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Solute and sediment export from Amazon forest and soybean headwater streams

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Abstract. Intensive cropland agriculture commonly increases streamwater solute concentrations and export from small watersheds. In recent decades, the lowland tropics have become the world's largest and most important region of cropland expansion. Although the effects of intensive cropland agriculture on streamwater chemistry and watershed export have been widely studied in temperate regions, their effects in tropical regions are poorly understood. We sampled seven headwater streams draining watersheds in forest (n = 3) or soybeans (n = 4) to examine the effects of soybean cropping on stream solute concentrations and watershed export in a region of rapid soybean expansion in the Brazilian state of Mato Grosso. We measured stream flows and concentrations of NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+}, Fe^{3+}, and dissolved organic carbon (DOC) biweekly to monthly to determine solute export. We also measured stormflows and stormflow solute concentrations in a subset of watersheds (two forest, two soybean) during two/three storms, and solutes and $\delta^{18}O$ in groundwater, rainwater, and throughfall to characterize watershed flowpaths. Concentrations of all solutes except K^+ varied seasonally in streamwater, but only Fe^{3+} concentrations differed between land uses. The highest streamwater and rainwater solute concentrations occurred during the peak season of wildfires in Mato Grosso, suggesting that regional changes in atmospheric composition and deposition influence seasonal stream solute concentrations. Despite no concentration differences between forest and soybean land uses, annual export of NH_4^+, PO_4^{3-}, Ca^{2+}, Fe^{3+}, Na^+, SO_4^{2-}, DOC, and TSS were significantly higher from soybean than forest watersheds (5.6-fold mean increase). This increase largely reflected a 4.3-fold increase in water export from soybean watersheds. Despite this increase, total solute export per unit watershed area (i.e., yield) remained low for all watersheds (<1 kg NO_3^- N·ha^{-1}·yr^{-1}, <2.1 kg NH_4^+-N·ha^{-1}·yr^{-1}, <0.2 kg PO_4^{3-}-P·ha^{-1}·yr^{-1}, <1.5 kg Ca^{2+}·ha^{-1}·yr^{-1}). Responses of both streamflows and solute concentrations to crop agriculture appear to be controlled by high soil hydraulic conductivity, groundwater-dominated hydrologic flowpaths on deep soils, and the absence of nitrogen fertilization. To date, these factors have buffered streams from the large increases in solute concentrations that often accompany intensive croplands in other locations.

Key words: *agroecosystems; biogeochemistry; Brazil; hydrology; land-use change; streams; watershed.*

Introduction

Expansion and intensification of crop agriculture often increase nutrient runoff and sediment export from watersheds, which has caused widespread decreases in water quality (Carpenter et al. 1998, Galloway et al. 2003, Jacobson et al. 2011). Most examples of how crop expansion and intensification affect stream chemistry and watershed export are from the temperate zone and are often associated with high fertilizer inputs (Jordan et al. 1997, Turner and Rabalais 2003, Billen et al. 2007). During the past few decades, however, most new land conversion to intensive agriculture has occurred in the tropics (FAO 2009, Foley et al. 2011), where the effects of agricultural intensification on the quality of surface waters remain poorly known. Growing global demand for food, animal feed, biofuel, and fiber will likely lead to continued expansion and intensification of tropical crop agriculture, particularly in rapidly developing countries.

The Amazon Basin of Brazil has seen extensive, recent expansion of large-scale soybean cropland into the world's largest remaining tropical forest (Morton et al. 2006, Nepstad et al. 2006). From the 1970s to the late 1990s, land-use change in the Brazilian Amazon was driven predominantly by the expansion of cattle ranching

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on slashed and burned forest (Skole and Tucker 1993, Fearnside 2005). During the last 20 years, however, soybean cultivation has expanded and intensified, especially at the Amazon's eastern and southern edge (Fearnside 2001, 2005, Nepstad et al. 2006). From 2001 to 2004, more than 87% of this expansion of cropland in the Amazon occurred in the Brazilian state of Mato Grosso (Morton et al. 2006). Between 2001 and 2010, three million ha were converted to soybean cultivation, with soybean production in the state nearly doubling over the same period (Macedo et al. 2012). At the same time, the proportion of new cropland sourced from already cleared land (primarily pastureland) increased from 74% (2001–2005) to 91% (2005–2010) (Macedo et al. 2012) in the forested region of the state. The effects of this new land-use transition (from pasture to intensively cropped agriculture) on streamwater chemistry and export have not been examined previously.

Small headwater streams connect terrestrial environments with surface waters and provide a major conduit for solute and sediment export from landscapes (Bormann et al. 1968, Vannote et al. 1980, Peterson et al. 2001). The hydrology and solute chemistry of headwater streams respond rapidly to land-use change and land disturbance (Likens et al. 1970, Webster et al. 1992). Comparisons of solute or sediment concentrations and export in headwater streams draining agricultural landscapes have been widely used to assess the effects of agriculture on water quantity and chemistry (Dillon and Kirchner 1975, Smart et al. 1985, Jordan et al. 1997).

Previous studies in Amazonia have shown that conversion of headwater catchments from forest to pasture produces an initial increase in solute transport and export (Williams and Melack 1997, Neill et al. 2006). In pastures, grazing by cattle decreases soil infiltrability and hydraulic conductivity (Zimmermann et al. 2006) while increasing overland flow (Germer et al. 2010), as well as hydrologic, solute, and sediment export (Biggs et al. 2006, Germer et al. 2009). Additionally, clearing for pasture has been shown to increase solute concentrations in larger Amazonian streams and rivers (Ballester et al. 2003, Biggs et al. 2002). However, pasture catchments can have lower export of some solutes, particularly NO_3^-, when aquatic grasses infill stream channels running through pastures (Neill et al. 2001, Deegan et al. 2011).

There are several indications that watershed hydrology and solute transport in southeastern Amazonia may respond differently to crop conversion compared with conversion to pasture in other parts of Amazonia. First, in Mato Grosso highly weathered soils, 45% of which are Oxisols, cover most of the land area (Soil Survey Staff 1999, FAO 2011). They tend to be up to several meters deep (Negreiros et al. 2009), and in some places display a pronounced microaggregation (pseudosand, Schaefer 2001). This creates high infiltrability, reduces surface compaction, and leads to streams dominated by groundwater flows (Cassel and Lal 1992, Elsenbeer 2001). The increased resistance to surface compaction and high infiltrability of these soils has been observed to reduce the production of overland flow despite large increases in streamflow in cropland compared to forests (Hayhoe et al. 2011, Scheffler et al. 2011).

Second, crop management may lead to relatively low solute export. Nitrogen (N) fertilizer is not applied (or applied in very small amounts) to soybean crops in this region (Galford et al. 2010) and farmers rely on N fixation to meet crop N demand. Phosphorus (P) fertilizer inputs to soybeans are high, ~ 40–50 kgP/ha (Riskin et al. 2013*a*, Roy et al. 2016), but soils strongly fix added P. Following (at least) the first five years of cultivation soil available P does not increase below the tilled layer (30 cm; Riskin et al. 2013*b*), and soil erosion, which dominates sediment (and hence P) delivery to streams in other regions (Sharpley et al. 1992). Except for one or two years following conversion from forest or pasture, crop management is almost exclusively by minimum tillage (Neill and Macedo, *unpublished manuscript*), which further reduces the potential for overland flow and erosion.

We examined the effect of Amazon soybean agriculture on watershed hydrology and solute export in three lowland forested catchments and four soybean catchments in a region of rapidly expanding soybean cropping in northern Mato Grosso, Brazil. We monitored watershed hydrology, solute and sediment concentrations, and export for a year. We also measured stream solute and sediment concentrations during periods of baseflow and during rain events to quantify the potential importance of stormflow. We focused on the following key questions: (1) Do streamwater solute and sediment concentrations vary between land uses? Do streamwater solute and sediment concentrations vary seasonally? (2) Does the decrease in evapotranspiration in cropped watersheds lead to an increase in stream discharge? (3) Does the annual yield of solutes and sediment vary between land uses?

Based on previous hydrological data (Hayhoe et al. 2011) and the unique properties of the well-drained, highly weathered soils of this region, we hypothesized that soybean watersheds would be buffered from the typical consequences of large-scale agricultural development such that (1) streamwater and sediment concentrations would vary seasonally but not between land uses, (2) changes in land cover would decrease evapotranspiration and increase discharge in soybean watersheds compared with forested watersheds, and (3) this increase in discharge would increase the annual yield of solutes and sediments from soybean watersheds compared with forested watersheds. We discuss the management implications of our results in the context of ongoing agricultural conversion in the Amazon region.

Methods

Field site

We worked at Tanguro Ranch, an 800 km^2 soybean farm in Mato Grosso, Brazil, that includes about 500 km^2

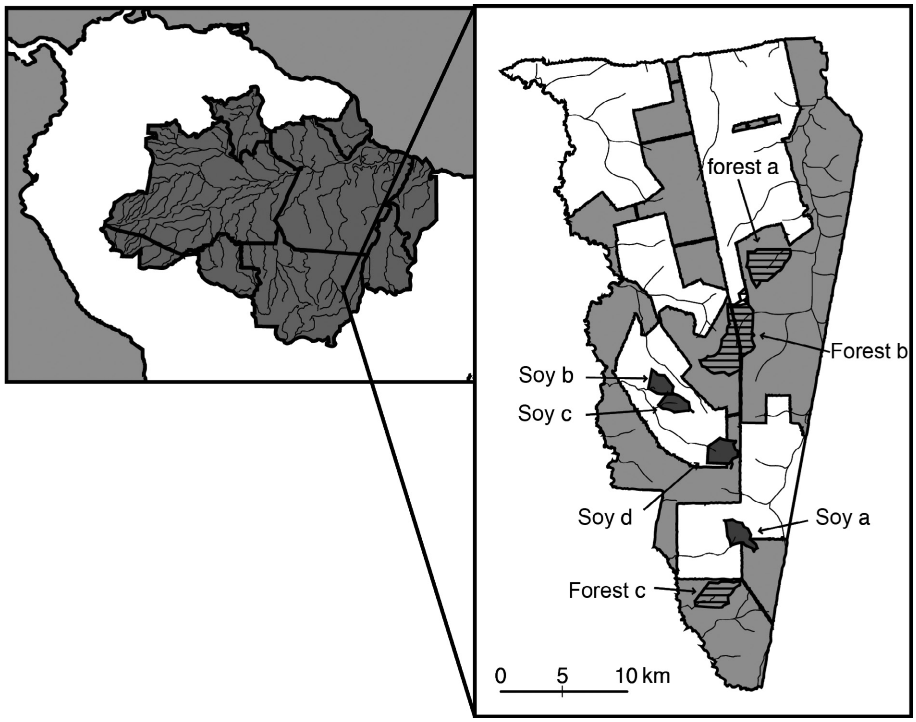

FIG. 1. The location of Tanguro Ranch within the Brazilian Legal Amazon. Inset map shows Tanguro Ranch indicating locations of three forest and four soybean watersheds.

of forest and 300 km^2 of cultivated soybeans in a single annual rotation (Fig. 1). Mean annual temperature is 27°C and mean annual precipitation is 1,800 mm/yr (1987–2010 mean; Tanguro Ranch, *unpublished data*), almost all of which falls from September to April. Tertiary and Quaternary fluvial deposits cover Precambrian gneisses of the Xingu Complex (Projeto Radambrasil 1981). The region lies in the headwaters of the Xingu River, the fifth largest tributary of the Amazon River by watershed size (basin area, 446,203 km^2; length, 1,640 km; average discharge, 8,665 m^3/s). The landscape at Tanguro Ranch is undulating, with wide interfluves that grade to streams with generally less than 65 m in elevation change and channel slopes between 0.3° and 1.9° (Hayhoe et al. 2011). Topographic differences between plateaus and stream channels indicate the depth to the water table ranges from 20 to more than 40 m (Hayhoe et al. 2011).

Soils along geographic plateaus are medium textured, highly weathered, base-poor ustic Oxisols (Soil Survey Staff 1999), which is equivalent to Latossolo vermelho-amarelo distrófico in the Brazilian classification (Embrapa 2013). Soils are deep and well drained on plateaus and grade into aquic Inceptisols (Soil Survey Staff 1999), or Gleissolos (Embrapa 2013), along stream channels and riparian zones. Plateau soils have a mean soil texture of 55% sand, 2% silt, and 43% clay across all land uses (Riskin et al. 2013*a*).

We sampled seven first-order headwater streams, three in forest and four in soybean catchments (Fig. 1), from August 2008 to August 2009. Riparian forest vegetation is perennially evergreen and has a relatively low diversity of tree species (Shannon diversity index ~3.13; Nagy et al. 2015), typical of the transitional forests between cerrado woodlands and central Amazon evergreen forest (Ivanuskas et al. 2004). Watersheds now planted in soybeans were originally cleared for pasture in the early 1980s and then converted to soybean cultivation between 2003 and 2008. All contained a narrow (50–200 m) band of riparian forest. Three of the soybean watersheds monitored in this study (b–d) were converted in 2004 and one (a) was converted in 2007. We sampled each stream between 420 and 2,000 m from its source. All soybean watersheds had a small impoundment at the headwaters. These were created to provide water for cattle when the land was pasture and they occur in nearly all headwater streams in former pasturelands of the region (Macedo et al. 2013). We sampled soybean streams between 10 m and 360 m downstream of these impoundments.

When pastures were converted to soybean cropland, woody vegetation was burned, soil was tilled to 50 cm, and lime was incorporated. Soils were then disked to 30–40 cm for 1–2 yr and subsequently managed by no-tillage. Lime was added at approximately 1,500 kg/ha every other year following conversion. Approximately 50 kg/ha P (as rock phosphate, single super phosphate, or triple super phosphate) and approximately 70 kg/ha potassium (as KCl) were added annually (Scheffler et al. 2011; Tanguro Ranch, *unpublished data*).

Flow measurements

We established monitoring sites within each stream for measurement of stream stage and discharge. Stream stage was measured hourly with HOBO pressure loggers (Onset Computer, Bourne, Massachusetts, USA). We used a reference logger that recorded ambient air pressure and temperature to correct for atmospheric pressure and convert pressure to water level. We calculated hourly discharge from rating curves extrapolated with power functions based on periodic measurements of stream cross-sectional area and water velocity across a range of discharges (Gore 2007, Hayhoe et al. 2011; Appendix S1: Fig. S1). Although hourly measurements might underestimate peak flows that occur within an hour in small watersheds, this hourly time-step appears to capture most high flows in our study system (Appendix S1: Fig. S2). Flow in each watershed was standardized to watershed area. We delineated watershed areas using a digital elevation model and standard Hydrology Tools in ArcGIS (Hayhoe et al. 2011). We filled one gap in stage data (967 h in watershed Soy b) using the mean annual flow rate for each missing hourly datum. We compared four gap-filling methods: (1) taking the mean proportional change in flow of the two closest streams, (2) removing the hours from the year of discharge, (3) using the mean baseflow rate from 500 h of dry season baseflow, and (4) using the mean annual flow rate. Although method 4 (mean annual flow rate) increased the total annual flow compared with methods 2 and 3 and decreased mean daily flow rates compared to methods 1 and 3, we selected it because the change in standard deviation for the year of daily flows was least influenced using this method and, compared to using only base flow, seemed more representative of discharge over the period of the gap. We performed a hydrograph separation based on the local minima method of Sloto and Crouse (1996) to partition discharge into baseflow and stormflow (methods described in Hayhoe et al. 2011).

Because these watersheds consist of deep sediments and lack impermeable bedrock in stream channels, it is likely that some flow leaves the watershed as groundwater, which would not be captured by our surface discharge measurements. To account for this possibility, we compared measured stream discharge with the expected streamflow (ESF), calculated from observed rainfall (PPT) and modeled regional evapotranspiration (ET) data for each watershed (ESF = PPT − ET). This allowed us to estimate any runoff that bypassed small stream channels as underflow, i.e., groundwater that exits the watershed boundary without interacting with surface water. To estimate annual rainfall (PPT), we took the mean of two daily rainfall datasets, one from a recording weather station at Tanguro Ranch (IPAM, *unpublished data*) and the other from a network of 23 rainfall collectors in soybean fields on the farm (Tanguro Ranch, *unpublished data*). We combined monthly rainfall totals from each collector to generate a monthly average. We estimated monthly watershed ET during the study period using the Global Terrestrial ET Data Set (MOD16), which models monthly ET using satellite data from the Moderate Resolution Imaging Spectroradiometer (MODIS) and an algorithm based on the Penman–Monteith equation (Mu et al. 2011). To estimate ET for each study watershed, we took an area-weighted average of monthly ET values for all pixels (1-km^2 resolution) intersecting the watershed, using standard tools in the Raster package in R (Hijmans and van Etten 2012). Using the above datasets, we calculated the expected streamflow (ESM) in each of our study watersheds at monthly intervals.

Baseflow sampling

We collected baseflow samples from each of the seven watersheds every 2–4 weeks between August 2008 and August 2009 (Appendix S1: Fig. S1). At each location, we collected four water samples from a 1-L polyethylene bottle that we triple rinsed with streamwater. We poured a 25-mL subsample into a vial with no headspace and no preservative for isotopic analysis ($\delta^{18}O$). We filtered a second using a Swinnex syringe filter cartridge (Millipore, Bilercia, Massachusetts, USA) and an ashed 25-mm glass fiber filter (Whatman GF/F) into a 40-mL glass vial with a Teflon-lined lid. We preserved this sample with 250 μmol/L $HgCl_2$ for analysis of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). We filtered a third subsample for analysis of anions and cations into an acid-washed 60-mL plastic bottle and preserved it with a small amount of thymol (to inhibit microbial activity) and froze it generally within 4 h. We measured pH and conductivity in a field laboratory (Orion meters, Thermo Fisher Scientific, Waltham, Massachusetts, USA) on the 1-L sample. We measured total suspended solids (TSS) by filtering a separate measured volume of water through a pre-weighed glass fiber filter, which was then dried at 60°C and reweighed.

Stormflow sampling

We instrumented two forest watersheds and two soybean watersheds with Isco automated water samplers (Teledyne Isco, Lincoln, Nebraska, USA). We captured between two and four rain events in each watershed during either the early wet season (between September and November 2008) or the late wet season (between January and March 2009; Appendix S1: Fig. S1). The samplers were set to trigger at the beginning of a rain event to capture the chemistry of both the ascending and descending limbs of storm hydrographs. Based on our previous observations of hydrograph responses to large rain events, we set the samplers to collect the first 15 samples every 15 min and the last nine samples following 30, 30, 60, 60, 120, 120, 180, 180, and 360 min. We collected stormflow samples from the samplers within 12 h of the end of the 23-h sampling event and processed the samples following the same procedure previously described.

Rain, groundwater, and throughfall sampling

We collected rainwater samples during a subset of storms from the early wet season (September and October 2008) and the late wet season (January and February 2009). We used three rain collectors in an open field more than 1 km from any forest edge. Rain collectors were 1.5 m long PVC pipes and ~15 cm in diameter with three rectangular openings cut along one axis of the pipe (Germer et al. 2009). The pipe was suspended horizontally approximately 1 m above the ground. One end of the PVC pipe was capped while the other was attached to a funnel, lined with mesh, and connected to a collection bucket by a plastic hose. For each sampled event, we filtered and preserved samples for analysis like other water samples.

We installed three shallow groundwater wells in 2008 at field edges about 50 m from the stream edge in each watershed. Wells were constructed of PVC and installed by hand augering wells 2 m below the water table, to a total depth of 4–6 m. We sampled groundwater twice, in October 2008 at the beginning of the rainy and soybean cropping seasons, and in February 2009 late in the rainy season and at the end of the cropping season. We collected samples by bailer or battery pump, and we flushed wells for three well volumes before collection. Samples were preserved and analyzed as previously described.

Throughfall was collected from one large and intact forest site on Tanguro Ranch from September 2008 to February 2009. We placed three throughfall collectors 200 m from the forest edge. We collected water after eight sizable rain events (>20 mm) during the rainy season (two events in September, one in October, one in January, and four in February). Samples were filtered and preserved as previously described. We assumed that throughfall chemistry was not modified by the litter layer and hence that the throughfall collected represented the ultimate input into the soil.

We analyzed water samples at the Centro de Energia Nuclear na Agricultura (CENA) at the University of São Paulo, Brazil. We analyzed anions and cations (NH_4^+, NO_3^-, NO_2^-, SO_4^-, PO_4^{3-}, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, Fe^{3+}) using inductively coupled plasma optical emission spectroscopy (Ultima 2, Horiba Jobin Yvon, São Paulo, Brazil). We measured DOC and DON with a TOC analyzer (TOC-CPH, Shimadzu, Columbia, Maryland, USA) and $\delta^{18}O$ using laser mass spectrometry (DLT-20, Los Gatos Research, Mountain View, California, USA).

Data analyses

We tested for seasonal and land use differences in solute concentrations with a repeated measures univariate split-plot approach that compares changes in solute concentrations both between land uses and over time within a single model (Quinn and Keough 2002, Hayhoe et al. 2011). We fit an equation of the form

$$Y_c = \beta_0 + \beta_1 x_{\text{landuse}} + \beta_2 x_{\text{time}} + \beta_3 x_{\text{landuse}} \times x_{\text{time}} + \varepsilon,$$

where Y_c is the predicted concentration of the solute, x_{landuse} is a binomial variable indicating the land-use type as soybean or forest, x_{time} is the rank of the sampling event in the course of the year of sampling (e.g., first event, fifth event, etc.), and ε is the associated error term. The interaction term, $x_{\text{landuse}} \times x_{\text{time}}$, was included to test whether seasonal patterns in concentrations differed between land uses. The error term used was the individual effect of each watershed nested within land use and specified as a random effect. After running this model for pH, conductivity and 11 solutes, we used the Bonferroni correction to correct for multiple comparisons (JMP 9.0.2, SAS Institute, Inc. Cary, NC, USA).

We examined the effects of stormflow by quantifying the relationship between flow and concentrations of solutes and sediments, analyzing nine rain events for which we had flow data and samples from the rising limb of the storm hydrograph. Four of the storms were collected in forest watersheds (three in Forest a, two in Forest b) and five in soybean watersheds (three in Soy a, two in Soy b). To find instantaneous discharge for each collected sample, we interpolated flow using a cubic spline function, creating a continuous curve through all points and fitting a unique cubic polynomial for each segment to minimize bending (Matlab 7.7.0, Mathworks, Natick, MA, USA). Because of the hysteresis between discharge and concentrations, we isolated those samples that were collected during the rising limb of the storm hydrograph (Whitfield and Schreier 1981, Prowse 1984). We used linear regression to look individually at the relationship between rising-limb discharge and concentration in each storm for pH, conductivity, 13 solutes, and TSS. The regressions were done separately, using discharge as the explanatory variable and the measured streamwater variable as the response variable (JMP 9.0.2). We compared results visually to identify patterns among streams, storms, and solutes (Appendix S1: Fig. S3).

To analyze groundwater concentrations, we used a mixed effects model with land use and season as fixed factors to evaluate the differences in groundwater solute concentrations among wells. This model included a random effect for stream site to account for multiple samples taken in each watershed. The relative importance of land use and season were assessed using likelihood ratio tests. We used the lme4 package (Bates et al. 2014) to do the mixed effects analysis and all analyses were done in R (R Core Team 2016).

Annual solute yield

Previous work has demonstrated that flow in these streams was barely affected by storms. Stormflow made up less than 13% of annual water yield and did not differ between soybean and forest watersheds (Hayhoe et al. 2011). Thus, we used our 14–17 collections of baseflow concentrations in each watershed and hourly discharge to calculate annual yield of each solute from each watershed.

Table 1. Watershed area, percentage of baseflow, annual discharge, and mean daily discharge for three forest and four soybean watersheds between August 2008 and August 2009.

Stream	Area (km^2)	Baseflow (%)	Annual discharge (mm/yr)	Mean daily discharge (mm/d)
Forest a	8.32	95	320	0.88
Forest b	13.12	99	45	0.12
Forest c	5.13	96	59	0.16
Forest mean	8.86	96	141†	0.39†
Soy a	3.56	99	569	1.56
Soy b	1.98	98	577	1.58
Soy c	2.06	88	831	2.28
Soy d	4.11	100	478	1.32
Soy mean	2.93	96	614†	1.69†

†Statistically significant differences between land uses.

Measured stream discharges were higher than those predicted for all streams based on the calculated regional water balance, so we did not include a water volume underflow term in our estimates of annual yield. Because the concentrations of most solutes varied seasonally and independently of discharge, we did not use a regression-based interpolation between flow and concentrations. Instead, for the gap between each pair of samples, we split the time in half and applied the concentrations from the nearest sample date. We did this for 20 August 2008–20 August 2009. We then converted the concentrations and water flows to kg solute·ha^{-1}·yr^{-1}. For TSS, where concentrations varied inconsistently with season and independently of discharge, we used mean annual concentrations across land uses combined with mean annual discharge. We used single factor ANOVAs to compare annual yield from forest and soybean watersheds for each solute (JMP 9.0.2).

Because of the hysteretic nature of solute–discharge relationships that we observed (Riskin 2012), we estimated base- vs. stormflow-driven solute yield by multiplying the percent discharge from either storm or baseflow (Table 1) by the annual mean concentration of solutes (Appendix S1: Table S1) to calculate a potential percent contribution from storms and baseflow. This approach generated an estimate of stormflow-driven yield for four of our seven study streams.

Results

Precipitation and discharge

Total annual rainfall measured 1,170 mm at the Tanguro Ranch weather station and 1,300 mm across the distributed network of rain gauges, for an average of 1,235 mm that was heavily concentrated between October and April (Fig. 2). Annual streamflow was stable in forest watersheds across seasons but increased in soybean watersheds during the rainy season, with a 1-month lag after the start of the first heavy rains (Fig. 2). Soybean streams exported 4.3 times more water per hectare than forest streams (ANOVA, $P < 0.01$; Table 1). Measured mean stream discharge was 140 mm/yr from forest watersheds and 610 mm/yr from soybean watersheds (Table 1).

Water balance calculations based on observed rainfall (PPT) and streamflow (SF) data yielded evapotranspiration (ET) estimates of 1,095 mm/yr in forest watersheds and 625 mm/yr in soybean watersheds (ET = P−SF). Annual ET estimates based on the MOD16 data product were considerably higher, averaging 1,300 mm/yr in forest watersheds and 1,000 mm/yr in soybean watersheds. Although expected streamflows (calculated using MOD16) were lower than measured stream discharges, both expected and observed stream discharges were higher in soybean compared with forest watersheds. Stormflow contributed little to streamflow and did not vary significantly between forest and soybean watersheds. Baseflow contributed 88–100% of total streamflow across all watersheds (Table 1).

Streamwater solute and sediment concentrations

The mean streamwater concentrations of solutes and TSS did not differ between soybean and forest watersheds, with the exception of Fe^{3+} (Table 2). The concentrations of all solutes except K^+ varied seasonally in streamwater ($P < 0.004$ for all solutes except K^+, where $P > 0.05$; Fig. 3). Peaks in NO_3^-, NH_4^+, PO_4^{3-}, and Cl^- concentrations occurred in the early rainy season between mid-October and early November, while SO_4^- concentrations decreased during this time (Fig. 3). Concentrations of Al^{3+} and DOC peaked slightly later in November and December and the peak of Al^{3+} occurred later in soybeans than in forest streams (Fig. 3). Concentrations of Fe^{3+}, Na^+, Mg^{2+}, and Ca^{2+} varied during the year but generally did not have a distinct period of peak concentrations (Fig. 3).

We found inconsistent patterns of solute concentrations in the ascending limb of storm hydrographs across land uses or within individual streams (Riskin 2012; Appendix S1: Fig. S3). Furthermore, the response of solutes to increased discharge varied among storms: no solute concentration varied significantly with discharge during every storm, and where solutes did vary significantly with discharge, most relationships were not consistently positive or negative (Riskin 2012; Appendix S1: Fig. S2). Increases in solute concentrations during storms were larger on average in soybean streams (Riskin 2012; Appendix S1: Fig. S2). Stormflow concentrations of NO_3^-, NH_4^+, and PO_4^{3-} increased in soybean streams but not in forest streams (Appendix S1: Table S1). Stormflow and baseflow concentrations of Na^+, Ca^{2+}, Al^{3+}, Fe^{3+}, and TSS were relatively similar, and stormflow DOC concentrations were lower than in baseflow (Appendix S1: Table S1).

Rain and throughfall concentrations

Rainwater concentrations of NO_3^-, NH_4^+, Cl^-, PO_4^{3-}, Al^+, and Fe^{3+} were substantially higher in October than February with up to a sixfold decrease over that time period (Appendix S1: Table S2), but differences were

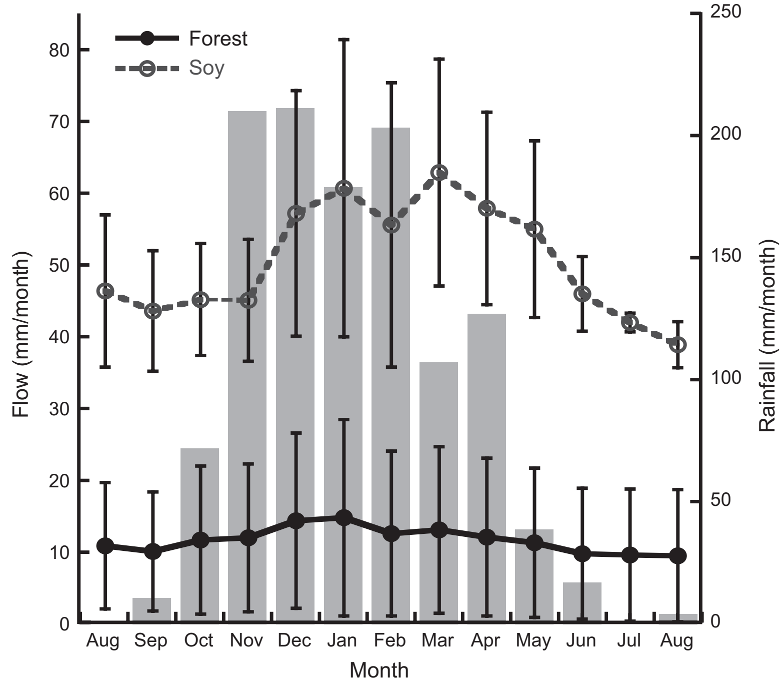

FIG. 2. Mean discharge for soybean ($n = 4$) and forest ($n = 3$) watersheds and monthly rainfall (gray bars) between August 2008 and August 2009. Error bars represent the maximum and minimum discharges measured among streams for each month.

TABLE 2. Annual mean pH, conductivity, solute concentration, and total suspended solids (TSS) for three forest and four soybean watersheds.

	Forest a	Forest b	Forest c	Forest mean	Soybean a	Soybean b	Soybean c	Soybean d	Soybean mean
pH	5.12 (0.06)	5.12 (0.06)	5.22 (0.09)	5.15	5.17 (0.08)	5.29 (0.08)	5.24 (0.11)	5.13 (0.07)	5.21
Cond µS/cm	4.26 (0.21)	4.31 (0.27)	3.86 (0.26)	4.14	3.75 (0.15)	3.24 (0.10)	4.24 (0.36)	4.19 (0.48)	3.86
NO_3^--N µmol/L	5.07 (2.92)	6.47 (3.48)	4.05 (2.40)	5.2	3.04 (2.47)	8.56 (5.63)	8.48 (5.78)	4.82 (3.68)	6.23
NH_4^+-N µmol/L	17.3 (5.6)	11.2 (2.61)	11.3 (2.34)	13.29	12.9 (3.31)	12.6 (3.46)	15.3 (4.56)	15.0 (4.55)	13.94
Cl^- µmol/L	14.2 (8.37)	19.0 (10.4)	10.7 (6.71)	14.65	11.3 (8.08)	15.1 (8.71)	21.8 (7.00)	8.58 (3.94)	14.18
PO_4^{3-}-P µmol/L	0.71 (0.35)	0.58 (0.32)	0.49 (0.29)	0.59	0.72 (0.53)	0.56 (0.32)	0.79 (0.57)	0.33 (0.19)	0.6
Al^{3+} µmol/L	0.42 (0.09)	0.66 (0.31)	1.06 (0.58)	0.71	0.23 (0.03)	0.43 (0.17)	0.18 (0.02)	0.46 (0.23)	0.33
Ca^{2+} µmol/L	2.07 (0.34)	2.2 (0.37)	2.97 (0.89)	2.41	2.55 (0.18)	2.74 (0.67)	3.51 (0.83)	2.76 (0.39)	2.89
Fe^{3+} µmol/L	0.37 (0.04)	0.27 (0.03)	0.32 (0.03)	0.32†	0.22 (0.03)	0.21 (0.03)	0.22 (0.03)	0.20 (0.03)	0.21†
K^+ µmol/L	5.03 (0.93)	3.71 (0.79)	5.25 (2.86)	4.66	1.5 (0.45)	3.34 (0.92)	7.52 (2.90)	2.89 (0.49)	3.81
Mg^{2+} µmol/L	0.72 (0.12)	0.78 (0.12)	1.09 (0.75)	0.86	0.67 (0.14)	0.81 (0.16)	1.24 (0.6)	0.80 (0.25)	0.88
Na^+ µmol/L	9.72 (0.89)	9.1 (1.00)	7.32 (0.85)	8.71	8.13 (0.96)	10.1 (2.01)	8.49 (1.61)	8.42 (0.86)	8.78
SO_4^{2-}-S µmol/L	2.67 (0.28)	2.77 (0.27)	2.87 (0.35)	2.77	2.82 (0.33)	3.01 (0.39)	2.76 (0.26)	2.76 (0.26)	2.84
DOC µmol/L	750 (185)	695 (198)	676 (236)	707	593 (285)	696 (288)	634 (234)	734 (220)	664
TSS mg/L	12.4 (7.6)	11.8 (7.65)	16.6 (9.8)	13.6	10.1 (6.2)	11.6 (5.9)	8.7 (5.6)	11.8 (7.8)	10.6

Note: Standard error is shown in parentheses.
† Significant differences between forest and soybean watersheds.

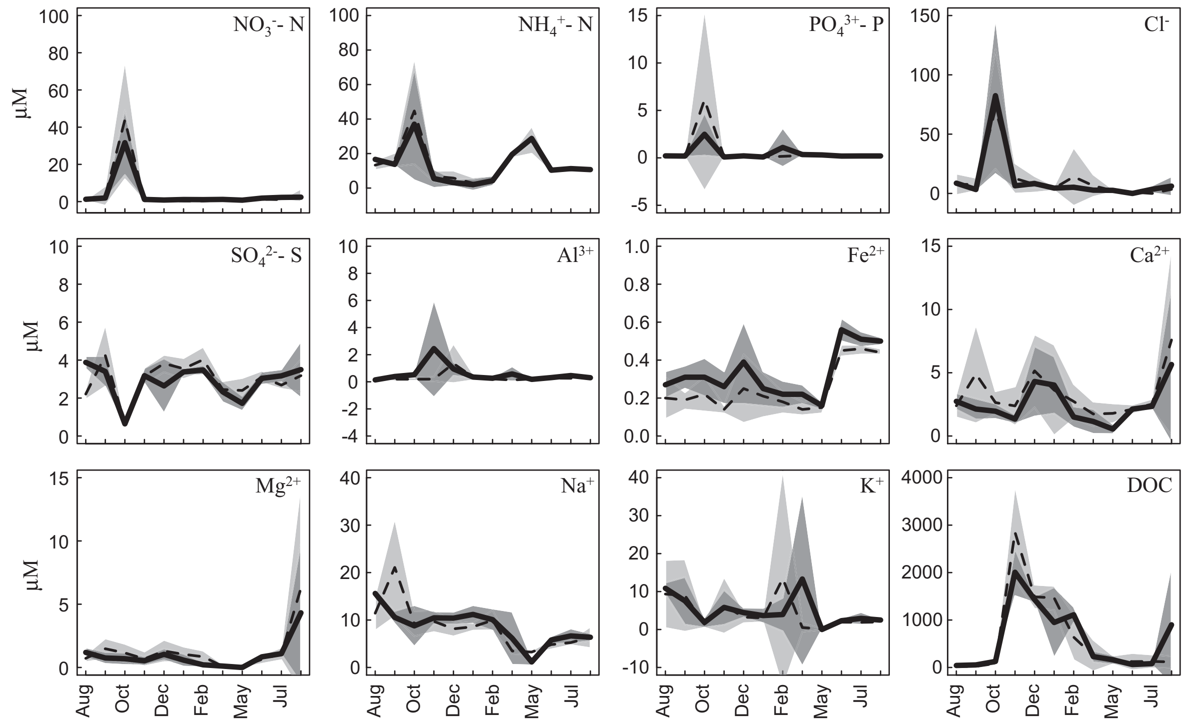

Fig. 3. Average monthly solute concentrations during baseflow in forest (solid line) and soybean (dashed line) watersheds. Envelopes represent standard deviation around average concentrations. Dark gray polygon is forest error, and light gray polygon is soybean error).

only statistically different for Cl^-, SO_4^{2-}, Al^{3+}, and Fe^{3+}. Throughfall concentrations were also higher during September/October rains, especially during the first rainstorm captured in late September. Concentrations progressively declined through the measurement period until February (Appendix S1: Table S2).

Groundwater solute concentrations

The $\delta^{18}O$-H_2O signatures of streamwater in forested and soybean streams were nearly identical to groundwater, indicating that groundwater inputs were dominant over rain or throughfall (Fig. 4). Groundwater solute concentrations varied by land use or time, depending on the solute (Appendix S1: Table S3). For example, NO_3^- and NH_4^+ concentrations remained constant or decreased in forest watersheds from October to February but increased in soybean watersheds during the same time, suggesting that groundwater in soybean watersheds accumulated NO_3^- during a single growing season. Potassium, which is added as fertilizer, was higher in soybean watersheds during both periods, as were Mg^+ and Na^+. Patterns were inconsistent for other solutes (Appendix S1: Table S3).

Annual solute yield

Annual solute yield from forested watersheds was very low (Table 3). All forest watersheds exported less than 0.2 kg NO_3^--N·ha^{-1}·yr^{-1}, less than 0.6 kg NH_4^+-N·ha^{-1}·yr^{-1} and less than 0.2 kg PO_4^{3-}-P·ha^{-1}·yr^{-1} and low amounts of base cations (Table 3). Although solute concentrations did not differ between land uses, the average

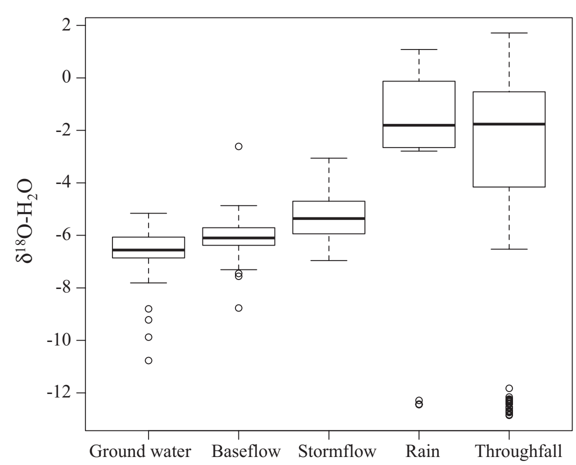

Fig. 4. The isotopic signature of water flowpaths of Tanguro Ranch in Mato Grosso, Brazil. All samples taken between August 2008 and August 2009. The dark line in each box represents the median value, the top and bottom of the boxes represent the 75th and 25th quartiles of the data range, respectively, the 'whiskers' extend the length of 1.5 times the interquartile range (represented by the box), and the individual points are data points that lie outside this range.

Table 3. Annual solute yield ($kg \cdot ha^{-1} \cdot yr^{-1}$) from three forest and four soybean watersheds.

	Forest a	Forest b	Forest c	Forest mean	Soybean a	Soybean b	Soybean c	Soybean d	Soybean mean
NO_3^--N	0.15	0.04	0.02	0.07 (0.02)	0.14	0.81	0.55	0.14	0.41 (0.16)
NH_4^+-N	0.59	0.08	0.09	0.25† (0.10)	0.91	2.04	1.14	0.91	1.25† (0.27)
Cl^-	1.02	0.26	0.16	0.48 (0.16)	1.47	8.03	2.51	1.47	3.37 (1.57)
PO_4^{3-}-P	0.05	0.01	0.01	0.02† (0.01)	0.08	0.17	0.09	0.08	0.11† (0.02)
Al^{3+}	0.03	0.01	0.02	0.02 (0.00)	0.03	0.04	0.08	0.03	0.05 (0.01)
Ca^{2+}	0.2	0.04	0.06	0.1† (0.03)	0.53	1.43	0.75	0.53	0.81† (0.21)
Fe^{3+}	0.05	0.01	0.01	0.02† (0.01)	0.06	0.12	0.08	0.06	0.08† (0.01)
K^+	0.43	0.06	0.15	0.21 (0.06)	0.29	3.47	0.84	0.29	1.22 (0.76)
Mg^{2+}	0.04	0.01	0.01	0.02 (0.01)	0.07	0.22	0.13	0.07	0.12 (0.04)
Na^+	0.52	0.09	0.1	0.24† (0.08)	0.92	1.89	1.52	0.92	1.31† (0.24)
SO_4^{2-}-S	0.37	0.07	0.09	0.18† (0.06)	0.81	1.59	1.17	0.81	1.1† (0.19)
DOC	20.0	3.86	4.73	9.54† (3.03)	43.4	81.6	NA	43.4	56.1† (11.0)
TSS	30.4	5.42	9.22	15.0† (4.48)	50.5	110	57.5	50.5	67.1† (14.4)

Note: Standard errors shown in parentheses.
† A significant difference between forest and soybean solute yield.

annual watershed yield of all solutes was higher from soybeans than from forest watersheds (Fig. 5). Average solute yield was 5.6 times greater in soybean watersheds, ranging from a 2.3-fold to 8.1-fold increase (Table 3, Fig. 5). This difference was significant for NH_4^+, PO_4^{3-}, Ca^{2+}, Fe^{3+}, Mg^{2+}, Na^+, SO_4^-, and DOC (Fig. 5). Average annual yield of TSS was low from all watersheds but significantly higher from soybeans than forest (Table 3).

We found that a larger proportion of annual solute yields could be attributed to stormflow in soybean streams compared with forest streams, but solute export attributable to stormflow varied from 0 to 50% in the two soybean streams in which we measured stormflow (Appendix S1: Table S1). It was therefore difficult to conclude whether soybean streams had greater stormflow-related yield in general.

Discussion

Solute concentrations vary seasonally but not with land use

Despite dramatic changes in land cover between forest and soybean watersheds, we found no difference in streamwater concentrations of any solutes or sediment with the exception of lower concentrations of Fe^{3+} in soybean streams. This differed from patterns found in other Amazon headwater streams following deforestation. For example, Williams and Melack (1997) found higher concentrations of Na^+, Ca^+, Mg^+, Cl^-, SO_4^{2-}, and K^+ in streams draining recently burned, deforested watersheds. Biggs et al. (2002) found higher Cl^- and Na^+ concentrations in pasture streams compared with forest streams in Rondônia, which they attributed to the widespread use of supplemental salts in cattle feed. Neill et al. (2001) found lower concentrations of NO_3^- but higher concentrations of PO_4^{3-} in pasture compared with forest streams in the same region. In these and other locations on Ultisols in Rondônia, overland flow was common in pasture watersheds because of a combination of soil compaction and perched water tables (Biggs et al. 2006, Germer et al. 2010). It is likely that deep soils and vertical flowpaths currently buffer the influence of soybean croplands on stream solute concentrations at Tanguro Ranch (Mato Grosso) compared with these other locations (Scheffler et al. 2011), but this has yet to be empirically demonstrated.

Interestingly, Fe^{3+} concentrations were consistently higher in forest streams. We don't have a clear understanding of the mechanism for this difference. In fact, this result contrasts with another study in lowland Amazon forest, where concentrations were higher in pasture streams than forested streams (Neill et al. 2006). One potential hypothesis for the decrease in Fe^{3+} we observed is that riparian zones of soybean streams had lower redox potential due to their higher water tables (Nagy et al. 2015) reducing Fe^{3+} to Fe^{2+}, which we did not measure. It has been shown that frequent reducing conditions in humid tropical forest soils, in combination with pulses of labile carbon, drives the reduction of Fe^{3+} phosphates to Fe^{2+} and bioavailable phosphate (Chacon et al. 2006). This pattern will likely be more common to forests, where pulses of labile carbon from litter leachate are more common. Other factors such as pH, temperature, or interactions with organic carbon may have influenced the patterns we observed, but understanding the full extent of these controls on iron biogeochemistry was beyond the scope of our work and merits further study.

While we did not find differences in streamwater solute concentrations between land uses, we did observe significant differences in groundwater NO_3^- and K^+ concentrations between forested and soybean watersheds. This could occur for a number of reasons. First, there is likely a temporal delay in runoff from fields reaching streams. At the time of the study, fields had been planted in soy for less than four years. Given the deep soils, predominantly vertical flowpaths, and low gradient topography, it is likely that most of the soil amendments applied to fields had not yet emerged in streams (Scheffler et al. 2011). Hayhoe et al. (2011) found that flow responses in streams were best predicted using a model that included a two-month lag between

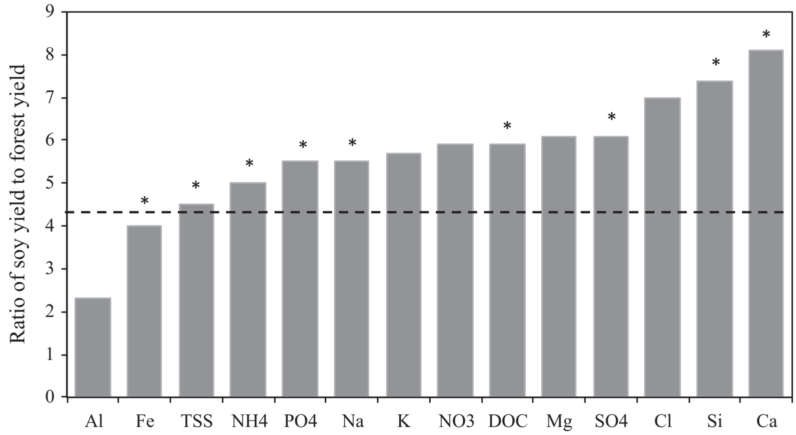

Fig. 5. Ratio of average soybean watershed solute yield to average forest watershed yield. Asterisks denote significant increases in solute yield in soybean over forest watersheds. Dashed line signifies proportional increase in discharge in soybean watersheds over forested watersheds (~4.3 times).

precipitation and streamflow response, indicating that the deep, vertical flowpaths substantially delayed water reaching streams and altered flow and solute loads. A significant degree of processing (e.g., denitrification) may also occur along groundwater flowpaths from fields to streams (R. Fox, *personal communication*). Even if soybean agriculture enriches groundwater with solutes, it is thus possible that processing in transit removes them before they reach streams.

Concentrations of almost all solutes varied significantly over the year. Peaks in concentrations of NO_3^-, NH_4^+, PO_4^{3-}, and Cl^- during October corresponded consistently with the first heavy rains, suggesting relatively fast flow through the groundwater. Throughfall solute concentrations in fragmented Amazon forest regions can be very high during the first rains after a long dry season (Germer et al. 2007). This occurs both because of flushing of accumulated material from leaf surfaces and because solute concentrations in rain are also elevated at that time, presumably because of flushing of the atmosphere during a time of high biomass burning (Germer et al. 2007). This was consistent with our findings that solute concentrations in rainwater were higher during the first rains at the end of the dry season (October) compared with the middle of the wet season (February; Appendix S1: Table S2) and that streamwater concentrations of NO_3^-, NH_4^+, PO_4^{3-}, and Cl^- decreased after the onset of regular rains (Fig. 3).

The number of fires in Mato Grosso also peaks during the late dry season (Appendix S1: Fig. S4). Biomass burning in Amazonia increases aerosol concentrations of black carbon, organic compounds, Cl, S, and K (Artaxo et al. 1998, Yamasoe et al. 2000), as well as NH_4^+ and NO_3^- (Andreae et al. 1988). Our observed peaks in rainwater Al and Fe concentrations, elements common in soils of the region, also suggest that increased dust fluxes (e.g., from field tilling or unpaved road use) contribute to increased atmospheric aerosols during the transition from the dry to the wet season. Observations from Rondônia and Mato Grosso suggest that increased dust levels during the dry season may also increase regional P concentrations in aerosols (Mahowald et al. 2005), which may explain higher PO_4^{3-} concentrations in early wet season rain samples.

In contrast to other solutes, concentrations of NH_4^+ and DOC were higher in our study than in other studies from the Amazon region (Davidson et al. 2004, Markewitz et al. 2004). Concentrations of NH_4^+ were lowest in groundwater and highest in stormflow (Appendix S1: Tables S1 and S3), suggesting that NH_4^+ entered streams from the headwaters and stream channels rather than from groundwater as hypothesized for other solutes (Fig. 4). A seasonal peak in streamwater DOC concentrations during the wet season increased mean annual concentrations, and was also measurable in groundwater. This suggests that DOC inputs from rain and possibly throughfall contributed to DOC concentrations in both groundwater and streamwater.

Discharge increases and ET decreases in soybean watersheds

Groundwater sources dominated baseflow in both forest and soybean watersheds (Fig. 4), and streamflows varied little across seasons despite a strong dry season of four months with little or no rain (Fig. 2). This dominance of baseflow as a proportion of total hydrologic yield from both forest and soybean watersheds was similar to previous measurements from Tanguro Ranch (Hayhoe et al. 2011). It was also consistent with high rates of soil infiltrability and subsurface saturated hydraulic conductivity measured in forest and soybean fields in the region (Scheffler et al. 2011). Deep, well-drained soils with predominantly vertical flowpaths occur on broad areas of forested Amazon Oxisols (Elsenbeer and Vertessy 2000, Elsenbeer 2001). Although conversion to soybean cultivation at Tanguro Ranch decreased infiltrability and saturated hydraulic conductivity, these rates remained high enough to absorb even the most intense rainfalls (Scheffler et al. 2011). As a result, conditions needed to generate excess overland flows (either infiltration or saturation) are unlikely and contributions of streamwater from sources other than deep groundwater (as observed at baseflow; Fig. 4) are rare or ephemeral. Brief increases in streamflow associated with individual rains likely result from runoff generated from relatively small, saturated areas adjacent to stream channels (Hewlett and Hibbert 1967). This contrasts with many studies from the Amazon showing that conversion of forests to pasture and subsequent cattle grazing results in the activation of near-surface flowpaths (Biggs et al. 2006, Moraes et al. 2006, Zimmermann et al. 2006, Neill et al. 2011). However, these studies were all conducted on Ultisols or plinthic Oxisols in contrast to the well-drained Oxisols that occur on Tanguro Ranch.

Our observation of higher discharge in deforested watersheds was consistent with studies in other forest types that documented lower evapotranspiration and increased discharge after forest clearing (Bosch and Hewlett 1982, Hornbeck et al. 1993, Sahin and Hall 1996, Brown et al. 2005). For example, in the central Amazon, Williams and Melack (1997) observed similar increases in discharge in response to deforestation in the watersheds of small streams. These patterns were consistent with observations in two large eastern Amazon region rivers, the Tocantins and Araguaia, where discharge increased substantially following large-scale deforestation (Costa et al. 2003, Coe et al. 2011).

Although the change in discharge was consistent in both our field measurements and estimated water balance, our estimate of expected streamflow was lower than measured discharge. This discrepancy may result from underestimation of rainfall by weather gauges, uncertainty in the modeled ET data (see Mu et al. 2011), and/or a lag time in water export to streams due to changes in soil water storage (Panday et al. 2015). For example, other work at Tanguro suggests that it can take up to a year for streamflow to recover after a significant drought, suggesting that there is a temporal mismatch between measured discharge and the total water balance. While measured discharge remains the most direct means of calculating solute yields downstream, these other hydrological and soil characteristics are key to understanding the longer-term implications of land-use change for nutrient processing and yield, and merit further work.

It is unlikely that year-to-year variations in rainfall substantially alter the relative distribution of baseflow and stormflow. Annual rainfall during the year of sampling was low (1,170 mm) relative to the long-term average (1,800 mm) and to the previous water year sampled by Hayhoe et al. (2011). Although that year received an above-average 1,900 mm of rain, stormflows contributed on average only 2% of total flow.

Increased discharge increases annual solute yield from soybean watersheds

Significantly greater annual yield of NH_4^+, PO_4^{3+}, Ca^{2+}, Fe^{3+}, Na^+, SO_4^-, Si, and DOC from soybean watersheds was driven primarily by the 4.3-fold increase in stream discharge in soybean vs. forest streams, despite little change in the concentration of most solutes and sediments. However, the yield of TSS, NH_4^+, PO_4^{3-}, Na, K, and DOC in soybean streams was proportionally greater than the increase in discharge in soybean watersheds, and the increased water volume did not dilute solute concentrations as typically occurs with increased discharge (Lewis et al. 1999). These observations suggest that soybean cultivation generates additional sources of these solutes (Fig. 5). The sources and the mechanisms by which solutes are transferred from watershed soils to streams were not investigated, however, and likely differ among solutes.

Despite increased annual yield of most solutes from soybean watersheds, annual yields were still low compared with other tropical watersheds. Export of all base cations (Na^+, Mg^{2+}, K^+, and Ca^{2+}), NO_3^- and Cl^- was lower from both soybean and forest watersheds than from other watersheds in the lowland Amazon, montane Ecuador, or Puerto Rico (McDowell and Asbury 1994, Williams and Melack 1997, Markewitz et al. 2004, Bücker et al. 2011). Low solute yield typifies streams and rivers draining the highly weathered soil of the Brazilian shield (Stallard and Edmond 1983, Markewitz et al. 2001, 2006), and the observed concentrations of cations, NO_3^- and PO_4^{3-}, were within the range reported at other lowland shield sites (Davidson et al. 2004, Markewitz et al. 2004). This was true in soybean watersheds, despite biannual additions of approximately 1,500 kg/ha of agricultural lime and annual additions of 50 and 70 kg/ha of P and K, respectively (Riskin 2012).

Though we did find higher average concentrations of some solutes during storms, which resulted in higher storm-related yields (Appendix S1: Table S1; notably in one of the two soybean watersheds), the variability within and among streams made it difficult to draw clear conclusions about stormflow concentration–discharge relationships (Appendix S1: Fig. S3). In fact, we saw large differences in the storm-related water and solute yield from the two soybean watersheds that we monitored (Soy c and Soy d). For example, Soy c had up to ~50% solute yield from storms, while Soy d had uniformly zero contribution from storms to both water and solute yield (Table 1; Appendix S1: Table S1). These two streams were physically very different: Soy c had a relatively small and well-defined channel, while Soy d had diffuse channel boundaries and a large area of saturated side-channel habitat. This likely makes discharge in Soy d much more stable during storm events, resulting in very little response of solute yields to storm events. Germer et al. (2009) also found weak relationships among NO_3^- and cations with discharge during most storm events. This may be because factors like antecedent moisture conditions and flowpath saturation alter concentration–discharge relationships among storm events (Meyer et al. 1988). Further, the combination of base-poor status of the soils at Tanguro Ranch, high soil infiltration rates, and very low overland flow, may mitigate the decrease in rock-derived elements and the increase in organic material often observed in response to stormflow discharge in some locations (Meyer et al. 1988, Hornberger et al. 1994, Lewis et al. 1999). This may also prevent flow-related increases in base cations that have been observed elsewhere in the Amazon, which resulted from increased contact of water with surface soils during periods of high rainfall (Markewitz et al. 2001).

The presence of small impoundments in soybean watersheds has the potential to decrease sediment and solute yields in those watersheds. Other studies have found that the presence of reservoirs decreases nutrient yields from catchments (Pedrozo et al. 1992, Bonetto et al. 1994, Vörösmarty et al. 1997) because they increase water residence time and facilitate sedimentation and biotic uptake (Dudgeon et al. 2008). At Tanguro Ranch, the reservoirs are relatively small (up to several ha) and shallow, with low residence time, perennially flowing outlets and limited storage capacity to buffer stormflows. Our surveys of solute chemistry upstream and downstream of impoundments showed no differences (Appendix S1: Table S4). At the scale of the Upper Xingu watershed, small impoundments in deforested headwater watersheds are a ubiquitous legacy of the cattle ranches that preceded soybean cropping. Macedo et al. (2013) mapped more than 10,000 impoundments in the approximately 70,000 km^2 of land in the Upper Xingu watershed that was cleared in 2010. At this density, almost all soybean headwater streams contain at least one impoundment, and their presence in the watersheds we measured was typical of the larger landscape.

Land use and management applications

Despite deforestation, tilling during conversion from pasture to cropland, and no-till cropping with large inputs of lime, potassium, and phosphorus fertilizer for two to four years, this soybean cropping system did not alter stream sediment or solute concentrations. Vertical water flowpaths through deep soils appear to buffer streamwater against changes to sediment and solute concentrations. This contrasts with the effects of intensive cropping in other regions where nutrient-enriched overland flows and drainage have increased nutrient loading to streams and degraded the quality of downstream receiving water bodies (Jordan et al. 1997, Turner and Rabalais 2003, Billen et al. 2007).

Further, despite large changes to streamflows caused by conversion of forest to cropland, the landscape at Tanguro Ranch was resistant to changes in hydrograph patterns and streamwater solute concentrations over the short term. We do not yet know the effects over a longer time scale because the soybean watersheds we studied were cropped for only a few years. The higher concentration of some solutes in the groundwater in soybean watersheds (Appendix S1: Table S3) suggests that there may be a pulse of contaminated groundwater that hasn't yet reached the stream or is being processed in route. Depending on future agricultural management and soil properties, several different alternative future outcomes could occur.

One potential outcome is that infiltrability and high solute retention will be sustained because of the particular chemical and mineralogical characteristics of weathered Oxisols (Soil Survey Staff 1999). For example, many high-clay soils such as these have small aggregates that remain very stable with cultivation (Six et al. 2000), which explains the high infiltrability regardless of land use. Previous research showed that six years of additions of 50 kg P/ha to soybean fields at Tanguro Ranch did not result in movement of P below 20 cm soil depth, which was attributed to its chemisorption by iron and aluminum oxides (Riskin et al. 2013*a, b*). Furthermore, the presence of anion exchange in highly weathered Oxisols (Sanchez 1977) may increase nitrate retention in deep soils and act as a brake on N losses at watershed scales (Lohse and Matson 2005).

Another possible outcome is that neither infiltrability nor solute retention will be sustained over the long term. Although these watersheds were deforested in the early 1980s, they were only recently converted to soybean cropping (from 2003 to 2008). Therefore, the capacity of soils to absorb water and retain solutes could eventually be reduced. Oxisols with stable microaggregate structure can succumb to compaction (Cassel and Lal 1992), and it is possible that infiltrability may eventually decrease enough to lead to more frequent overland flow in cropland that bypass deep soils and deliver materials directly to streams. A change in the rainfall regime with climate change, specifically an increase in high-intensity, short-duration rain events that exceed soil infiltration capacity, could also generate more frequent overland flows. It is also possible that nutrient leaching may increase with time because capacity on exchange sites is exceeded. Weathered soils with low effective cation exchange capacities have a limited ability to retain cations, which then may be lost to leaching (Sanchez and Logan 1992). Solute retention capacity associated with anion exchange and when it could be exceeded, are not known.

These potential outcomes are now relevant over wide portions of the Amazon territory. There are now more than 70,000 km^2 of soybean cropland in the Brazilian states of Mato Grosso and Pará (IBGE 2014). The vast majority of this cropland occupies level, well-drained Oxisols (Soil Survey Staff 1999) that are in the same soil classification units as those at Tanguro Ranch (Embrapa 2013) and on which similar hydrological and biogeochemical responses to cultivation are likely. Lastly, while we examined watersheds managed with a single crop of soybeans per year, the double cropping of soybeans with corn (and less extensively cotton) during the same growing season has expanded rapidly in recent years, increasing from less than 15% of Mato Grosso's soybean croplands in 2001 to 50% in 2011 (Spera et al. 2014). Unlike leguminous soybeans that require application of no or little nitrogen fertilizer, many second crops require nitrogen fertilization, which may fundamentally change the solute yield from double-cropped watersheds in the future.

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Supporting Information

Additional Supporting Information may be found online at: http://onlinelibrary.wiley.com/doi/10.1002/eap.1428/full

Data Availability

Data associated with this paper are available in Dryad: http://dx.doi.org/10.5061/dryad.d4f4s