Discharge-calcium concentration relationships in streams of the Amazon and Cerrado of Brazil: Soil or land use controlled.

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Abstract

Stream discharge-concentration relationships are indicators of terrestrial ecosystem function. Throughout the Amazon and Cerrado regions of Brazil rapid changes in land use and land cover may be altering these hydrochemical relationships. The current analysis focuses on factors controlling the discharge-calcium (Ca) concentration relationship since previous research in these regions has demonstrated both positive and negative slopes in linear $\log_{10}$discharge-$\log_{10}$Ca concentration regressions. The objective of the current study was to evaluate factors controlling stream discharge-Ca concentration relationships including year, season, stream order, vegetation cover, land use, and soil classification. It was hypothesized that land use and soil class are the most critical attributes controlling discharge-Ca concentration relationships. A multilevel, linear regression approach was utilized with data from 28 streams throughout Brazil. These streams come from three distinct regions and varied broadly in watershed size (<1 to >10^6 ha) and discharge ($10^{-5.7}$ to $10^{3.2}$ m^3 sec^{-1}). Linear regressions of $\log_{10}$Ca versus $\log_{10}$discharge in 13 streams have a preponderance of negative slopes with only two streams having significant positive slopes. An ANOVA decomposition suggests the effect of discharge on Ca concentration is large but variable. Vegetation cover, which incorporates aspects of land use, explains the largest proportion of the variance in the effect of discharge on Ca followed by season and year. In contrast, stream order, land use, and soil class explain most of the variation in stream Ca concentration. In the current data set, soil class, which is related to lithology, has an important effect on Ca concentration but land use, likely through its effect on runoff concentration and hydrology, has a greater effect on discharge-concentration relationships.

Introduction

Streamwater discharge-concentration relationships are indicators of terrestrial ecosystem function (Bond, 1979). The slope of the discharge-concentration relationship, whether positive or negative, has been used to infer the sources and flowpaths of dissolved constituents to streams (Saunders and Lewis, 1989). Source waters that travel long flowpaths such as groundwaters and interact with primary minerals in bedrock tend to contribute high concentrations of the rock derived elements (e.g., Ca^{+2}, Mg^{+2}, and Si) during low flow (Drever, 1997). In contrast, source waters that are quickly transported to streams during runoff events may be dilute in the rock derived elements but rich in organic carbon or nitrogen due to interaction with the soil O horizon (Hornberger et al., 1994). In this case, organic C and N may have a positive discharge-concentration relationship, at least during the earlier stages of storm runoff, while the rock derived elements present a negative discharge-concentration relationship as groundwaters are diluted by surface waters (Lewis and Grant, 1979). Empirical studies commonly observe negative discharge-concentration relationships for the rock derived elements with positive relationships being atypical (Meyer et al., 1988).

The current analysis focuses specifically on discharge-Ca concentration relationships in the Amazon and Cerrado of Brazil since previous research in a watershed on highly weathered soil, which is common in both regions, demonstrated a positive discharge-Ca concentration relationship (Markewitz et al., 2001). Positive slopes in Ca-discharge concentration relationships were reported by Meyer et al. (1988) but no mechanism was identified. In the Amazonian watershed where a positive slope in Ca-discharge was observed, two competing hypotheses were proposed: 1) it is possible that these positive relationships could result where soils and underlying parent material have become so depleted of Ca that surface runoff concentrations exceed groundwater concentrations or 2) land use conversion through slash-and-burn practices can so enrich surface soils in Ca that surface runoff concentrations exceed groundwater concentrations (Markewitz et al., 2001). Significant differences in stream water Ca concentrations (as well as other cations) have been demonstrated to vary with lithology in the Amazon Basin but effects on discharge-concentration relationships has not been thoroughly investigated (Stallard and Edmond, 1983). The prevalence of positive slopes in discharge-Ca concentration relationships in the Amazon and Cerrado is unknown and whether these slopes result from differences in lithology and soil type or from land use conversion remains uncertain.

Throughout the Amazon and Cerrado regions of Brazil rapid changes in land use and land cover (INPE, 2006) are altering the hydrological (Moraes et al., 2006; Williams and Melack, 1997) and hydrochemical (Germer et al., 2009; Neill et al., 2001) relationships in these streams and possibly altering the expected discharge-concentration relationships in these water bodies. As the landscape of Brazil continues to be altered in the coming decades it will be important to understand regional differences in stream water chemistry (Richey et al., 1990; Stallard, 1985) and differences in processes of land-water coupling (Biggs et al., 2002). Regulatory agencies in Brazil will be tasked with assessing changes in water quality with continued land use conversion and will need to be able to interpret concentration differences with lithology, season, or flow from those changes due to human alterations.

The objective of the current study is to evaluate slopes (+/-) of discharge-calcium concentration relationships for previously studied streams and evaluate the influence of year, season, stream order, vegetation cover, land use, and soil classification on the regression relationship. A multilevel linear regression approach is utilized.

Methods

Data from 28 different streams with 51 total sampling stations (i.e., >1 sampling station/stream) were utilized in this analysis (Table 1). These streams are situated in eight different locations and three distinct regions (Figure 1). Site descriptions and specific details of stream water sampling and analysis within each watershed are available in references provided in Table 1. At all sites investigators identified current land use and existing soil types. In many cases stream waters were collected as grab samples on a weekly or biweekly basis, while at Rancho Grande an automated ISCO sampler was utilized. A number of sites also had automated stage height recorders while others recorded stage height during collections. In all cases waters were filtered prior to analysis and all sites used ion chromatography for Ca analysis. Stream Ca concentration data were available for all sampling stations while discharge was measured in 18 of the streams at 28 sampling stations. Sampling stretched over 12 yrs (1994, 1996-2007) and all months of the year (i.e., season).

Stream order and land use were taken from site descriptions. Land use was comprised of seven total categories; four within lowland moist tropical forest and three within Cerrado savannah. Within these two land use classes some watersheds were nearly 100% natural vegetation (broadleaf forest (Forest) or Cerrado scrub savannah (Cerrado)) while many others possessed some natural vegetation (34-70% primary or secondary forest or 12-50% Cerrado) mixed with pastures (19-46%) and agricultural (5-50%) land uses (Fmixed or Cmixed). Some lowland forest watersheds in the Amazon had been nearly 100% converted to pasture (Pasture). Finally, if forested or Cerrado watersheds in either location possessed substantial urban development they were classified as Furban (1-2%) or Curban (6-27%).

Vegetation Cover of each watershed was characterized based on the 1988 Mapa de Vegetacão do Brasil at a 1:5,000,000 scale (http://na.unep.net/datasets/datalist.php). Soil classification was similarly obtained from the 1981 Mapa de Solos do Brasil at a 1:5,000,000 scale. Given the available map scales each watershed and thus all the sampling stations were within a single class. Furthermore, all vegetation cover and soil class designations were generally consistent with site specific descriptions.

To analyze individual station regressions where there was sufficient data, simple linear least square regression was utilized on the $\log_{10}$Ca (in μM) - $\log_{10}$Q (in $m^3 sec^{-1}$) relationship. To analyze the data from all stations simultaneously, a multilevel modeling approach (Congdon, 2001) was utilized to estimate a linear model for prediction of $\log_{10}$Ca. The main predictor variable was discharge or $\log_{10}$Q, which was centered by subtracting the mean of the $\log_{10}$Q and dividing by the range. If discharge was recorded as zero (n=56) discharge was considered a missing value.

In the Bayesian multilevel modeling approach, which is nearly identical mathematically to the classical random effect model (Clayton, 1996), adjustments to the regression relationship between the dependent variable $\log_{10}$Ca and the independent variable $\log_{10}$Q are incorporated for covariates at all levels, including observation and higher level groups (i.e., stream order, soil class, etc). This approach allows for the simultaneous accounting of contextual and individual variability in the outcome (Congdon, 2001). Adjustments to the linear regression parameters β_0 (the intercept) and β_1 (the slope) were estimated at all levels. In contrast, a multivariate regression using a completely pooled regression model would use each factor as a separate predictor but would have little chance of satisfactory results using data from such a large region. Implicit in using a pooled model would be an assumption that a single slope and intercept could describe the relationship everywhere. Since there is evidence to the contrary, the multilevel approach utilized allows for some variability in parameters, based on the chosen factors.

In the current analysis, year, season, stream order, land cover, land use, and soil class were the factors, and each factor had multiple levels (e.g., season has 12 monthly levels). As such, the observation model for $\log_{10}$Ca was

$$\log_{10}(\text{Ca conc. } \mu\text{M}_{\,i}) \sim N(\mu_i\,,\ \tau_1), \tag{1}$$

where τ_1 is the error precision, and $\tau_1 = 1/\sigma_1^2$. A uniform prior was used on σ_1 (Gelman, 2005b). The mean of the normal distribution for observations i (μ_i) was given by a linear regression which specifies the mean, conditional on the covariate $\log_{10}$Q such that:

$$\mu_i = \beta_0 + \beta_1 * \log_{10}\text{Q}_\text{i}\,, \tag{2}$$

where,

$$\beta_0 = \mu_{\beta 0} + \beta_0\text{year}_{\,j} + \beta_0\text{seas}_{\,k} + \beta_0\text{order}_{\,l} + \beta_0\text{cov}_{\,m} + \beta_0\text{use}_{\,n} + \beta_0\text{soil}_o \tag{3}$$

$$\beta_1 = \mu_{\beta 1} + \beta_1\text{year}_{\,j} + \beta_1\text{seas}_{\,k} + \beta_1\text{order}_{\,l} + \beta_1\text{cov}_{\,m} + \beta_1\text{use}_{\,n} + \beta_1\text{soil}_o \tag{4}$$

and:

$$\begin{aligned}\mu_i = {} & (\mu_{\beta 0} + \beta_0\text{year}_{\,j} + \beta_0\text{seas}_{\,k} + \beta_0\text{order}_{\,l} + \beta_0\text{cov}_{\,m} + \beta_0\text{use}_{\,n} + \beta_0\text{soil}_o) + \\ & (\mu_{\beta 1} + \beta_1\text{year}_{\,j} + \beta_1\text{seas}_{\,k} + \beta_1\text{order}_{\,l} + \beta_1\text{cov}_{\,m} + \beta_1\text{use}_{\,n} + \beta_1\text{soil}_o) * \log_{10}\text{Q}_\text{i}\end{aligned} \tag{5}$$

and j = 1, …, 12 years, k = 1,…,12 seasons (months), l = 1, …,5 stream orders, m = 1,…,7 vegetation covers, n = 1, …,7 land uses, and o = 1,…,7 soil classes. In the multilevel model of equation 5, $\mu_{\beta 0}$ is an overall mean intercept term, while $\beta_0\text{year}_j$, $\beta_0\text{seas}_k$, $\beta_0\text{order}_l$, $\beta_0\text{cov}_m$, $\beta_0\text{use}_n$, and $\beta_0\text{soil}_o$ are adjustments to this overall intercept due to the six factors year, season, order, cover, use, and soil, respectively. Similarly, $\mu_{\beta 1}$ in equation 5 is an overall mean slope for the $\log_{10}$Q term, while $\beta_1\text{year}_j$, $\beta_1\text{seas}_k$, $\beta_1\text{order}_l$, $\beta_1\text{cov}_m$, $\beta_1\text{use}_n$, and $\beta_1\text{soil}_o$ are additive adjustments to this overall mean according to the same six factors, respectively. The sample size for each level of a factor can vary and will influence the uncertainty within the parameter estimates. Similarly, the matrix of all combinations of all factors may not be fully represented within the observational data.

A non-informative, proper prior distribution was utilized for the regression coefficients, such that each coefficient was assumed to have a normal distribution, with a separate mean (μ) and precision ($\tau = 1/\sigma^2$). The use of a normal distribution for the regression coefficients stems from the usual assumptions made regarding regression residuals. Regression coefficients of a linear model are linear functions of the residuals, and if we assume the residuals are normal *iid*, then so are the regression coefficients. Again, a uniform prior on each σ (in units of $\log_{10}$Ca concentration) was used (Gelman, 2005a), such that $\sigma \sim U(0,100)$, and an initial value of 0 was used for μ.

The model was estimated using a Markov Chain Monte Carlo (MCMC) simulation following Lamon and Qian (2008). MCMC is a simulation technique for solving high dimensional probability distribution problems. The basic idea of MCMC is to find a numeric algorithm to make probabilistic inference on random variables with algebraically intractable probability distributions. The Bayesian Analysis Using Gibbs Sampler (BUGS) project distributes and supports flexible software for the Bayesian analysis of complex statistical models using MCMC methods (http://www.mrc-bsu.cam.ac.uk/bugs/ welcome.shtml), and winBUGS is for use on PC platforms (Spiegelhalter et al., 2003). The model was initiated by sampling from the prior distributions for each estimated coefficient and distributions were updated based on the log-likelihood estimations for the observed and predicted values. As presented here, a posterior distribution of all model coefficients was obtained after 100,000 iterations.

To evaluate parsimony, the six factor adjustments were compared to other five, four, and three factor adjustment models (e.g., without season or soil, etc.). The deviance information criterion (DIC) is a hierarchical modeling generalization of the Akaike information criterion (AIC) and the Bayesian information criterion (BIC). It is particularly useful in Bayesian model selection problems where the posterior distributions of the models have been obtained by MCMC simulation, as was done here (Spiegelhalter et al., 2002).

The deviance information criterion was calculated as

$$DIC = p_D + \bar{D} \tag{6}$$

The deviance *D* is a measure of model fit analogous to a residual standard deviation. It is estimated by the log-likelihood after each iteration and is defined as

$$D(\theta) = -2\log\left(p(y|\theta)\right) + C \tag{7}$$

where y are the data, θ are the unknown parameters of the model including β, σ, and τ, and $p(y|\theta)$ is the likelihood function. C is a constant that cancels out in comparison of different models. The expectation of *D*

$$\bar{D} = E^{\theta}[D(\theta)] \tag{8}$$

is an average of the log-likelihoods and is a measure of how well the model fits the data; the larger this value the worse is the fit. The effective number of parameters of the model was computed as

$$p_D = \bar{D} - D(\bar{\theta}) \tag{9}$$

where $\bar{\theta}$ is the expectation of θ. This is a measure of model complexity that is particularly useful in hierarchical models where the number of independent parameters may be difficult to determine. A larger p_D implies that more parameters are being used in the model and thus the model is better able to fit the data.

The idea is that models with smaller DIC should be preferred to models with larger DIC. Models were evaluated both by the value of D, which favors good fit, but also by model complexity, as measured here by the effective number of parameters p_D. Since D will tend to decrease as the number of parameters in a model increases, the p_D term compensates for this effect by favoring models with a smaller number of parameters.

Results

Data Distribution

Across the dataset (n=3155) $\log_{10}$Ca in μM ranged over two orders of magnitude with a mean of 1.32 (Table 2) and discharge (m^3 sec^{-1}) ranged more broadly covering five orders of magnitude with a mean $\log_{10}$Q of -1.70 (Table 2). The data covered 1994 to 2007 with 1994 and 2007 having fewer samples and 2005 the most (Table 3). All months of the year were well represented and there were five stream orders in the dataset (1, 2, 3, 5, and 6) with the majority of data points from 1st or 2nd order streams (Table 3). Urupá and Ji-Paraná@Cacoal are the 5th and 6th order streams, respectively.

There were seven vegetation covers identified from land cover maps with a majority of samples from dense tropical forest with secondary forest and agricultural activities. This land cover class D included all the Paragominas and Igarapé-Açu samples. Land use as identified by researchers working within each site (see references in Table 1) was also comprised of seven classes with forest watersheds under mixed land use being in greatest abundance, which included many of the same samples identified above under dense tropical forest with secondary forest and agricultural activities. Samples classified under Cerrado land uses comprised 17% of the dataset.

Finally, there were seven soil types classified in the watersheds with the largest number of sample points represented by Latossolos amarelos distrófico which were predominant in all the Paragominas streams and Juruena B1 (Table 3). Argissolos vermelho-amarelos eutróficos were next most common being present in both Rancho Grande and Juruena B2. Latossolos vermelho escuro represented most of the Cerrado samples. Two other soil orders were also present with Cambissolos identified in two Cerrado watersheds (Pulador and Capão da Onça) and Neossolos found in a single watershed in the Ji-Paraná basin (Ji-Paraná@Cacoal). Latossolos, Argissolos, Cambissolos, and Neossolos are generally equivalent to Oxisols, Ultisols, Inceptisols, and Entisols in US Soil Taxonomy (Soil Survey Staff, 1997).

From a design standpoint, it would be best to have observations for all combinations of factor values. In other words, the ideal would be to have samples from every vegetation type, on every soil type, under all land uses, for every stream order, month and year. This is seldom the case for studies using observational data. The configuration of samples in the matrix of all possible sampling combinations of the various factors (i.e., yr x month x stream order x land cover x land use x soil class) is an important attribute of the analysis and can affect the uncertainty in the estimated beta adjustments. For example, if there are certain months or soil types or month x soil type combinations that are not represented by actual samples there is little information with which to estimate adjustments and there is large uncertainty. The multidimensional matrix is difficult to represent in total (i.e., 246,960 combinations from 12 yrs x 12 months x 5 stream orders x 7 land covers x 7 land uses x 7 soil classes) but coplots can represent three factors simultaneously (Figure 2). The coplots indicate that while every combination of factors is not represented in every month, the data are far from perfect colinearity among the factors. In the case of perfect colinearity, the coplots would show one and only one factor value on the y axis corresponding to each factor value on the x axis. The coplots indicate, however, that soil and land use are well represented in most years and months but are sparser with stream order or with vegetation cover (Figure 2, coplots by year and cover not shown).

Discharge-Concentration Regression Analysis

$Log_{10}Ca–log_{10}Q$ relationships for 25 stream stations with sufficient data were analyzed for each stream-station (Table 4). Within these individual station regressions for the 25 streams, 13 regressions had slopes significantly different from zero with a clear preponderance having negative slopes (Figure 3). Ji-Paraná@Cacoal and IG54-S5 (IG54 at station 5) were the only stream stations with significant positive slopes. Of the available stations that had both discharge and concentration data but slopes not different from zero only the Rancho Grande Forest stream had large sample size (n=187); all others had <13 samples.

Using various combinations of the available factors to analyze the $Log_{10}Ca–log_{10}Q$ regression relationship across all streams and stations the multilevel linear model was utilized to partially pool the data. Using the available factors (i.e., year, season, order, cover, use, and soil) the model search results suggest that the complete model is the best (i.e., lowest DIC) at predicting Ca concentration (Table 5). A number of the five component models provide good fits but each is improved by inclusion of the additional adjustment parameter. Comparison of some of the 3, 4, or 5 factor models with or without land use or soil class (e.g., season veg soil vs season veg use) suggest that models including land use were slightly improved.

To investigate the relative contribution of the various factors (i.e., year, season, order, cover, use, and soil) to the overall variance in the $log_{10}Ca$ concentration response an ANOVA decomposition analysis was utilized to interpret the multilevel linear model results (Figure 4).

For the model containing all variables, the graphically based ANOVA decomposition indicates that variance explained by the model intercept term (Int) exceeds the unexplained variance (s.y.). In addition, discharge (i.e., FLOWREG) has a relatively large effect on Ca, although over this broad data set, this slope term is not extremely well defined. The intercept is affected by stream order, soil type, land use, and land cover. Season and year have a small but measureable effect on the intercept. In contrast, land cover, season, and year have a larger effect on the $\log_{10}$Ca-$\log_{10}$Q regression slope than do soil type, stream order, or land use (Figure 4).

Individual adjustments for each class of each factor to the mean intercept or slope are estimated and presented such that their mean is zero (Figure 5 and 6). In other words, the mean intercept and slope terms from Equation 5 ($\mu_{\beta 0}$ and $\mu_{\beta 1}$, respectively) have not been added to the values in Figures 5 and 6. Instead the means for $\mu_{\beta 0}$ and $\mu_{\beta 1}$ have been noted on the "zero" (vertical dotted line) in these graphs. The individual adjustments for the intercept demonstrate small adjustments for all months and all years (Figure 5a and b). Within the other factors a number of adjustments are substantial, for example, 1st order streams, mixed forest (fmixed) land use, and Cambissolos soil classes (Figure 5d, e, and f). For these three highlighted classes, adjustments were negative and thus are a subtraction from the mean value. The individual adjustments for each class of each factor for the slope demonstrate some different patterns with effects being evident for both season and year (Figure 6a and b). May and April have the largest positive adjustments and October and November the most negative. Adjustments for 1st order streams, mixed forests, and Cambissolos are still evident, although positive in this case. In addition, a substantial positive adjustment for open tropical forest (vegcode A) is evident.

The additive effects of the adjustments on the $\log_{10}$Ca–$\log_{10}$Q relationship predicted over all years and seasons at each station (Figure 7) indicate an overall preponderance of positive slopes (i.e., 29 positive, 13 negative). For locations with individual station regressions (Table 4), these multilevel predictions are largely consistent except for Ji-Paraná@Cacoal, which had a positive individual regression slope but is poorly defined in the multilevel model, and for Taquara, which had a negative individual regression slope at p=0.07 (Table 4) but is predicted to be positive by the model. Given the mapping scale used for each stream-station classification, adjustment factors and thus slopes are similar in some cases for all stations (e.g., Capitão Poço (CP 1-4)) but may differ if, for example, stream order changes downstream (e.g., Igarapé Sete (IG7 1-7)).

Discussion

Discharge-Concentration regressions

This study considers many of the major controls on element supply to streams including stream hydrology (discharge), stream geomorphology (order), landscape vegetation (land cover), land-use practices, soil type and interannual variance (year) as they affect discharge-concentration relationships. Discharge-concentration relationships are element specific but in the case of rock-derived elements such as Ca there is typically a dilution of rock-derived, element-enriched groundwaters by surface or stormflow runoff such that concentration decreases with increasing flow (i.e. negative slope) (Drever, 1997). This pattern was observed in regressions by individual station for 11 of the 13 stream datasets available (Figure 2). The two streams with positive slopes (IG54-S5 and Ji-Paraná@Cacoal) were quite distinct from each other in location (eastern vs western Amazon), stream order (1 vs 6), land cover (dense vs open forest), and soil classification (Latossolos amarelo distrófico and Argissolos/Neossolos). In fact, Ji-Paraná@Cacoal was distinct from all other streams in having Neossolos, which have a high sand content. On the other hand, Ji-Paraná@Cacoal and IG54-S5 are somewhat similar in having large portions of non-forest land uses (i.e., 30 and 40% pasture, respectively) in their watersheds with Ji-Paraná@Cacoal possessing ~1% urban land use (Ballester et al., 2003) while IG54 has ~22% row-crop agriculture (Figueiredo et al., 2010). These watersheds provide some support for the proposed hypotheses regarding controlling factors of positive slopes in Ca-discharge relationships (i.e., soils and underlying parent material or land use conversion) with the Ji-Paraná@Cacoal watershed providing support for both alternatives and IG54-S5 providing more support for the latter.

Multilevel Analysis

Rather than seeking to explain positive or negative slopes to the Ca-discharge regression within individual streams based on site-specific factors, the multilevel analysis pools the available data and interprets the relative effect of the various model factors on the overall regression intercept and slope. The multilevel analysis clearly demonstrates an overall strong effect of discharge (i.e., $\log_{10}Q$) on Ca concentration (Figure 4) with an overall mean slope that is negative (Figure 6). In the intercept of the discharge concentration regression, stream order explains the greatest amount of variation with 1^{st} order streams requiring a large negative adjustment (Figure 5d) indicating these streams have lower Ca concentrations. There are a limited number of studies that have directly investigated the effect of stream order on stream water concentration mostly focusing on N and P (Kang et al., 2008). A few studies have demonstrated declining N concentration with increasing stream order while the trend for P has been reversed. In the Seine River in France Ca concentrations had little variance with increasing stream order (Meybeck, 1998). Data presented by Ballester et al. (2003) for the Ji-Paraná river from 3^{rd} to 7^{th} order streams do possess increasing mean Ca concentrations. Increasing Ca concentration in larger streams may reflect a greater contribution of groundwater relative to surface water throughout the year.

Soil type and land use also affect the mean concentration of Ca. In the current analysis the scale of soil maps used for classification was quite coarse but was consistent with observations made within each watershed. The effect of lithology on stream chemical concentrations, at least within the main tributaries of the Amazon, has been well investigated and increasing Ca concentration with base-rich bedrock has been well demonstrated (Gibbs, 1967; Mortatti and Probst, 2003; Richey et al., 1990; Stallard, 1985; Stallard and Edmond, 1987). At a smaller scale (<13,000 km^2) the effect of base –rich soil types on increasing Ca concentration in the western Amazon has also been demonstrated (Biggs et al., 2002). In the present analysis, Argissolos vermelho-amarelo eutrófico (ArgissolosVeAmEut) are in a eutrophic or base rich soil group but do not require a positive adjustment that would reflect a higher Ca concentration. The Latossolos amarelo escuro/Cambissolos association (LatossolosAmEsc/Cambissolos) and the Argissolos/Neossolos association are classifications that include soils that have weak horizon development and likely reflect sandy substrates. As such, these soils should be base poor with potentially lower Ca concentrations. In these soils, the Cambissolos type had a negative adjustment indicating a Ca concentration lower than the mean.

The effects of interannual variation or season on mean Ca concentration are limited for explaining the variation in mean Ca concentrations across the data set. A similar pattern was demonstrated for the main stem Amazon and its tributaries where inter- or intra-annual variance within a river sampling station was small relative to the variance among the rivers (Mortatti and Probst, 2003).

Interpretation of adjustment parameters on the slope of the discharge-concentration relationship differs from those discussed above for the intercept term. In the case of the slope adjustment, year and season explain much of the variation along with vegetation cover. Seasonal adjustments in stream chemical compositions in the form of 12 monthly parameters are commonly utilized to estimate changes in seasonal processes including discharge (StatSoft, 2010). Presently, the seasonal adjustments to slope are well defined for each month of the year with the adjustment being positive in April and May (Figure 6a), which are rainy season months in all locations other than the Cerrado (Markewitz et al., 2006).

The importance of vegetative cover to the slope adjustment as compared to land use was unexpected although the vegetative cover classes do include an aspect of land use. Both the land cover vegetation classes A (open tropical forest with secondary forest and agricultural activity) and D (dense tropical forest with secondary forest and agricultural activity) have greater land cover conversion than classes As (open tropical forest) and Ds (dense tropical forest). In fact, the A and D classes both have positive slope adjustments where As and Ds are negative (Figure 6c). This change in adjustment is consistent with the hypothesis of land use conversion increasing surface runoff concentrations. Increases in surface runoff with forest conversion to pasture have been demonstrated in a number of Amazonian locations with responses being most evident on watersheds < 1 km^2 (Biggs et al., 2006; Germer et al., 2009; Moraes et al., 2006). Only in the case of Rancho Grande have concentration-discharge relationships been quantitatively evaluated with land use change (Germer et al., 2009). At this site during a number of storm-event hydrographs Ca concentration increased initially with stormflow runoff in both the forest and pasture watershed and remained elevated throughout the storm with Ca exports in storm flow from the pasture being greater. Despite these increased Ca fluxes during the storm both the forest and pasture watershed had a net Ca retention relative to inputs. In the current analysis, which combined both storm-event and non-event data from Rancho Grande for analysis, a similar increase in Ca concentration with increasing discharge was not evident (Figure 3).

In the land use classes some similar evidence for an effect of forest conversion is apparent with the Fmixed, Curban, and Cmixed classes all requiring positive adjustment to slope (Figure 6e). On the other hand, the Pasture and Furban adjustment are not positive, although Furban is very poorly defined (i.e. few samples and large variance). Of course, there are many studies that have demonstrated an increase in stream solute concentrations with land use conversion (Likens and Bormann, 1995; Williams and Melack, 1997) but few that have specifically observed changes in discharge-concentration relationships with changing land use (Germer et al., 2009; Markewitz et al., 2001).

The predictive multilevel model indicates that the additive adjustments of all the factors (year, season, stream order, land cover, land use, and soil class) on $\log_{10}$Ca, in many cases, results in positive slopes for $\log_{10}$Ca vs $\log_{10}$Q. The model, of course, reflects the data of which nearly 1/3 are from IG54. This stream has a significant positive slope and shares many attributes (i.e., soil, land use, land cover) with the other streams in the eastern Amazon (i.e., Region C in Figure 1) and thus influences these predictions. It is uncertain how representative IG54 is for this region (Davidson et al., 2010; Figueiredo et al., 2010). As such, one value of the multilevel model is knowledge gained about where future sampling should occur to best learn about the factors and relationships of interest. Clearly, sampling of additional streams in this rapidly changing portion of the eastern Amazon would be valuable.

Conclusion

Across the Amazon and Cerrado of Brazil the hydrology of many low order streams is being impacted by land use conversion as evidenced by studies demonstrating increasing surface runoff, peak flows, and water yield. The factors controlling the expected responses in stream concentration or concentration-discharge relationships, however, are only beginning to be elucidated. In the present study the role of year, season, stream order, vegetation cover, land use, and soil type were investigated for 28 streams. Ca concentrations and discharge varied across three and six orders of magnitude, respectively. In 13 streams with significant concentration-discharge relationships in the individual station regressions, 11 had negative slopes while two had increasing concentrations with discharge. There were no readily apparent similarities between these two stream watersheds and competing hypothesis of soil or land use control in affecting these positive slopes were not well differentiated. Multilevel analysis of the pooled data, however, indicated that soils and land use as well as stream order all explained portions of the variance in mean Ca concentrations while season, year, and vegetative cover explained much of the variance in the slope of the discharge-concentration regression. The utilized vegetative cover classes incorporate aspects of land use and thus suggest a larger role for land use in discharge-concentration slopes than soil classes.

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Table 1. Brazilian streams utilized for multilevel analysis of discharge-Ca concentration relationships. Sta-is number of stations on each stream.

Location, State	Stream/River	Latitude	Longitude	Yr	Sta	Order	Ppt	Basin area	Land Cover	Land use	Soil	Ref
							cm	ha				
Ji-Paraná, Rondonia	Urupá	11°40' S	61°30' W	99/00	1	5	241	420900	A	Furban	AVAE	1,2
	Ji-Paraná@Cacoal	10°80' S	61°80' W	"	1	6	"	1755900	A	Furban	Ag/Ne	"
Juruena, Mato Grosso	B1	10°28' S	58°28' W	03/06	1	1	258	2	As	Forest	LAD	3
	B2	10°25' S	58°46' W	"	1	1	"	2	As	Forest	AVAD	"
Faz. Rancho Grande,	Forest	10°18' S	62°52' W	04/05	1	1	230	1.4	Ds	Forest	AVAE	4
Rondônia	Pasture	"	"	"	1	1	"	0.7	Ds	Pasture	AVAE	"
Fazenda Nova Vida,	Forest1	10°30' S	62°30' W	94/01	1	2	220	1740	A	Forest	AVAE	5
Rondônia	Pasture1	"	"	"	1	2	"	720	A	Pasture	AVAE	"
	Forest2	"	"	"	1	2	"	250	A	Forest	AVAE	"
	Pasture2	"	"	"	1	1	"	130	A	Pasture	AVAE	"
Paragominas, Pará	IG54	2°59' S	47°31' W	96/05	5	2	180	14000	D	FMixed	LAD	6,7
	Sete	3°16' S	47°23' W	03/05	7	3	"	16143	D	FMixed	LAD	7
	Pajeú	3°10' S	47°17' W	"	3	2	"	3246	D	FMixed	LAD	"
Capitão Poço, Pará	CP1	2°10' S	47°15' W	"	2	1	260	20	D	Forest	LAD	"
	CP2	"	"	"	2	1	"	20	D	Forest	LAD	"
Igarapé-Açu, Pará	Cumaru	1°11' S	47°34' W	06/07	4	2	251	1850	D	FMixed	AAD	8
	Pachibá	1°10' S	47°37' W	"	2	1	"	323	D	FMixed	AAD	"

	São João	1°10' S	47°30' W	"	2	1	"	570	D	FMixed	AAD	"
Brasilia, Distrito	Roncador	15°56' S	47°53' W	98/00	1	3	147	2000	Sa	Cerrado	LVE	9
Federal	Pitoco	15°55' S	47°52' W	05/06	2	1	138	80	Sa	Cerrado	LVE	10
	Taquara	15°57' S	47°53' W	"	2	1	"	150	Sa	Cerrado	LVE	"
	Vereda Grande	15°32' S	47°34' W	"	1	1	"	3850	Sa	Cerrado	LVE	"
	Estanislau	15°47' S	47°37' W	"	2	1	"	390	S	Cmixed	LVE	"
	Barreiro do Mato	15°48' S	47°36' W	"	1	1	"	250	S	Cmixed	LVE	"
	Capão da Onça	15°38' S	48°10' W	"	1	1	"	720	S	Cmixed	LVE/C	"
	Pulador	15°40' S	48°1' W	"	1	1	"	170	S	Curban	LVE/C	"
	Mestre D'Armas	15°36' S	47°40' W	"	1	1	"	5740	Sa	Curban	LVE	"
	Atoleiro	15°37' S	47°38' W	"	1	1	"	2030	Sa	Curban	LVE	"

Furban – forest watershed intermixed with urban areas

Fmixed – forest watershed intermixed with pasture and agricultural areas

Curban – cerrado watershed intermixed with urban areas

Cmixed-cerrado watershed intermixed with pasture and agricultural areas

A- Floresta ombrofila aberta (Floresta de transição) – Vegetação secundária e Atividades agrícolas (Open tropical rainforest (transition forest) – secondary vegetation and agricultural activities).

As- Floresta ombrófila aberta (Floresta de transição) – Submontana (Open tropical rainforest (transition forest) – sub-mountain).

ON-Áreas de tensão ecologica (contatos entre tipos de vegetação)-Floresta Ombrófila-Floresta Estacional (Ecotone {contact between two vegetation types}-tropical rainforest-seasonal forest.

Ds-Floresta ombrófila densa-submontana (Dense tropical forest – submountain).

D- Floresta ombrófila densa- Vegetação secundária e Atividades agrícolas (Dense tropical forest –secondary vegetation and agricultural activities).

Sa- Savana-Arbórea Aberta (Savannah-open woodlands).

S- Savana- Atividades agrícolas (Savannah –agricultural activities).

LAD – Latossolos amarelo distrófico (distrophic yellow latosol)

LVE- Latossolos vermelho escuro (dark red latosol)

LVE/C – Latossols vermelho escuro/Cambissolos (dark red latosol/cambisol)

AVAE –Argissolos vermelho-amarelo eutrófico (eutrophic red yellow argisol)

AAD-Argissolos amarelo distrófico (distrophic yellow argisol)

AVAD - Argissolos vermelho-amarelo distrófico (distrophic red yellow argisol)

Ag/Ne – Argissolos/Neossolos (argisol/neosol)

1 (Krusche – unpublished data); 2 (Ballester et al., 2003); 3 (Johnson et al., 2006); 4 (Chaves et al., 2008); 5 (Neill et al., 2001); 6 (Markewitz et al., 2001); 7(Figueiredo et al., 2010) ; 8 (Figueiredo - unpublished data); 9 (Markewitz et al., 2006); 10 (Silva et al., In press)

Table 2. Descriptive statistics for $Log_{10}Ca$ concentration and $Log_{10}Q$ for 28 streams in Brazil sampled between 1994 and 2007. Total sample size is 3155.

Statistic	**log_{10} Ca**	**$log_{10}Q$**
	μM	**$m^3\ sec^{-1}$**
n	2734	2062
Minimum	-0.432	-6.00
1^{st} Quartile	1.08	-3.243
Median	1.38	-1.200
Mean	1.32	-1.707
3^{rd} Quartile	1.64	-0.072
Max	2.43	3.238
Missing values	421	1093

Table 3. Sample size available for multilevel analysis from 28 streams in Brazil sampled between 1994 and 2007.

Year		Month		Stream Order		Land Use		Land Cover		Soil Class	
ID	N	ID	N	ID	N	ID	N	ID	N	ID	N
1994	21	1	291	1	1502	Forest	712	A	276	LAD	1336
1996	124	2	450	2	1407	Fmixed	1224	As	83	LVE	489
1997	271	3	366	3	198	Furban	48	D	1389	LVE/C	42
1998	340	4	206	5	24	Pasture	640	Ds	792	AVAE	1044
1999	217	5	181	6	24	Cerrado	350	ON	84	AAD	136
2000	148	6	213			Cmixed	105	S	126	AVAD	84
2001	73	7	172			Curban	76	Sa	405	Ag/Ne	24
2003	171	8	203								
2004	589	9	273								
2005	820	10	241								
2006	305	11	385								
2007	40	12	172								

Furban – forest watershed intermixed with urban areas

Fmixed – forest watershed intermixed with pasture and agricultural areas

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A- Floresta ombrófila aberta (Floresta de transição) – Vegetação secundária e Atividades agrícolas (Open tropical rainforest (transition forest) – secondary vegetation and agricultural activities).

As- Floresta ombrófila aberta (Floresta de transição) – Submontana (Open tropical rainforest (transition forest) – sub-mountain).

ON-Áreas de tensão ecologica (contatos entre tipos de vegetação)-Floresta Ombrófila-Floresta Estacional (Ecotone {contact between two vegetation types}-tropical rainforest-seasonal forest.

Ds- Floresta ombrófila densa-submontana (Dense tropical forest – submountain).

D- Floresta ombrófila densa- Vegetação secundária e Atividades agrícolas (Dense tropical forest –secondary vegetation and agricultural activities).

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AVAD - Argissolos vermelho-amarelo distrófico (distrophic red yellow argisol)

Ag/Ne – Argissolos/Neossolos (argisol/neosol)

Table 4. Linear regression statistics for $Log_{10}Q$ (m^3 sec^{-1}) vs $Log_{10}Ca$ (μM) for individual stream stations. Statistics include adjusted R^2, y intercept (y_0) and standard error (SE_{y0}), slope and standard error (SE_{slope}), p-values for tests of y-intercept (P_{y0}) and slope (P_{slope}) different from zero.

ID	Adj. R^2	y_0	SE_{yo}	Slope	SE_{slope}	P_{yo}	P_{slope}
Urupá	0.50	2.550	0.105	-0.186	0.038	0.0001	0.0001
Ji-ParanáCa	0.80	1.019	0.067	0.262	0.027	0.0001	0.0001
JuruenaB1	0.59	-1.043	0.251	-0.713	0.072	0.0001	0.0001
JuruenaB2	0.79	-0.253	0.096	-0.719	0.030	0.0104	0.0001
RGForest	0.00	1.446	0.076	-0.008	0.017	0.0001	0.6621
RGPasture	0.02	1.302	0.024	-0.027	0.007	0.0001	0.0002
FazNVFor1	0.62	1.779	0.015	-0.122	0.014	0.0001	0.0001
FazNVPas1	0.23	1.696	0.046	-0.152	0.040	0.0001	0.0004
FazNVFor2	0.38	1.880	0.030	-0.076	0.019	0.0001	0.0004
FazNVPas2	0.18	1.714	0.080	-0.158	0.059	0.0001	0.0119
IG54-S5	0.20	1.282	0.010	0.996	0.086	0.0001	0.0001
IG54-S3	0.00	1.466	0.100	0.296	0.279	0.0001	0.3139
Sete-S2	0.08	0.691	0.340	-1.684	1.073	0.0691	0.1477
Sete-S4	0.11	2.465	0.721	-2.915	1.711	0.0066	0.1192
Sete-S5	0.03	0.676	0.419	1.883	1.553	0.1381	0.2533
Sete-S6	0.00	1.673	0.717	-1.204	1.585	0.0445	0.4670
Pajeú-S2	0.00	1.065	0.304	0.183	0.392	0.0057	0.6504
CumaruA	0.00	0.549	0.690	-0.024	0.127	0.4170	0.8512
CumaruB	0.00	0.833	0.700	0.086	0.132	0.2593	0.5290
CumaruC	0.00	1.160	0.129	-0.037	0.038	0.0001	0.3579
CumaruD	0.67	0.169	0.230	-0.337	0.073	0.4799	0.0013
Roncador	0.22	1.426	0.044	-0.342	0.043	0.0001	0.0001
Taquara	0.16	-3.850	2.164	-2.908	1.483	0.0970	0.0700
Pachibá	0.00	0.818	0.367	0.037	0.093	0.0546	0.6947
São João	0.00	0.893	0.163	0.015	0.043	0.0028	0.7501

Table 5: Results of the model search within the ANOVA models using year, season, stream order, vegetation cover, land use, and soil type. DIC is an estimate of expected predictive error (lower including more negative deviance is better). Dbar is a Bayesian measure of fit, while pD (pD = Dbar-Dhat) is the estimated number of independent parameters (complexity) of the multilevel model. C is an indicator for convergence; M is an indicator that Markov chains have mixed during simulation.

Model	Dbar	Dhat	pD	DIC	C	M
Season Veg Soil	1581.99	1445.78	136.21	1718.20	1	0
Season Veg Use	1473.75	1269.96	203.79	1677.53	1	1
Year Season Order	726.960	619.82	107.140	834.100	0	0
Year Season Soil	386.899	189.674	197.225	584.123	1	1
Season Veg Use Soil	1431.81	1294.59	137.22	1569.03	1	0
Year Season Use Soil	-372.663	-722.334	349.671	-22.992	1	1
Year Season Order Soil	-280.310	-609.287	328.976	48.666	1	0
Year Season Order Use	470.518	215.02	255.497	726.015	1	1
Year Season Order Veg	-607.721	-1090.06	482.338	-125.383	1	1
Year Season Veg Soil	3.994	-260.95	264.942	268.936	1	1
Year Season Veg Use	-581.756	-893.92	312.166	-269.589	0	0
Year Season Order Veg Soil	-688.375	-1157.03	468.654	-219.721	1	0
Year Season Order Veg Use	-835.041	-1296.67	461.634	-373.407	1	1
Year Season Order Use Soil	-560.757	-610.80	50.042	-510.714	0	0
Year Season Veg Use Soil	-746.277	-962.58	216.302	-529.976	1	1
Year Season Order Veg Use Soil	-991.330	- 1237.39	246.062	-745.268	1	1

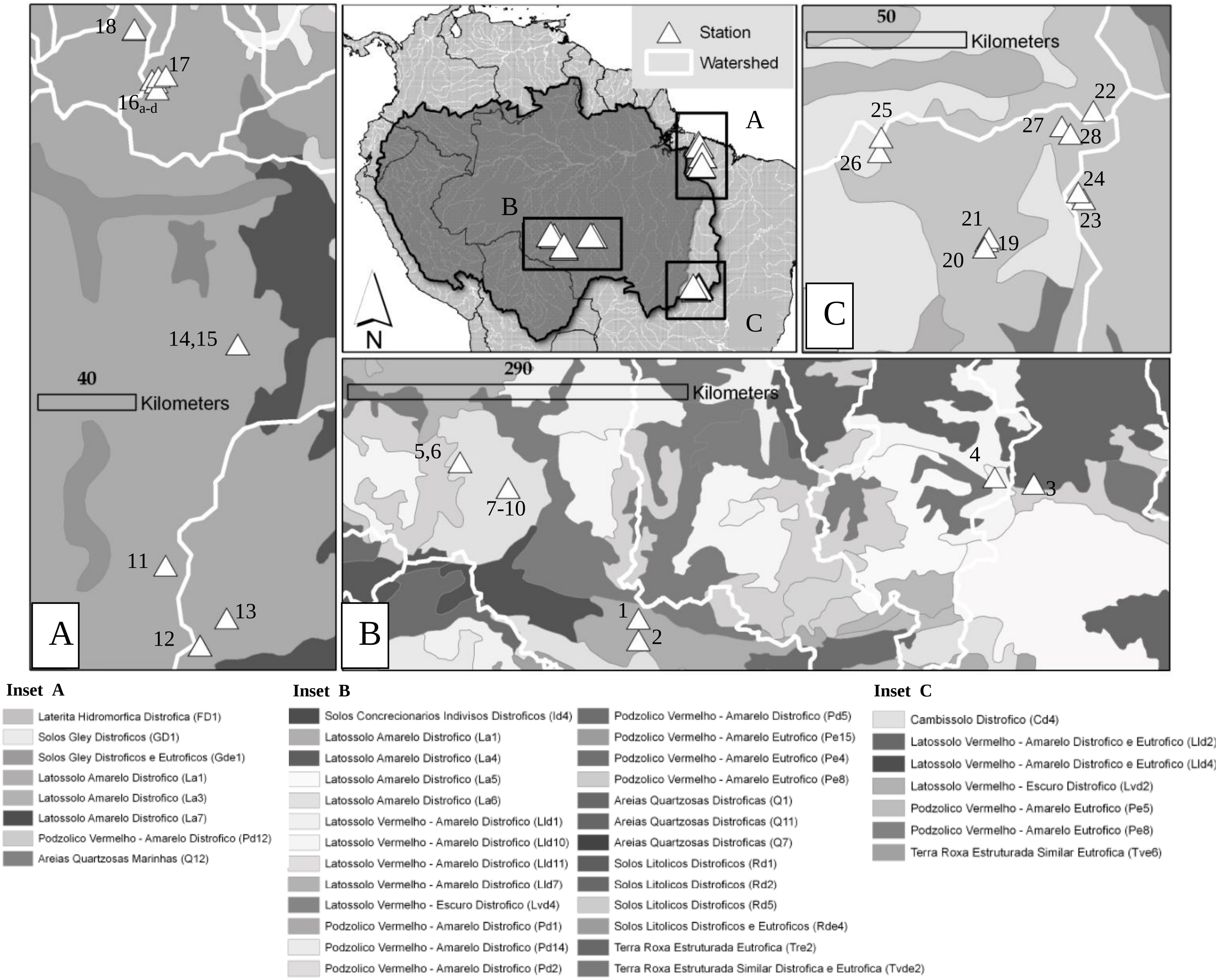

Figure 1. Locations of streams in the Amazon and Cerrado of Brazil. Underlying map is RADAM soil classifications. 1-Urupá; 2-Ji-Paraná@Cacoal ; 3-B1; 4-B2; 5,6-Rancho Grande; 7-10 Nova Vida; 11-IG54; 12-Sete; 13-Pajeú; 14,15 Capitão Poço; 16-Cumaru; 17-Pachibá; 18-São João; 19-Roncador; 20-Pitoco; 21-Taquara; 22-Vereda Grande; 23-Estanislau; 24-Barreiro do Mato; 25-Capão do Onça; 26-Pulador; 27-Mestre D’Armas; 28-Atoleiro.

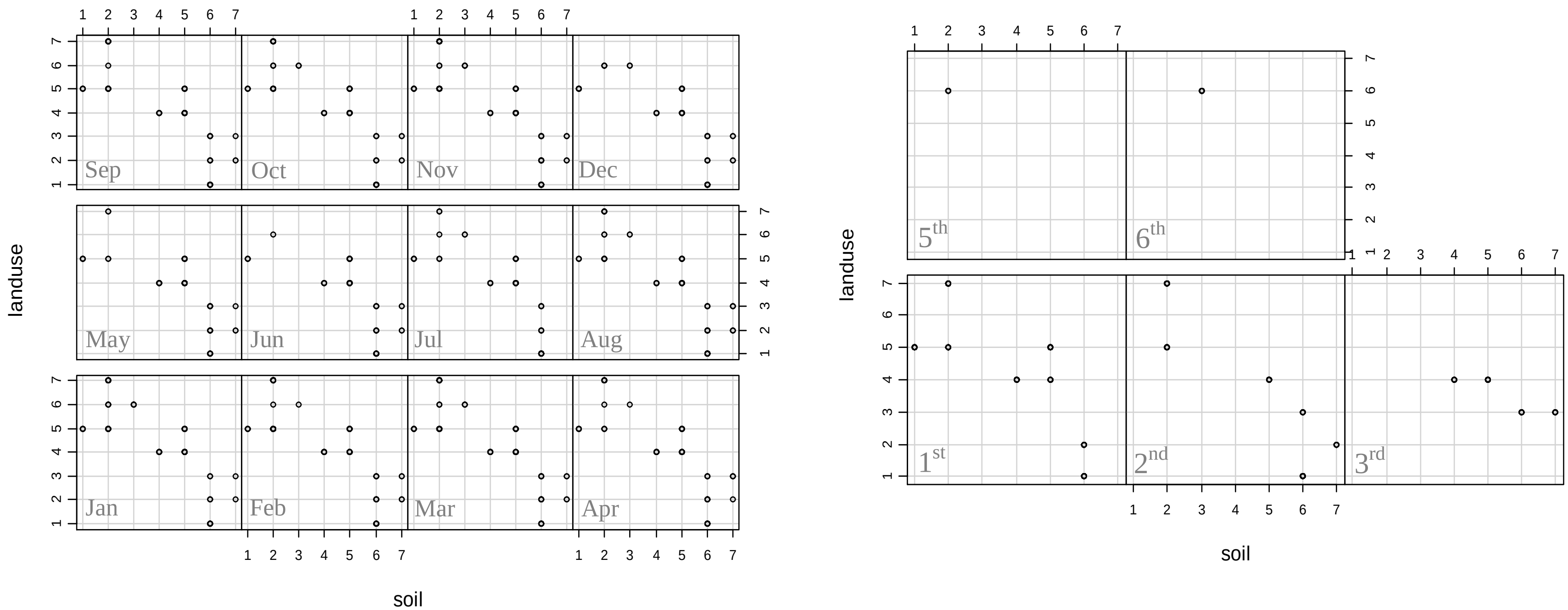

Figure 2. Coplots for landuse and soil given A) season (i.e., month) or B) stream order. Circles indicate presence of data corresponding to each soil type and land use, for each level of the marginal variable (i.e., season or order). Ideal would be a representative of each soil type in each land use for each season or stream order. Each month in season is well represented although July is missing soil type 7 (made up of land uses 2 and 3 in other months) and land use number 1 (Cerrado) is all in soil type 6, for all months. Stream order 1, 2, and 3 are well represented but order 5 and 6 are single soil and land use combinations.

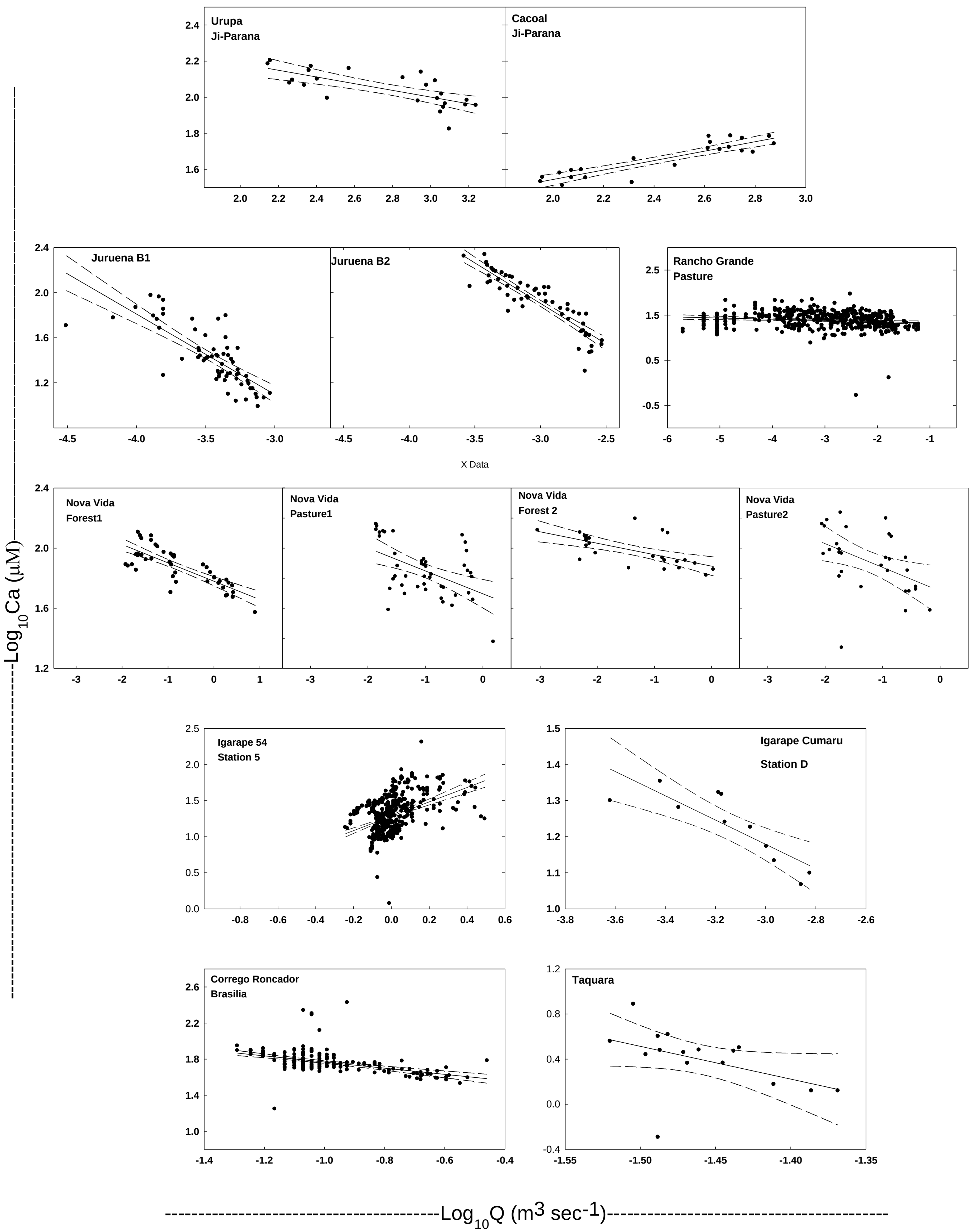
Urupa
Ji-Parana
Cacoal
Ji-Parana
Juruena B1
Juruena B2
Rancho Grande
Pasture
X Data
Nova Vida
Forest1
Nova Vida
Pasture1
Nova Vida
Forest 2
Nova Vida
Pasture2
Igarape 54
Station 5
Igarape Cumaru
Station D
Corrego Roncador
Brasilia
Taquara
$Log_{10}Ca$ (μM)
$Log_{10}Q$ (m^3 sec^{-1})

Figure 3. $Log_{10}Ca$ (μM) vs $Log_{10}Q$ (m^3 sec^{-1}) relationship for 13 streams in Brazil. Solid lines are least square linear regressions and dashed lines are upper and lower 95% confidence intervals. Data were collected between 1996 and 2005.

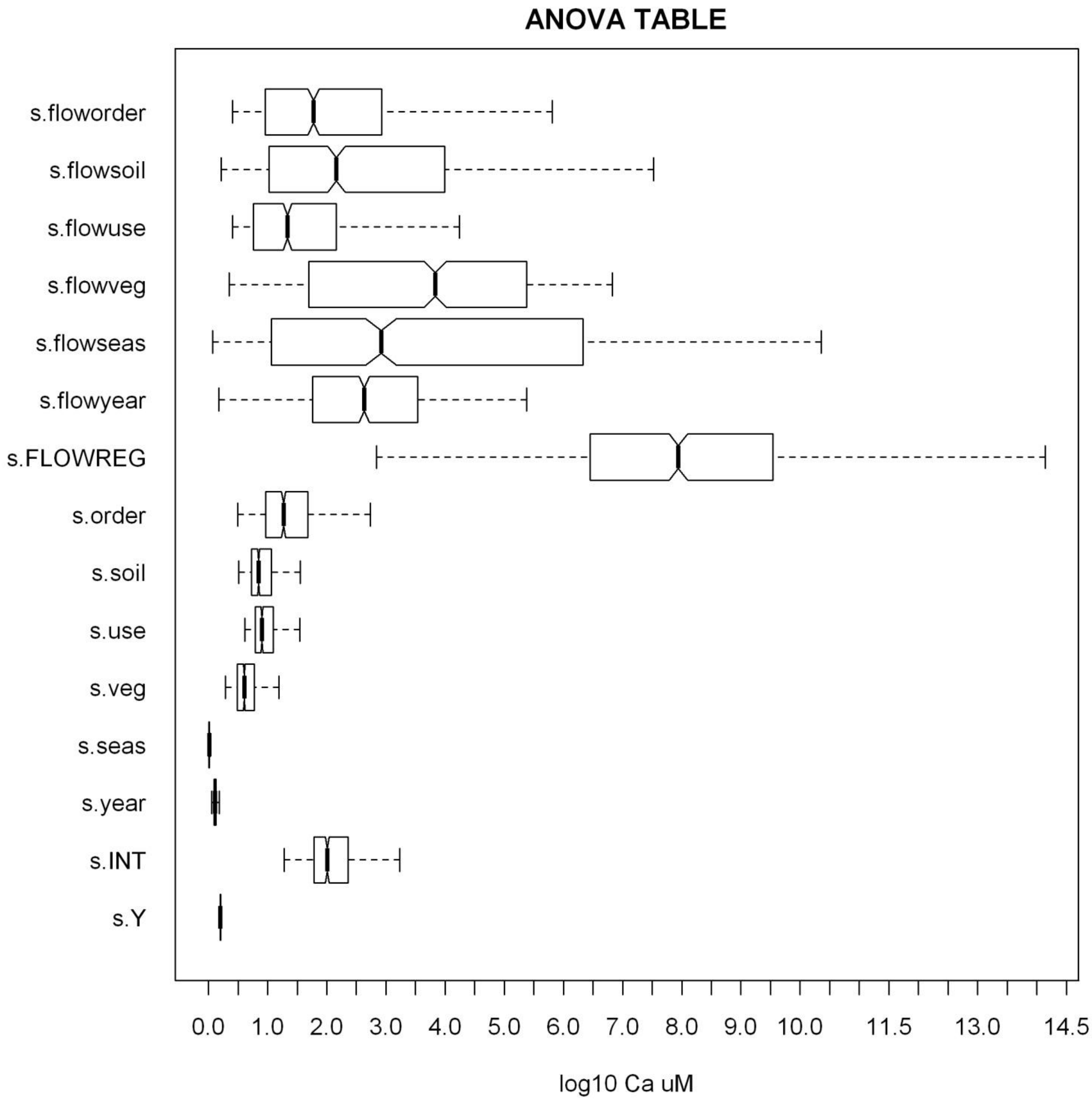

Figure 4 – ANOVA analysis for main effects on $Log_{10}Ca$ concentration (n=3155). The mean of the box plots represents the proportion of the standard deviation explained by each component and the distribution represents how well the effect is determined. The upper boxes (s.flow(factor)) represent the decomposition of the variance explained by the slope of the discharge-Ca regression slope (s.FLOWREG) and the lower boxes (s.(factors)) represent the decomposition of the variance in the intercept term (s.INT). The s.y. component identifies the unexplained variance.

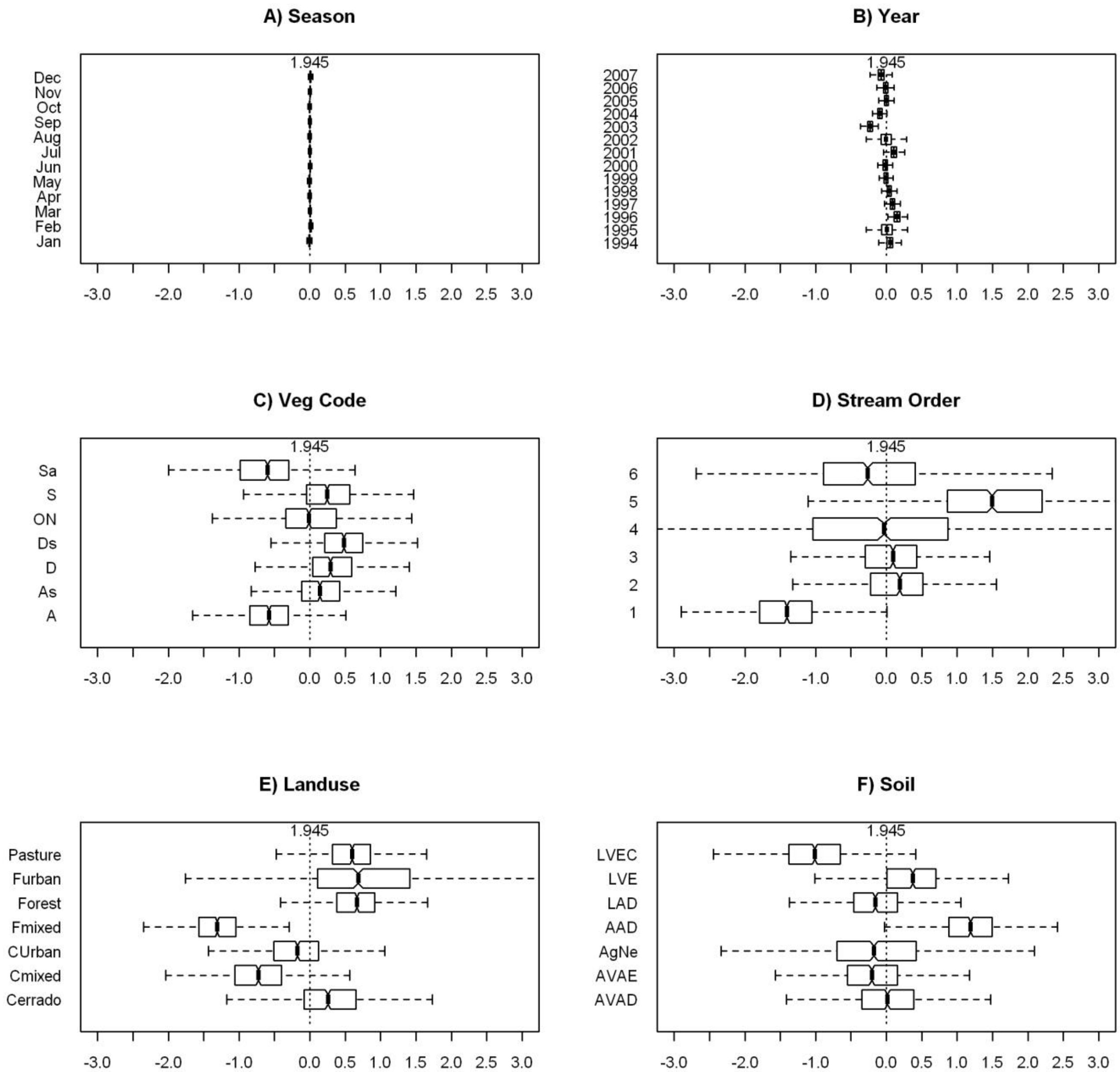

Figure 5 – Intercept adjustments associated with the $\log_{10}Q$ regression. The overall mean intercept is identified by the dotted line in each panel. A-Open tropical rainforest with secondary vegetation and agricultural activities); As-Open tropical rainforest – sub-mountain; ON-Ecotone tropical rainforest-seasonal forest; Ds-Dense tropical forest – submountain; D-Dense tropical forest –secondary vegetation and agricultural activities; Sa-Savannah-open woodlands; S-Savannah –agricultural activities). LAD – Latossolos amarelo distrófico; LVE- Latossolos vermelho escuro; LVE/C – Latossolos vermelho escuro/Cambissolos; AVAE –Argissolos vermelho-amarelo eutrófico; AAD-Argissolos amarelo distrófico; AVAD - Argissolos vermelho-amarelo distrófico; Ag/Ne – Argissolos/Neossolos.

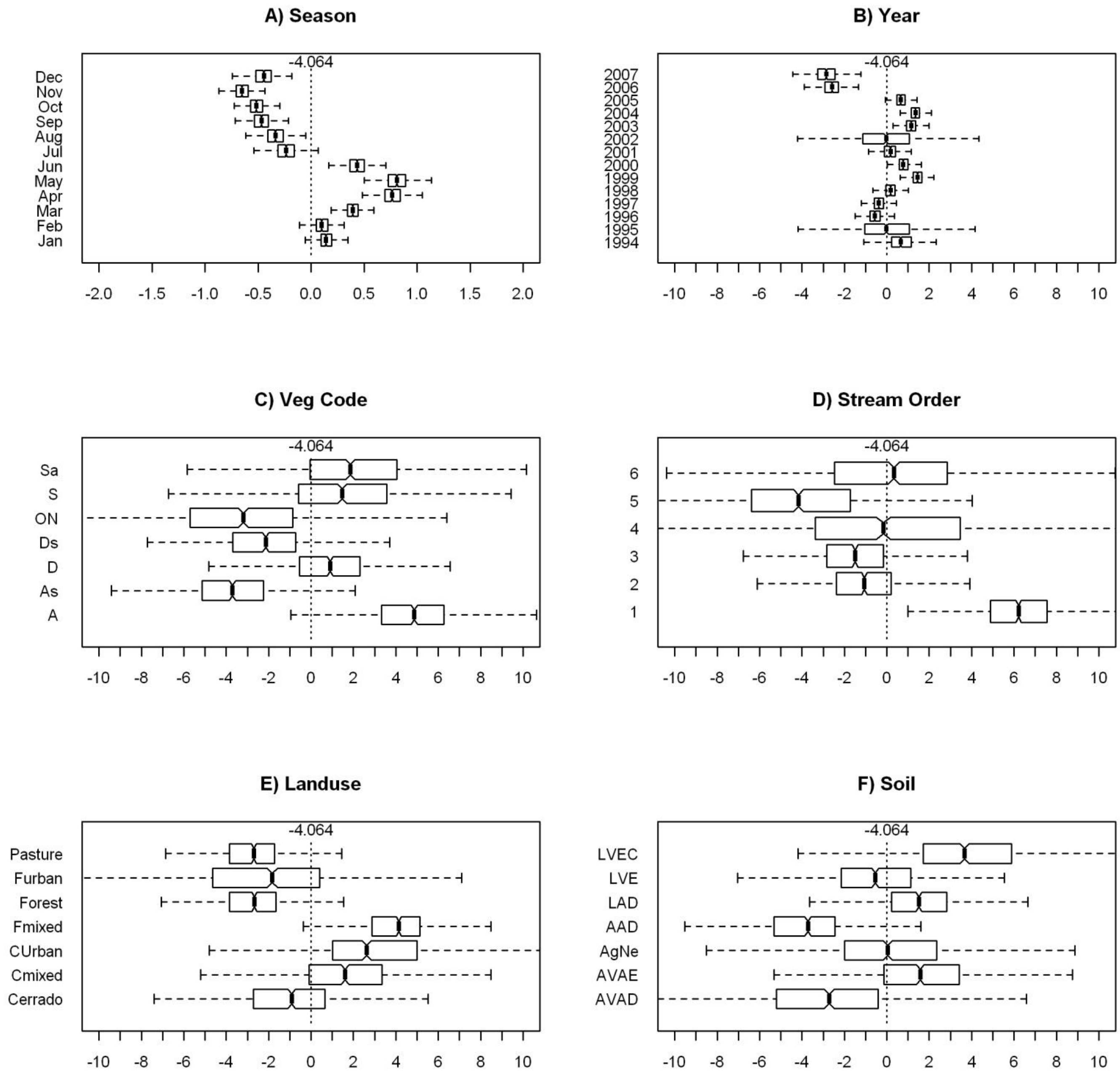

Figure 6 - Slope adjustments associated with the $\log_{10}$Flow regression. The overall mean Slope is identified by the dotted line in each panel. A-Open tropical rainforest with secondary vegetation and agricultural activities); As-Open tropical rainforest – sub-mountain; ON-Ecotone tropical rainforest-seasonal forest; Ds-Dense tropical forest – submountain; D-Dense tropical forest –secondary vegetation and agricultural activities; Sa-Savannah-open woodlands; S-Savannah –agricultural activities). LAD – Latossolos amarelo distrófico; LVE- Latossolos vermelho escuro; LVE/C – Latossols vermelho escuro/Cambissolos; AVAE –Argissolos vermelho-amarelo eutrófico; AAD-Argissolos amarelo distrófico; AVAD - Argissolos vermelho-amarelo distrófico; Ag/Ne – Argissolos/Neossolos.

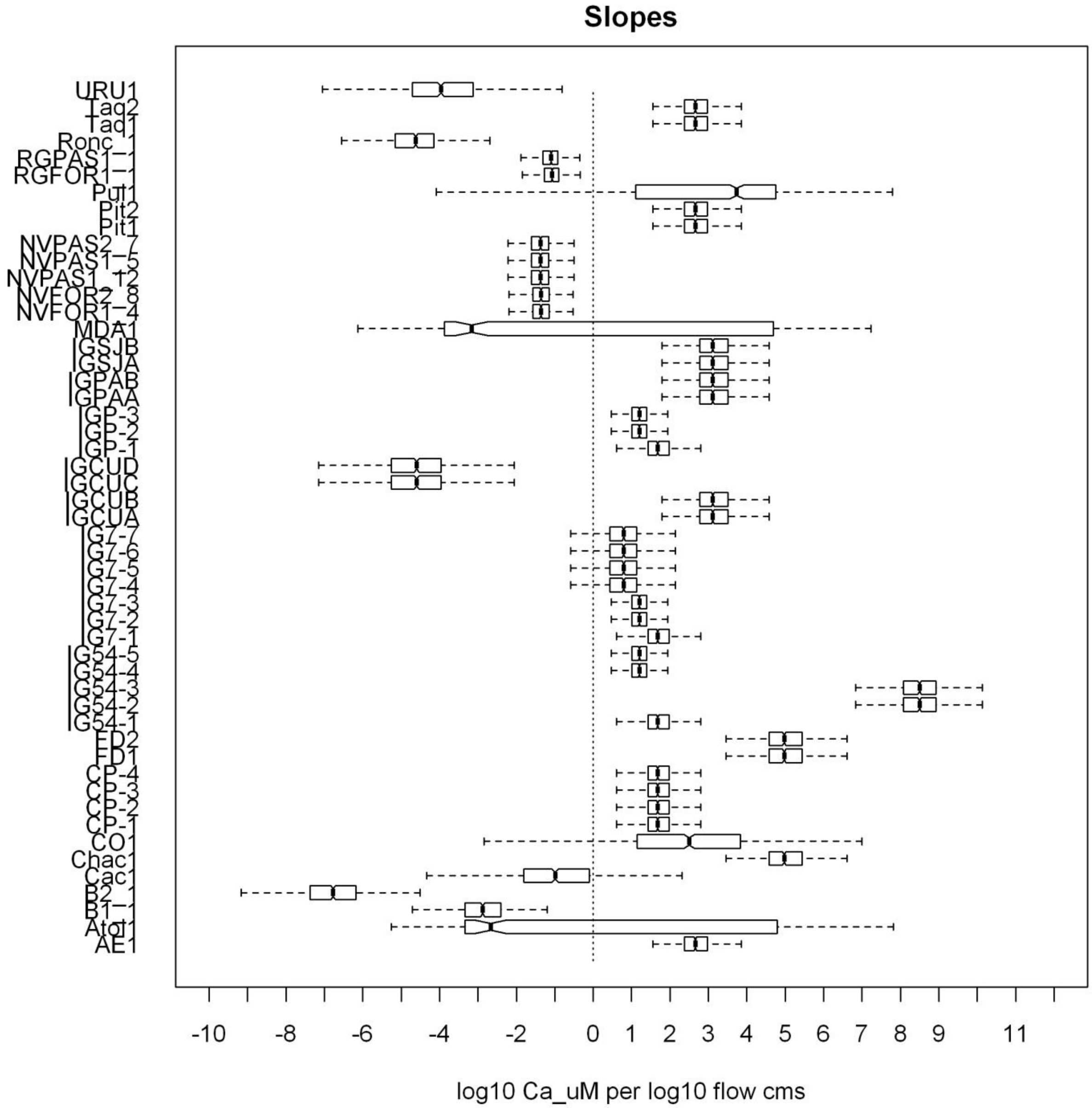

Figure 7. The log_{10}Ca vs log_{10}Q slopes for all stream stations predicted over all years from a multilevel model including adjustments for year, season, stream order, land cover, land use, and soil class. URU1-Urupa; Taq-Taquara; Ronc-Roncador; RGPAS-Rancho Grande Pasture; RGFOR-Rancho Grande Forest; Pul-Pulador; Pit-Pitoco; NVPAS-Nova Vida Pasture; NVFOR-Nova Vida Forest; MDA-Mestre D' Armas; IGSJ-São João; IGPA-Pachiba; IGP-Pajeu; IGCU-Camaru; IG7-Sete; IG54-Cinquenta e quarto; FD-Fazenda Dimas; CP-Capitão Poço; CO-Capão de Onça; Chac-Chacara; Cac-Ji-Paraná@Cacoal; B-Juruena; Atol-Atoliero; AE-Aguas Emendadas. Letters or numbers after abbreviations indicate stations within the stream.