (Creed and Band, 1998; Hillbricht-Ilkowska *et al*., 1995; Whelan *et al*., 2002).

Different solutes follow different hydrologic pathways and so interact with the biogeochemical environment in ways that affect their export from a hillslope via the upslope and near-stream pathways. Surface pathways that come into contact with organic material often dominate the export of more biologically active elements such as K, N, and P, while sub-surface pathways near weathering substrates dominate the export of more geochemically active elements such as Na and Si (Elsenbeer, 1995). Understanding the impact of land transformations on watershed biogeochemistry requires quantification of the contribution of different landscape components to water flow and solute export.

This study elaborates a conceptual model of hydrologic flowpaths for a hillslope containing upland and near-stream zones, and uses select field measurements of runoff volumes and the chemical composition of water in the various flowpaths to estimate the approximate magnitude of annual fluxes of solutes to streams from a hillslope under pasture in the southwestern Brazilian Amazon basin. The hydrologic pathways represented include precipitation, infiltration-excess overland flow, saturation overland flow (SOF), and groundwater flow upslope and through the near-stream zone. The objective of the paper is not to provide precise estimates of export values for a particular hillslope, but rather to use a conceptual model combined with a rapid and inexpensive field campaign to highlight the relative importance of different hydrologic pathways for fluxes of various solutes and nutrients. We highlight differences among various elements in the relative importance of different transport mechanisms and compare the broad patterns observed with results from more intensive sampling efforts reported in the literature.

STUDY AREA

The Nossa Senhora Ranch lies near the centre of the Brazilian state of Rondônia (Figure 1). A 53 ha rectangular field on the ranch extends over hillslopes that grade to streams on either side of a NW–SE trending interfluve. The field was deforested in several stages in the late 1970s and early 1980s, according to a time series of Landsat TM imagery of the area (Roberts *et al*., 2002), making the pasture approximately 18–25 years old at the time of sampling in October 2002. Since clearing, the plot was kept in pasture with *Brachiaria brizantha* grass (Hodnett *et al*., 1996). During the sampling period (October–November 2002) the field was grazed with 2·1 cattle/ha, which is at the upper end of cattle ranching densities in the Amazon basin (Chomitz and Thomas, 2001; Loker *et al*., 1997).

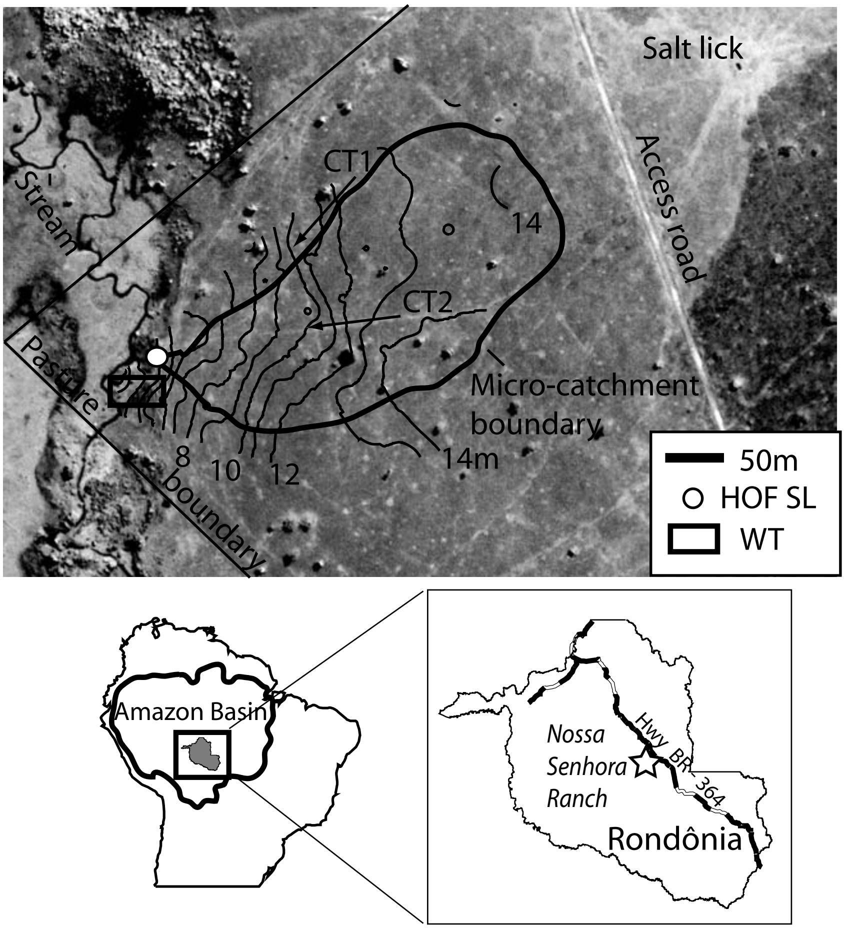

Figure 1. Location of the pasture field site on part of the Nossa Senhora Ranch, in central Rondônia. The micro-catchment boundary represents the area contributing to Horton overland flow during storm events. The contour lines indicate elevation above the stream bank. CT1 and CT2 are two of the main cattle trails that routed storm runoff to the sampling point at the natural lip. The black circle (HOF SL) indicates the HOF sampling location pictured in Figure 2, and WT is the well transect

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The sampling site consisted of an upslope micro-catchment, a near-stream zone, and a stream that flowed past the sampled hillslope (Figure 1). The stream drained a catchment area of 14·5 km^2 above the hillslope sampling location. The upland micro-catchment on the pasture hillslope had a network of cattle trails that accumulated runoff and routed it to a natural lip ~0·5 m high near the small stream at the southwestern end of the field (Figures 1, 2, marked HOF SL in Figure 1). Overland flow proceeded from east to west until it intercepted a large cattle trail (CT1) that cut across the hillslope and routed the runoff to the lip at HOF SL (Figure 1). CT1 defined the northwestern boundary of the micro-catchment, which drained 3·9

Figure 2. Photograph of the pasture hillslope as viewed from the overland flow sampling location, with runoff at the end of an 11-mm rainstorm (flow ~5 l/s). The lip is the sampling location for the HOF volume measurements and water sampling (marked HOF SL in Figure 1). The photo is taken facing northeast; the cattle trail conveying the water is marked CT1 in Figure 1

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hectares as mapped with a Total Station, and had a maximum hillslope length of 328 m. The slope was 0–1° in the upper northeastern half of the catchment and ∼1–3° in the lower southwestern half, with microtopography of 5–20 cm vertical amplitude caused by grass clumps and cattle trampling. An 11° slope defined the transition to a near-stream zone approximately 25 m wide with a 2·4° slope (Figure 3, WT1 in Figure 1).

The soil in the upslope portion of the micro-catchment was classified as a medium-textured red-yellow podzol, or Typic Paleudult in the US soil taxonomy (Hodnett *et al*., 1996a), formed on the gneissic basement of the Brazilian craton. Soil texture in the upper 0–15 cm in upslope positions was 50–85% sand and 7–15% clay, and the clay content increased to 15–30% at 35–50 cm in some locations. Soil structure was generally weak, progressing from fine granular in the topsoil to sub-angular blocky at 35–50 cm. Roots of the *Brachiaria* grass were most dense in the upper 15–20 cm of soil and thinned rapidly with depth, though some roots may be found below the 2-m depth (Hodnett *et al*., 1996a).

The near-stream zone below the natural lip (WT1) had a loam at the soil surface, changing to sandy loam at 25–35-cm depths, and dense growth of *Brachiaria* grass. Soil in the near-stream zone had organic horizons up to 10–30-cm depths and redoximorphic features below 15 cm depth, indicative of low redox potential. Bedrock underlied the soil at a depth of 70–120 cm (Figure 3). The streambed was granitic-gneiss with small patches of gravel and sand.

The water table in the near-stream zone ranged from 0 to 93 cm below the ground surface, sloped towards the stream, and fluctuated by 25–93 cm during the sampling period depending on location (Figure 3). Most (80–90%) of the near-stream zone was inundated with 2–50 cm of water for 1–2 days following large storms. Water levels in upslope wells were 50 cm and 138 cm below the ground surface and fluctuated less than the near-stream wells (Figure 3).

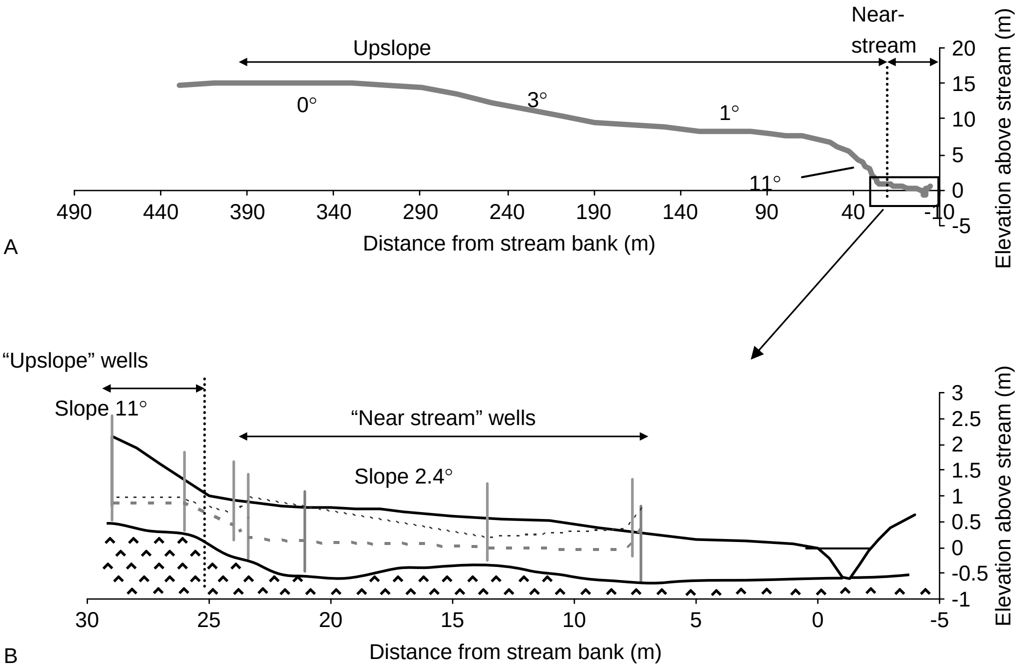

Figure 3. (A) Topographic profile of the micro-catchment and definition of the upslope and near-stream zones at WT1, as viewed from the north. (B) Topographic profile and well transect in the near-stream zone (WT1 in Figure 1). Horizontal dotted lines indicate the minimum and maximum water table depths during sampling

CONCEPTUAL MODEL AND METHODS

Water fluxes

A hillslope conceptual model (Figure 4) modified from Dunne (1978) framed the measurements and calculations of water and solute fluxes. In the model, the hillslope is divided into an upslope zone and a near-stream zone by a change in slope. Rainfall on the upslope zone either ran off as infiltration-excess (Horton) overland flow (Q_h) or entered the soil where it evaporated (ET), generated sub-surface stormflow (Q_{ss}), or recharged the groundwater and discharged to the near-stream zone (Q_{gup}). Rain on the near-stream zone (Q_{nz}) either fell on saturated surfaces and flowed over the surface to the stream (Q_{sof}), or fell on unsaturated portions of the near-stream zone, recharged the shallow water table and discharged to the stream, either through the sub-surface or as return flow (Q_{unz}). The definition of SOF used here included only precipitation falling on saturated parts of the near-stream zone. Other components of SOF, including exfiltration of groundwater from upslope and precipitation falling on saturated areas upslope (as described in de Moraes *et al*., 2006), were included as groundwater flow from upslope (Q_{gup}) or Q_h respectively. Groundwater flow from upslope (Q_{gup}) passed through the near-stream zone and not through a deeper, regional groundwater system, since the soils of the near-stream zone were relatively thin (0–3 m) and the channel bed was low-permeability crystalline bedrock. Upslope groundwater passed through the near-stream zone, where some of it evaporated before discharging to the stream (Q_{gs}). Annual changes in water storage in soil and groundwater were assumed minimal, as observed both at Nossa Senhora and in the central Amazon (Hodnett *et al*., 1996a; de Moraes *et al*., 2006), so the annual recharge upslope equalled the annual groundwater discharge from upslope (Q_{gup}).

Calculations of sub-surface stormflow from upslope positions (Q_{ss}) for a Rondônia pasture with similar soils and geomorphology (Elsenbeer *et al*., 1999) suggested that Q_{ss} was small. Even where impeding horizons

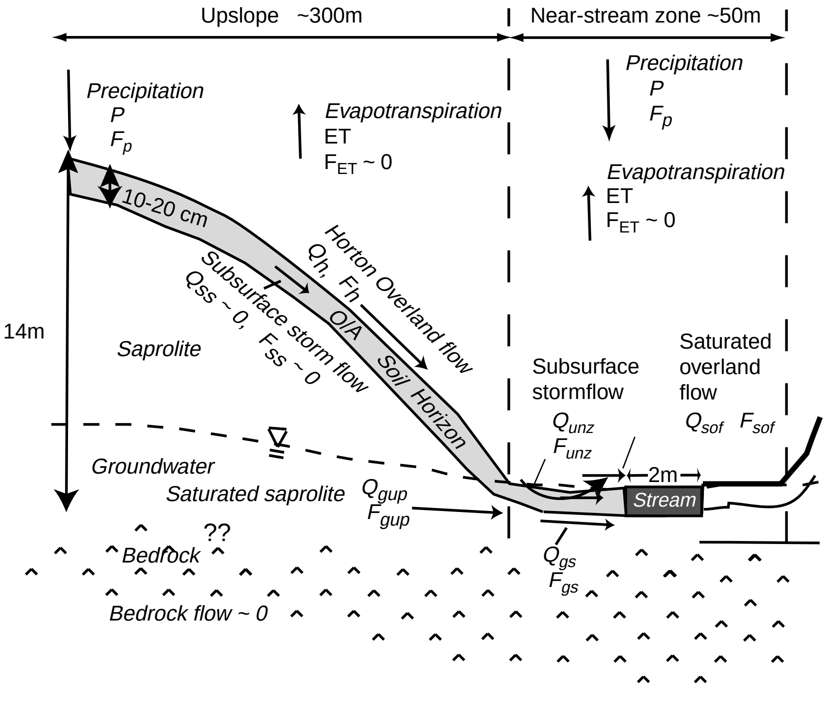

Figure 4. Hillslope conceptual model with fluxes estimated during the field campaign (not to scale). Q_i indicates annual water flows and F_i indicates annual solute or nutrient fluxes. The area in grey indicates the upper soil horizon. The depth of the boundary between saprolite and bedrock is not known

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existed, sub-surface stormflow in the upper meter of the soil was minimal (de Moraes *et al.*, 2006), so Q_{ss} is assumed to be zero. At Nossa Senhora, some macropores or pipes occurred at a natural scarp on the hillslope near the near-stream zone, but these did not produce any discharge during the storms that were measured.

Total annual discharge from the hillslope (Q_t) was the sum of the surface and sub-surface fluxes:

$$Q_t = Q_h + Q_{sof} + Q_{unz} + Q_{gs} \tag{1}$$

where Q_t is total annual water flux from the hillslope in mm, Q_h is infiltration-excess or HOF, Q_{sof} is SOF from rainfall on saturated areas in the near-stream zone, Q_{unz} is flow generated by rainfall on unsaturated portions of the near-stream zone, and Q_{gs} is the flow into the stream from upstream groundwater.

The two flowpaths generated in the near-stream zone were determined as follows:

$$Q_{sof} = \eta(1 - \lambda_{up})P \tag{2a}$$

$$Q_{unz} = (1 - \eta)(1 - \lambda_{up})P \tag{2b}$$

where λ_{up} is the fraction of the total hillslope defined as upslope, η is the average fraction of the near-stream zone saturated during storm events, and P is annual precipitation in mm. While the distinction between Q_{sof} and Q_{unz} does not affect the calculation of flow generation in the near-stream zone, it became important for calculating solute flux since solute concentrations differed in Q_{sof} and Q_{unz}. Values of η were determined from the minimum and maximum position of the water table observed from a well transect installed during the study (Figure 3), and from field surveys taken during storms in October–November. Values of η ranged from 0·3 to 0·8, which established a corresponding range of Q_{sof} and Q_{unz}.

Annual groundwater flow from upslope to the stream was calculated from the annual water balance:

$$Q_{gs} = \lambda_{up}(P - Q_h) - ET \tag{3}$$

ET was not multiplied by the upslope fraction (λ_{up}) because ET drew from upslope groundwater flowing through the near-stream zone. Though some ET in the near-stream zone may be abstracted from soil moisture due to rain falling on unsaturated portions of the near-stream zone (Q_{unz}), here we assumed that the residence time of Q_{unz} was short and that all ET in the near-stream zone was abstracted from Q_{gup}. A more detailed understanding of the residence time of Q_{unz} and its contribution to ET in the near-stream zone could be included in future revisions of the runoff values.

Evapotranspiration (ET) at the Nossa Senhora pasture was estimated as 1024 mm/year (2·8 mm/day, Kabat *et al.*, 1997; Waterloo, 1998), compared with 1387 mm/year (3·8 mm/day, (Kabat *et al.*, 1997)) and 1354 (3·7 mm/day, da Rocha *et al.*, 1996) at the Jarú forest site. ET at Nossa Senhora was 2·5 mm/day at the end of the dry season of 1993 *versus* a potential ET of 3·6 mm/day (Hodnett *et al.*, 1996), suggesting that 2·8 mm/day was a lower-bound estimate of ET at the pasture site. Soil moisture measurements suggested that pasture grasses experience water stress for 1–4 months annually (Hodnett *et al.*, 1996), which gives an ET range of 1156–1247 mm/year (3·2–3·4 mm/day). Here we used the full range of estimates (1024–1247 mm/year).

The total annual depth of HOF (Q_h) was calculated as follows:

$$Q_h = \lambda_{up} \sum_{i=1}^{n} q_{hi} N_i \tag{4}$$

where Q_h is the total annual depth of HOF, i is an index of storm size interval, n is the number of storm size intervals, q_{hi} is the depth of HOF from upslope generated by a storm in size interval i, and N_i is the annual frequency of storms in size interval i. The annual frequency distribution of storm sizes was derived from 0·5 hourly rainfall data from a tipping-bucket rain gauge at Nossa Senhora Ranch collected from 1999 to 2002 (LBA BR/EU Tower Consortium project; Von Randow and Silva Dias, 2004). Rainfall periods separated by any 0·5 h gap counted as separate events, so more than one event could occur in a single day. The probability distribution of storm sizes from 1999 to 2002 was scaled to the long-term average precipitation from 1970 to 1996 at Ji-Paraná station (1918 mm), which was 48 km from Nossa Senhora Ranch.

The Soil Conservation Service Curve Number method (SCS CN) (Mockus, 1964; Rawls *et al.*, 1993) for calculating HOF volumes (q_h) was calibrated with field measurements for ten storms at Nossa Senhora. Discharge was measured at the natural lip (HOF SL in Figures 1, 2) with a bucket and stopwatch every 0·5–5 min, depending on the rate of change in discharge. Rainfall depth and intensity during the rainfall events were measured with a tipping rain gauge or by a funnel and graduated cylinder for the dates without any rain-gauge data. The cattle trails that collected and routed the overland flow did not capture all of the overland flow from each event. During large storms, water filled the trails and some water passed over the trails and out of the micro-catchment at the northwestern boundary (labelled CT1 in Figure 1). The magnitude of the over-trail losses was estimated once or twice for each runoff event by recording the location, depth, and velocity of over-trail flow. The estimated over-trail losses increased as a function of discharge from 0 to 20%. The discharges reported here have been corrected to account for the losses. The estimates of the over-trail losses were rough given the limited sampling and rapid changes in the over-trail loss that occurred during runoff events.

Solute fluxes. The total solute flux from the hillslope was the sum of fluxes from each flowpath (cf. Equation (1)):

$$F_t = F_h + F_{sof} + F_{unz} + F_{gs} \tag{5}$$

where F_t is the total annual flux from the hillslope (mol/km^2-year). The other subscripts corresponded to the hydrologic pathways as described in the hydrologic model.

Fluxes via groundwater and near-stream pathways (F_{gs}, F_{sof}, F_{unz}) were calculated by multiplying the water fluxes (Q_i) by average solute concentrations measured in each pathway during the field sampling:

$$F_t = F_h + C_{sof}Q_{sof} + C_{gs}(Q_{unz} + Q_{gs}) \tag{6}$$

where C_i is the concentration of solutes or nutrients in a flowpath i, in μM. The chemical composition of water that fell on and flowed through unsaturated portions of the near-stream zone (Q_{unz}) was taken as the average chemical composition of shallow groundwater collected from wells in the near-stream zone ($C_{unz} = C_{gs}$), measured here as the average of the five wells in the near-stream zone (Figure 3).

We assumed that solute concentrations in the near-stream zone did not change rapidly over time, either through the season or during storms of different sizes. Intensive sampling efforts in a variety of landscapes suggest that spatial, intrastorm, and inter-storm variability in the chemical composition of pathways in the near-stream zone can be considerable (Elsenbeer *et al.*, 1995; Williams and Melack, 1997; Hedin *et al.*, 1998). Here, we assumed that the variability was sufficiently low to allow for useful calculations to be made on the relative importance of different transport pathways. The validity of this assumption was evaluated by sampling five wells three to five times during the sampling period.

The solute flux from upslope groundwater into the near-stream zone may be calculated separately as follows:

$$F_{gup} = \lambda_{up}C_{gup}(P - ET - Q_h) \tag{7}$$

where C_{gup} is the concentration of a solute in groundwater in upslope positions. The calculation of F_t (Equation (6)) did not include F_{gup}, since solutes entering the near-stream zone via groundwater (F_{gup}) were either retained in the near-stream zone or contributed to solute discharge to the stream, which was included in the calculation of F_{gs}.

The solute flux in HOF (F_h) was calculated with an additional model that took into account inter-storm variability in solute concentrations and fluxes. The volume-weighted mean (VWM) concentration of a solute in HOF for a given storm was assumed to vary as a power function of the total depth of overland flow generated by the storm:

$$c_h = a{q_h}^b \tag{8}$$

where c_{h} is the VWM concentration of solute in HOF for a single event (μM), q_{h} is the total depth of HOF for a given storm in mm, and a and b (dimensionless) are empirical constants determined by a regression of observed q_{h} and c_{h}. Though Equation (8) was often used to describe concentration variations within a single storm or seasonal hydrograph (Evans and Davies, 1998; Walling and Webb, 1986), it was used here to account for variability in VWM solute concentrations among storms of different sizes.

The flux of a solute per unit area for a given storm is the VWM concentration times the depth of HOF q (mm), which, combined with Equation (8), yielded:

$$f_{\mathrm{h}} = q_{\mathrm{h}}(aq_{\mathrm{h}}{}^{b}) \tag{9}$$

where f_{h} is the total flux of a solute in HOF for a runoff event of depth q_{h} in moles/km^2. The annual flux of a solute per unit area of the hillslope was computed as follows:

$$F_{\mathrm{h}} = \lambda_{\mathrm{up}} \sum_{i=1}^{n} aq_{\mathrm{h}i}{}^{b+1} N_i \tag{10}$$

where F_{h} is the total annual solute flux via HOF in moles/km^2, i is an index of rainfall depth interval (e.g. 0–2·5 mm), n is the number of rainfall depth intervals, $q_{\mathrm{h}i}$ is the depth of HOF generated by rainfall of depth interval i, and N_i is the annual frequency of storm events of depth interval i. f_{h} represented the flux per unit area upslope of the near-stream zone, so like Q_{h} it was multiplied by λ_{up} to give the contribution relative to the area of the entire hillslope (F_{h}).

Water sampling and chemical analysis

HOF was sampled in pre-rinsed HDPE bottles at the natural lip at 1–10 min intervals during ten storms for which discharge was measured. The solute concentrations in sub-surface pathways (C_{gup}, C_{gs}, C_{unz}) were determined using water samples on the well transect installed in the near-stream zone and upslope (WT1, Figures 1, 3). Seven wells made of 5-cm diameter PVC were spaced 2–8 m apart in a transect perpendicular to the stream, with two in the upslope positions and six in the near-stream zone (Figure 3). The bottom 15 cm of each PVC pipe was perforated with 1 mm holes, wrapped in 54-μm nylon mesh, and capped with flexible plastic. Wells were installed using a manual soil corer. Well bores were drilled down to bedrock. One pair of wells approximately 7 m from the stream sampled different depths (120-cm depth on bedrock and 50-cm depth in the lower soil horizon). The wells were sampled on five separate days during October and November, with 3–15 days between sampling. Wells were purged twice prior to sampling with a hand pump and nylon tubing.

Water samples for determination of C_{sof} were collected in the near-stream zone during two rainfall events, away from the location where HOF entered the saturated zone. Stream water was sampled once before and once after five storms. The stream samples may not be representative of the average chemical composition of total storm runoff, since maximum storm discharge in the stream typically occurred ~6–12 h after the storm sampling.

Water samples were filtered through Whatman GFF (0·7 μm) filters in the field. The unfiltered and filtered samples were kept frozen until they were analysed. Concentrations of K and Na in the samples were determined using flame photometry. K concentrations were analysed on the filtered samples, and Na on the unfiltered samples owing to contamination from the GFF filters. Dissolved Si, PO_4, and NH_4 were determined using flow injection analysis (FIA) and colorimetry, and Cl with mercuric thiocyanate colorimetry (APHA, 1989). Total and dissolved nitrogen and phosphorus were determined using persulfate digestion on unfiltered and filtered samples, with subsequent FIA colorimetry of nitrate and phosphate (Valderrama, 1981). Samples with high concentrations of total dissolved nitrogen (TDN), total nitrogen (TN), and total phosphorus (TP) were diluted 15 and 30 times to ensure complete digestion.

Pauliquevis *et al.* (2004) provided rainfall chemistry data for Nossa Senhora Ranch during the dry season (September–November, 2002) and the wet season (March–May, 1999). The calculation of annual solute flux

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in precipitation (F_p) used first the volume-weighted mean of wet and dry season values, and secondly the wet season values only.

RESULTS AND DISCUSSION

Horton overland flow and annual water fluxes

Total rainfall in the ten storm events sampled ranged from 2–35 mm (Table I, Figure 5). The storms were convective thunderstorms in the afternoons, typical of the diurnal cycle of precipitation and convective intensity over tropical landmasses, including the southwestern Amazon basin (Rickenbach *et al.*, 2002). HOF occurred during all storms larger than 5·5 mm. The SCS curve number calculated from the measured runoff volumes decreased from 86 to 76 with increasing rainfall depth, resulting in a composite SCS curve (Figure 6). On an annual basis, small storms (<5 mm) comprised 80% of the total number of storms and 16% of total precipitation at Nossa Senhora (Figure 7). Approximately 70% of annual rainfall occurred in storms less than 30 mm.

Evapotranspiration accounted for the largest fraction of the annual hydrologic budget (53–66% of precipitation, Table II). HOF (Q_{hof}) and flow originating in the near-stream zone ($Q_{sof} + Q_{unz}$) each accounted for ~8% of annual precipitation and 17–22% of annual runoff. These values are similar to those measured by de Moraes *et al.* (2006), who found that HOF and SOF together accounted for 17% of annual rainfall from a small watershed in the eastern Amazon basin *versus* the 16% observed at Nossa Senhora. The mechanisms producing runoff at the two sites differed; at the eastern Amazon site, SOF occurred in upslope positions due to a low-permeability horizon that favoured saturated conditions in the topsoil. By contrast, no impermeable layer was noted at Nossa Senhora, and SOF production at Nossa Senhora was observed only in the near-stream zone.

The calculation of Q_{hof} assumed that the composite SCS rainfall-runoff curve remained the same throughout the rainy season. The curve could change if vegetation or soil moisture changed over the rainy season. Cattle grazing resulted in a relatively constant grass height of 15–40 cm throughout the rainy season. By October 2002, the grass in nearby ungrazed pastures had grown to 70–100 mm, while the grass in the grazed pasture remained at 15–40 cm over the sampling period. This suggests that the grass in the pasture had reached its

Table I. Summary of rainfall events and Horton overland flow (q_h) observed during October–November 2002. Rainfall duration was defined as the duration of continuous precipitation in 10-s intervals. The numbers in parentheses are the depth, duration, or intensity calculated using the total time from the beginning of rainfall, including short dry intervals that occurred during the beginning and end of the storm. N-$_{HOF}$ is the number of water samples of HOF collected for chemical analysis

Date	N-$_{HOF}$ samples	Rainfall depth (mm)	Runoff depth (mm)	Rainfall duration (hours)	Rainfall Intensity (mm/h)	Maximum 5-min intensity (mm/h)
21 Oct	0	11·2	0·43	0·63 (0·82)	17·7 (13·7)	50
30 Oct	0	3·3	0·001	0·35 (0·90)	9·4 (3·7)	8
31 Oct	11	14·3	0·35	0·33 (0·63)	43·4 (22·6)	72
1 Nov	2	5·5	0·01	0·2 (0·5)	27·5 (11)	44
4 Nov	8	15·8 (11·6)	0·32	0·45 (0·55)	25·8 (21·1)	31
10 Nov	5	10·7	0·45	0·38 (0·48)	22·8 (28·8)	59
13 Nov	0	2·0	0·003	—	—	—
14 Nov	7	20[a]	2·07	—	—	—
16 Nov	4	25[b]	3·08	—	—	—
29 Nov	5	35[a]	3·71	—	—	—

[a] Rainfall measured with graduated cylinder and funnel, rain-gauge data missing.
[b] Rainfall estimated in field, rain-gauge data missing.

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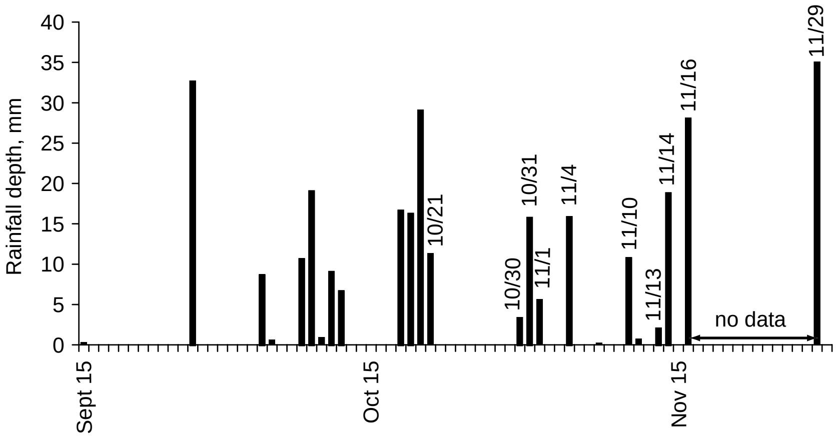

Figure 5. Precipitation events prior to and during the overland flow sampling period

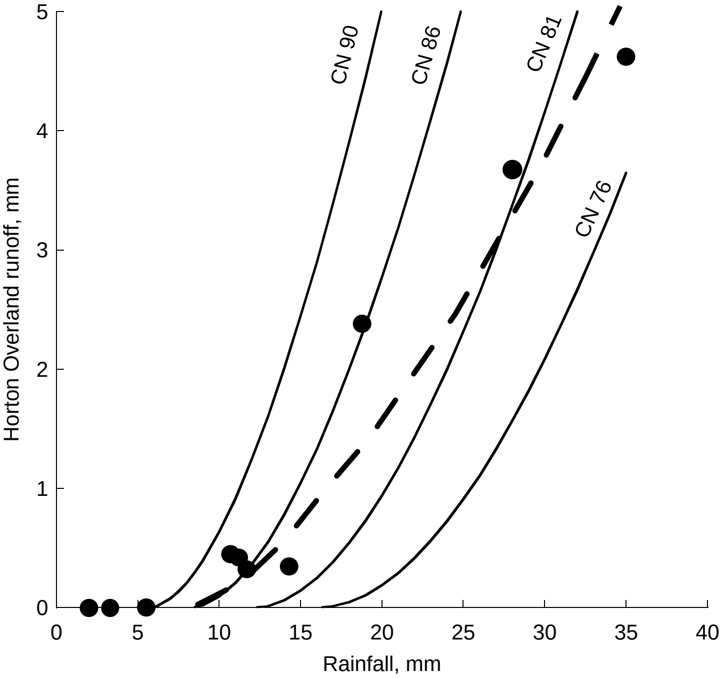

Figure 6. Rainfall-runoff relationship with Soil Conservation Service model curve for Horton overland flow (HOF). The dashed line incorporates varying curve numbers (CN) used to calculate annual HOF flows and fluxes

steady–state height for the wet season. HOF production may also increase with an increase in soil moisture (Bales and Betson, 1981; Perrone and Madramootoo, 1998). Soil moisture increased rapidly during the first few storms of the wet season, but varied only slightly during the wet season both at Nossa Senhora (Hodnett *et al.*, 1996) and in the eastern Amazon (de Moraes *et al.*, 2006). The sampling in October–November occurred one month after the first rains of the season, and immediately following several days of precipitation (Figure 5), so soil moisture status during the sampled storms was likely similar to wet season values. The SCS curve numbers calibrated to the October–November observations should therefore apply throughout the

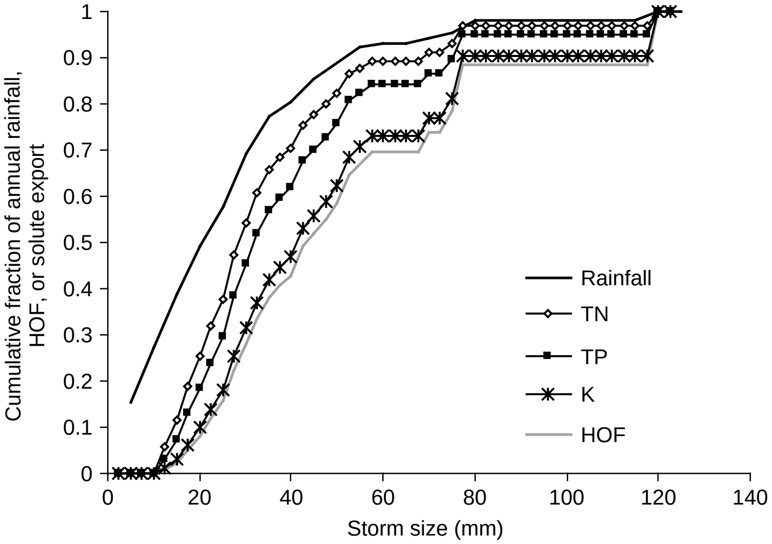

Figure 7. Cumulative depth of annual rainfall (solid line), Horton overland flow (HOF) (dashed line) and solute export via HOF, by storm size

Table II. Estimated hydrologic budget for the hillslope (in mm). The fraction of the hillslope that was upslope (λ_{up}) was 0·92. The range of values for groundwater flow from upslope (Q_{sof}) and sub-surface and return flow (Q_{unz}) were determined using a near-stream area saturated fraction (η) that ranged from 0·3–0·8

	Depth (mm)	Fraction of annual precipitation	Fraction of annual flow
Precipitation (P)	1918	1	—
Evapotranspiration (ET)	1024–1247	0·53–0·65	—
Groundwater flow from upslope to stream (Q_{gs})	368–591	0·19–0·30	0·55–0·66
Near-stream zone flow			
Saturated overland flow (Q_{sof})	46–123	0·02–0·06	0·05–0·18
Sub-surface and return flow (Q_{unz})	31–107	0·02–0·06	0·03–0·16
Overland flow (Q_h)	149	0·08	0·17–0·22
Total annual flow $Q_t = P\text{-}ET$	671–894	0·35–0·47	1

rainy season. More detailed investigations of runoff production for soils of different soil moisture status could test this assumption.

Changes in soil hydraulic properties and HOF production following deforestation were also observed in another pasture site in Rondônia (Rancho Grande), where the upper 10 cm of pasture soil had lower infiltration capacities than forest soils (Elsenbeer *et al*., 1999). Bare patches in the Rancho Grande pastures yielded HOF for rainstorms greater than 13 mm/h, which was exceeded in all but one of the rainfall events observed at Nossa Senhora (Table I).

The decrease in the SCS curve number with increasing storm depth was likely due to changes in the infiltration capacity of surfaces inundated during flows of different depths. During small rainstorms (<15 mm), HOF was generated on small bare patches and cattle trails. Areas covered by grass produced runoff during large storms (>20 mm), resulting in higher catchment-averaged infiltration and a lower SCS curve number. Measurements at the Rancho Grande site showed that bare areas had lower infiltration capacity (~13 mm/h) than grassy areas (~28 mm/h), (Elsenbeer *et al*., 1999). The bare areas generated runoff earlier in rainstorms

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than elevated clumps, and the infiltration capacity of the hillslope increases with storm size and depth of HOF, a process documented on pasture hillslopes in Africa (Dunne *et al*., 1991).

Solute concentrations in different flowpaths

Our purpose of calculating annual water fluxes was to frame the observations of HOF in a hillslope conceptual model of solute transport pathways to allow estimation of the relative magnitudes of solute export via each pathway. Spatial and temporal variability in solute concentrations along various pathways, especially in the near-stream zone, may be considerable, both within a single storm event and between storm events. Here we explicitly modelled the effect of storm size on solute concentrations in HOF, but the concentrations of solutes in the groundwater have been assumed constant in this rapid, single-season sampling effort. Flux calculations for the near-stream zone, in particular, were based on few samples. These estimates highlight dominant transport pathways and suggest where future sampling efforts could reduce uncertainties.

The biogeochemical composition of water differed by flow path (Figure 8). Water on the surface (SOF, HOF) was enriched in elements with high concentrations in biological material or fine-grained mineral particles, such as K, P, and N, and depleted in elements with lower biological activity such as Na and Si. Groundwater in the near-stream zone had higher concentrations of N, Na, and K than upslope groundwater (Figure 8). Solute concentrations varied little with depth in the near-stream zone. Concentrations of Si were 17% higher in the deep well (130 cm below ground surface) compared with the shallow well (50 cm below ground surface), and concentrations of K were 10% higher in the deep well compared with the shallow well. All other solutes differed by less than 5% between the shallow and deep well, suggesting that solute concentrations did not change markedly with depth in the near-stream zone.

In contrast with some other sites (Ann *et al*., 2000; Villapando and Graetz, 2001), groundwater in the Rondônia near-stream zone did not have appreciably higher total dissolved phosphorus (TDP) concentrations compared with upslope groundwater, despite evidence of low redox status in the soil. The abundance of Fe sesquioxides in these soils may explain the consistently low TDP concentrations in all sub-surface pathways.

Inter-storm variations in solute concentrations and flux calculations

Solutes in HOF were diluted during high discharges, both within a single event (Figure 9) and among events (Figure 10) of different runoff depths. The amount of dilution was less than that expected from a solute with a fixed rate of supply to the flow, and fluxes increased with discharge. TN showed the most dilution with increasing HOF depth (Table III) followed by Na $>$ TP $>$ Cl $>$ TDN $>$ TDP $>$ K $>$ Si. Most constituents showed concentration-discharge hysteresis (Figure 9), which is typical in the flushing of mobile material (Hyer *et al*., 2001; Nagorski *et al*., 2003; Walling and Webb, 1986). Suspended sediments showed the strongest hysteresis as quantified by the ratio of the concentration on the rising limb to concentrations on the falling limb (Table IV). K and Cl showed the least amount of hysteresis, and have relatively high resistance to dilution. The relatively high solubility of organically bound K may be the cause of the resistance of K to dilution with increasing HOF volume.

The calculations of solute flux in HOF assumed that the parameters of the concentration-discharge relationship (a and b in Equation (8)) did not change significantly during the rainy season. Solute fluxes in HOF for a given rainfall depth may not have been constant throughout the wet season, particularly during the first runoff events at the beginning of the wet season when mobile material that accumulated during the dry periods flushed from the land surface (Walling and Webb, 1986). Six intermediate-sized storms (8–33 mm) occurred prior to sampling (Figure 6) and likely flushed some of the mobile material. No large difference in runoff production or solute flux was observed for storms of similar sizes that occurred within 2–4 days of each other (e.g. October 31 and November 4, Table I). Solute flux measurements throughout the year, or another rapid sampling campaign at the end of the wet season could test for the effects of seasonality on the concentration-discharge relationship.

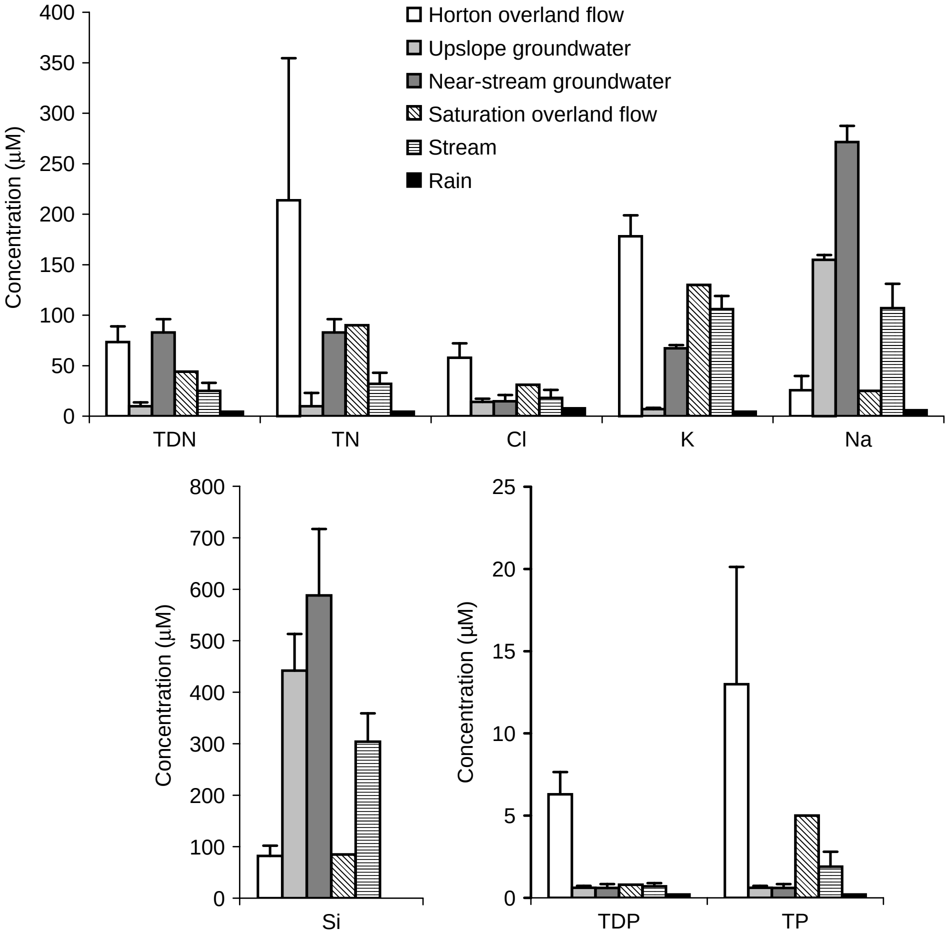

Figure 8. Comparison of solute concentrations in Horton overland flow ($n = 42$), upslope groundwater ($n = 5$), near-stream groundwater ($n = 11$), saturation overland flow ($n = 2$), stream water ($n = 15$), and rainfall (from Pauliquevis *et al*., 2004). Error bars indicate the standard deviation

The flux calculations assumed low inter-storm and seasonal variability in the solute concentrations in groundwater. The coefficient of variation for the five samples collected in the well nearest to the stream was lowest for K and Na (5%), mid-range for TDN and Si (10–20%), and highest for Cl and TDP (35–45%). There was no systematic variation with depth to water table or distance from the stream.

Annual solute export: comparisons by hydrologic pathway and landscape position

The relative dominance of HOF, upslope groundwater flow, and the near-stream zone for annual export differed among solutes, indicating preferential concentration, dilution, or retention along different pathways (Figure 11, Table V). Export of TDP and PP occurred mostly (48–68%) through HOF, owing to high concentrations in HOF and low concentrations in sub-surface pathways. K and N had high fluxes in the near-stream zone, and low fluxes through upslope groundwater. By contrast, geochemical elements, such as Na and Si were exported via upslope groundwater, and HOF accounted for only 1–7% of their annual export from upslope. Upslope groundwater accounted for less than 20% of the annual export of all solutes except Si and Na, indicating the importance of near-surface and near-stream zone pathways. These groupings

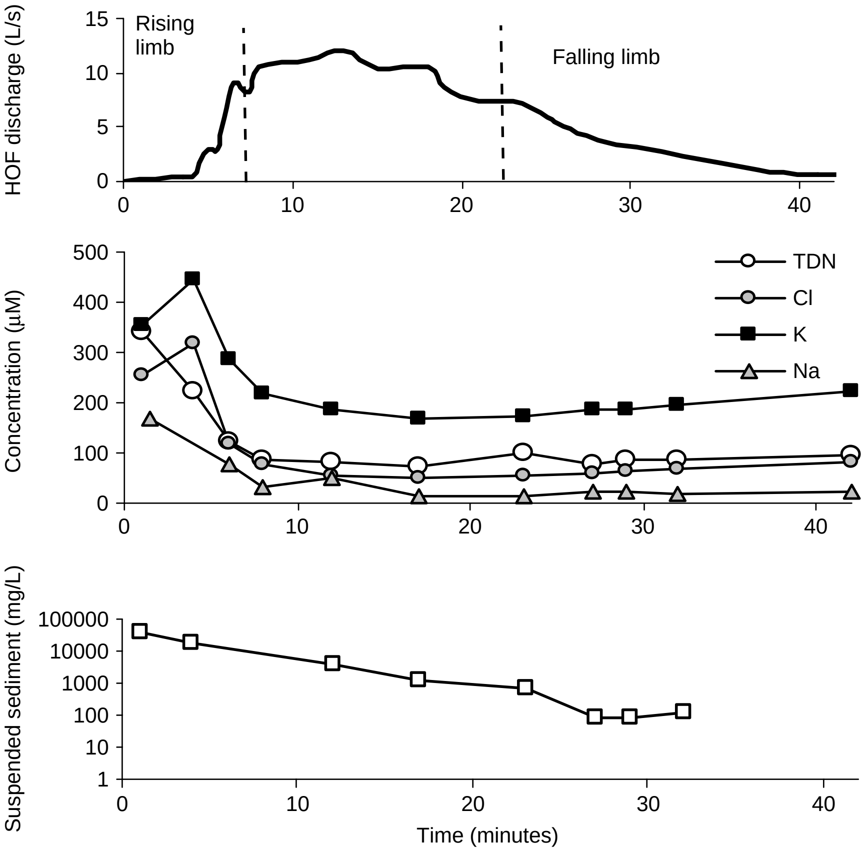

Figure 9. Horton overland flow and solute concentrations for the storm on October 31, 2002

remained consistent given the full range of possible values of ET and saturation status of the near-stream zone (Figure 11).

The observed patterns in solute concentrations and fluxes were based on relatively small sample sizes collected over a short period, but they nonetheless highlight broad differences in solute behaviour in different flowpaths. The estimates of export from HOF were likely the most robust, given the sample sizes and regularity of the relationship observed between precipitation and solute flux. The export estimates from the near-stream zone were the most uncertain, due to both the small sample size and possible inter-storm and seasonal variability in concentrations not captured during the sampling.

The patterns in solute transport by flowpath observed at the Nossa Senhora hillslope were consistent with those observed in other, more intensively sampled hillslopes. In another forested catchment in the Amazon basin, Elsenbeer *et al*. (1995) classified K as biochemically active and found that it was transported in near-surface 'fast' pathways such as overland flow. Na is more geochemically active and is transported in 'slow' pathways. This classification also applied to the Nossa Senhora hillslope, where biochemical elements (K, N, P) were transported in either HOF or the near-stream zone, while geochemical elements (Na, Si) were dominant in upslope groundwater that interacted with weathering saprolite and bedrock.

The importance of HOF for P export from agricultural watersheds has been noted in numerous studies (Gburek and Sharpley, 1998; McDowell *et al*., 2001). P is often bound to sediments, so its export depends on upslope erosion and sediment mobilization (Kronvang *et al*., 1997; Steegen *et al*., 2001). At the Nossa Senhora hillslope, concentrations and fluxes of P were low in sub-surface pathways, likely

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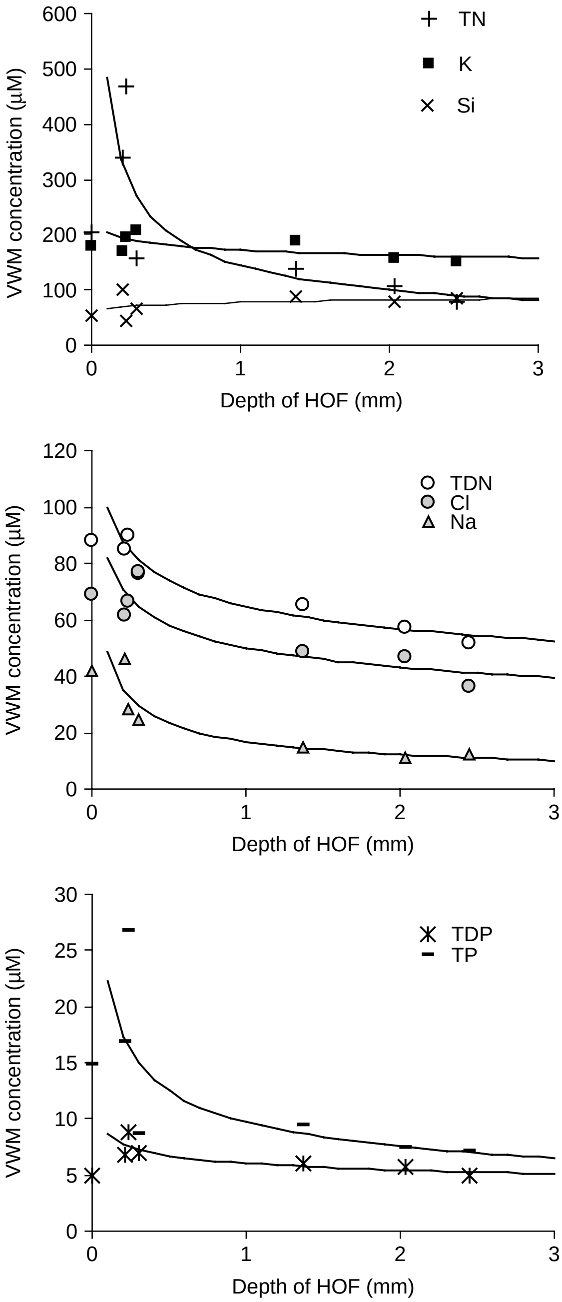

Figure 10. Volume-weighted mean concentration of solutes *versus* total event runoff depth. Lines represent the best-fit to Equation (8)

due to the high sorption capacity of the Al and Fe sesquioxides present in the soil (Reddy *et al*., 1999). Though P may be mobilized in soils with low redox potential (Carlyle and Hill, 2001) or low clay content (Graetz and Nair, 1995), the high clay, Al and Fe content of the Nossa Senhora soils resulted in low P concentrations in sub-surface water, even in near-stream soils with evidence of low redox potential.

Table III. Parameters of the concentration-discharge relationship (Equation (8)) for different solutes. Fits shown in Figures 9 and 10

	a	b
Si	77	0·07
K	170	−0·075
TDP	6·0	−0·15
TDN	65	−0·19
Cl	50	−0·21
TP	9·8	−0·36
Na	17	−0·46
TN	141	−0·53

Table IV. Ratio of concentrations of sediment and solutes in Horton overland flow during rising and falling discharge for the storm on October 31, 2002. The ratio was the average of three rising limb samples divided by the average of five falling limb samples

Sediment	164
TN	14
TP	8·4
Na	5·4
Cl	2·9
K	1·7

Measurements of infiltration capacities of forest and pasture systems suggest that HOF rarely or never occurs in forests (de Moraes *et al*., 2006; Elsenbeer *et al*., 1999). If F_h is close to zero in forest ecosystems, then conversion to pasture and enhanced HOF production more than doubles the loss of P to streams. In addition, the pasture at Nossa Senhora was 18–25 years old, suggesting that enhanced P export continued for decades following deforestation and pasture establishment.

Export of N from catchments covered in tropical rainforest is dominated by inputs in the near-stream zone (McDowell *et al*., 1992), or by inputs directly to the stream from litterfall (Brandes *et al*., 1996), due to high retention and removal rates in the near-stream zone. The Nossa Senhora hillslope showed similar evidence of low inputs of N from upslope groundwater and high fluxes of N through the near-stream zone (Figure 11). The conceptual model of the Nossa Senhora hillslope assumed that the mean N concentrations observed in the near-stream zone were representative of the N concentration of water entering the stream. Concentrations of TDN decreased slightly in the wells nearest the stream (∼75 μM) compared with wells further from the stream (∼93 μM), but K, Na, and Si concentrations decreased by similar amounts, suggesting that a significant removal of N did not occur in the sub-surface flowpath between wells in the near-stream zone. However, denitrification may remove N in the near-stream zone before it reaches the stream (Brandes *et al*., 1996), even within decimeters of the soil-stream interface (Hedin *et al*., 1998). Further sampling, particularly of gaseous N fluxes in near-stream areas could refine the estimates of fluxes from the near-stream zone.

The hillslope measurements detailed likely pathways for the land use signal in stream solute concentrations measured in synoptic surveys of large watersheds of 10–30 000 km^2. Elements having a large component of their export in HOF based on the hillslope measurements (K, Cl, TDP) had higher concentrations in deforested watersheds compared with forested watersheds during the wet season, while elements dominated by the near-stream zone or upslope groundwater (Na, Si, TDN) showed no detectable land use signal (Biggs *et al*., 2002; Biggs *et al*., 2004). The low response of TDN and N to land use in the wet season suggested that either the near-stream zone fluxes were similar in pasture and forest, or that significant retention or

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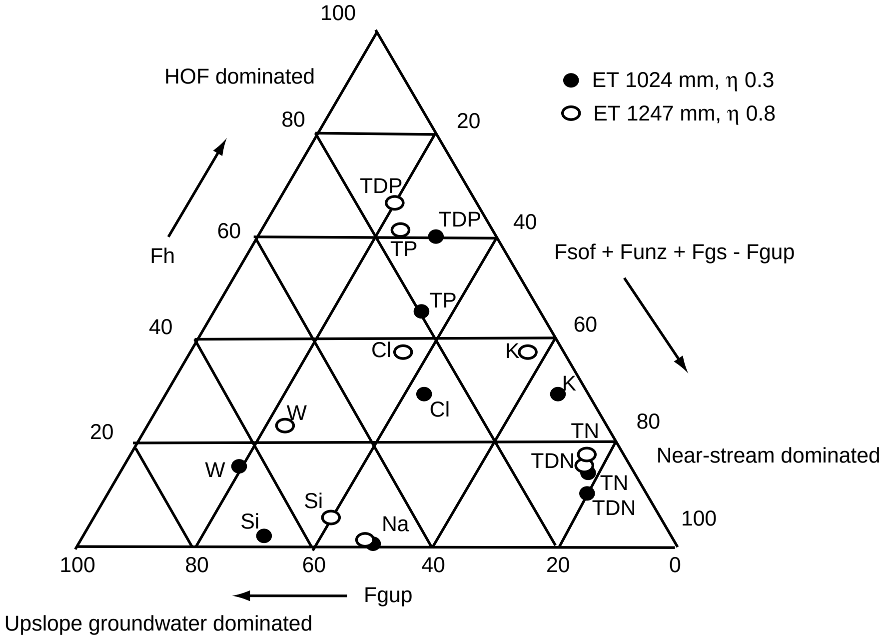

Figure 11. Ternary diagram of different flowpath contributions to runoff and solute export. Axes units are percent of the total annual hillslope flux (F_t). W indicates water. Dark circles indicate ET of 1024 mm/year and a near-stream area saturation fraction (η) of 0·3, and clear circles indicate ET of 1247 and η of 0·8

Table V. Annual solute and nutrient flux estimates, in moles/ha-year for the Nossa Senhora hillslope. The range of estimates for saturation overland flow (F_{sof}) and sub-surface flow (F_{unz}) were for near-stream area saturated fractions (η) of 0·3 and 0·8

	K	Cl	Na	Si	TDN	TN	TDP	TP
Rainfall	32–85	48–149	77–113	0	96–236[a]	—	3·8–4·4[b]	—
HOF (F_h)	220	51	12	134	69	96	6·8	8·1
Upslope groundwater to near-stream zone (F_{gup})	26–42	53–84	590–935	1681–2667	37–59	37–59	2·2–3·6	2·2–3·6
Near-stream groundwater to stream (F_{gs})	246–397	55–89	1000–1918	2170–3481	306–491	306–491	2·2–3·6	2·2–3·6
Saturation overland flow (F_{sof})	60–160	14–38	12–31	39–105	20–54	41–111	0·4–1·0	5·0–6·2
Near-stream sub-surface stormflow (F_{unz})	21–72	4–16	84–289	182–630	26–88	26–88	0·2–0·6	0·2–0·6
Total flux (F_t)	599–796	148–182	1124–1917	2584–4283	454–669	537–722	10–11	13–18
Net flux (F_t–F_{rain})	514–758	0–134	1011–1840	2584–4283	218–573	296–626	5·7–7·7	9–14

[a] Dissolved inorganic N (Pauliquevis *et al.*, 2004).
[b] PO_4.

denitrification occurred along the pathway from the near-stream zone to the channels of larger streams. The land use signals in stream chemical composition observed at the regional scale during the wet season were likely due to enhancement of solute transport in overland flow, rather than changes in the solute composition of upslope groundwater.

CONCLUSIONS

Significant uncertainties remain about the solute flux values from the pasture hillslope owing to the limited number of samples and short duration of sampling, but some broad conclusions may be drawn by considering the range of values observed. SOF and HOF occurred in roughly equal proportions, though sub-surface pathways dominated annual discharge. Solutes and nutrients fell into three categories depending on their dominant transport pathway: HOF from upslope dominated the export of P, the near-stream zone accounted for a large component of N and K export, and sub-surface pathways from upslope portions of the hillslope accounted for most of the Na and Si export. Solutes with a large HOF component (TDP, K, Cl) also had higher concentrations in streams draining large deforested watersheds (10–30 000 km^2) compared with streams draining forested watersheds, suggesting that deforestation and pasture establishment increases solute and nutrient export at the landscape scale by increasing solute fluxes in Horton overland flow. The increased export via HOF lasts for decades following pasture establishment.

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