Journal of Physical Chemistry & Biophysics

Zaffani et al., J Phys Chem Biophys 2014, 5:1
DOI: 10.4173/2161-0398.1000173

Research Article Open Access

Uncertainties in the Generation of Pollutant Loads in Brazilian Nested Catchment Experiments under Progressive Change of Land Use and Land Cover

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Abstract

River pollutant loads encompass a combination of natural and anthropogenic factors related to land use and land cover (LULC). Progressive changes in LULC can significantly alter pollutant behaviors of changing flows and pollutant concentrations, reducing biodiversity, and emerging uncertainties regarded to poor gauged basins. To assess the factors involved in the generation of pollutant loads, this paper examined empirical uncertainties from observed pollutant loads in river basins through nested catchment experiments (NCE). Monitored river flows, concentration and drainage areas of each NCE were associated with LULC in order to determine specific pollution generation coefficients per unit of drainage area (Ys) of BOD, a- chlorophyll, NTK, TSS, and Total Coliforms. Three Brazilian watersheds were tested with drainage areas ranging from 0.93 km² to 242 km², and under different conditions of: (1) LULC (urban, forest and agricultural), (2) numbers of NCEs (2 to 11), (3) sampling seasons (1 to 4), (4) antecedent precipitation index (dry or wet conditions) and (5) biomes (Atlantic Forest and Cerrado-savanna). LULC appraisal showed complex upstream-downstream uncertainties of BOD, a-chlorophyll, and TSS from both urban and rural areas. Therefore, limitations of addressing representative values of specific pollution loads were preliminarily regarded due to the lack of continuous spatiotemporal schemes of experimental data at NCEs linked to existing point-sources and progressive LULC.

Keywords: Land use and land cover; Pollutant load; Nested catchment experiments

Introduction

Changes in land use and land cover (LULC) have been recognized as stressors of aquatic ecosystems and drainage areas [1,2]. Some of the most relevant effects are reduced biodiversity and impacts on the quality and quantity of water [3-6]. These effects can be observed even in areas where the degree of urbanization is low [7], and which already have increased impermeable surfaces and structures implemented to increase the velocity and power of water runoff [8]. Increased runoff flow in urban areas is the main result from changing LULC, resulting in higher peak flows during rainfall events [9] and high transport of pollutants through runoff [10]. However, the practices used in rural areas also have negative effects on water resources qualitatively [5]. The different activities practiced in these areas also contribute significantly to the input of sediments and various potentially polluting substances from the use of fertilizers and pesticides applied to crops [11]. Nitrogen and phosphorus are the most common nutrients found in water bodies under agricultural influence [2,12]. According to Richardson et al. [13], the removal of riparian vegetation, which occurs in urban and rural areas, significantly impacts the water quality and biodiversity of the watercourses.

Given the known effects of increasing changes of LULC on water resources, it is vital to understand the processes involved and the factors influencing them [14-18]. DeFries and Eshleman [19] affirm that the identification and quantification of the hydrological consequences due to land use changes are difficult because of the small number of controlled experimental studies that have been performed.

According to Salmoral et al. [20], the impact extention of land use changes on hydrological responses of a basin depend on several variables such as the magnitude of the shift taking place, physical conditions like slope and soil, and ecological characteristics like vegetation types. Therefore, several studies are being developed in order to qualitatively and quantitatively determine the impacts of LULC. Hundecha and Bardossy [9] emphasized the growing interest of researchers in quantifying the effects of LULC on the flow dynamics – either through relationships between the physical characteristics of the drainage basin, such as topography, pedology, and flow generation [21]; by analyzing the influence of urbanization on the base flow of the natural watercourses [1]; or by discussing the role of different LULC classes as driving forces with impact on the water bodies [6].

Understanding the generation and transport of loads in drainage catchments and how they vary depending on the physical characteristics [15,22] can be linked to both progressive changes in LULC and climatic variations [5,23]. These impacts occur on a continuum of spatiotemporal scales. On the one hand, they occur from source to downstream areas, which are commonly poor-gauged in most osf river basins [24]. In addition, temporal experimental sampling, either in wet or even in dry seasons, are not systematically well-documented. Thus uncertainties of monitored evidences of pollution loads still remain. On that account, Hannah et al. [17] emphasize the need for implementing monitoring and data sharing networks so that the generation of pollutants can be evaluated and compared with different regions.

In the study of embedded or nested catchment experiments (NCE), in which there are substantial changes in the physical characteristics and

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Received: Aprile 29, 2014; **Accepted:** January 28, 2015; **Published:** January 30, 2015

Citation: Zaffani AG, Cruz NR, Taffarello D, Mendiondo EM (2015) Uncertainties in the Generation of Pollutant Loads in Brazilian Nested Catchment Experiments under Progressive Change of Land Use and Land Cover. J Phys Chem Biophys 5: 173. doi:10.4173/2161-0398.1000173

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scale of the drainage basins studied, evaluating and understanding the generation and transport dynamics of pollutant loads is complex, and depends on the availability of field data to have an integrated overview of the conditions of the drainage basin and the processes involved. Given the limitation of experimental information and the need to provide support for the conservation of water resources through adaptation and mitigation actions, an interesting alternative emerges to search for generation patterns of pollutant loads for catchments under specific LULC. Huang and Demuth [16] indicate the need to develop research to help explain the patterns and drivers of the hydrological responses observed, which according to them enables identifying locations and periods that are more sensitive to anthropogenic and climate actions, in addition to providing scientific information to the decision makers.

The focus of this paper is to discuss inherent uncertainties from experimental monitoring of pollutant loads through scales of NCEs and under progressive changes of LULC in selected Brazilian river basins. Thus the paper encompasses sections that analyzes the generation of pollutant loads in areas under different LULC with application of mass balance for spatial patterns of pollution generation across drainage areas of NCEs.

Methodology

Study Area

The methodology used in this work is to gather data from three different catchment areas (Canha Basin, Monjolinho Basin and Frutal Basin), obtained in four studies conducted between 2008 and 2012. The methodology presented herein can be applied to nested or embedded catchments in which the transfer of water and nutrients flow from upstream to downstream is influenced by different factors, and for which there are qualitative and quantitative data over points of interest, and also use and occupancy data. The drainage basins used in this study can be viewed in more detail at the link available in Appendix 1 (see Supplemental Material).

Figure 1 shows maps of each study area with its respective monitoring points and the delimitation of the drainage area. The Canha Basin has 8 analysis points that were sampled in four field campaigns. The Monjolinho River was analyzed in two different studies, in which one of them had three monitoring points with 4 campaigns in each one, and the second one had 14 points analyzed only once. The Frutal Basin has 28 monitoring points that were sampled qualitatively and quantitatively in one field campaign. Localizing the collection points in the study areas contributes toward understanding the LULC changes with regards to the generation of pollutants that are carried to the receiving water bodies.

Land uses in the study areas

To analyze the influence LULC changes had on the water resources, the usage ratio had to be estimated in the catchments under study. Using satellite images the land use was classified into three categories: forest, mixed farming (pasture, bare soil and crops) and urban. Table 1 shows that most of the area in the Canha Basin is occupied by forests (82%). In the Monjolinho Basin the largest percentage of the area is occupied by agriculture (48%), but there is also a significant percentage of the area that shows urban occupation (41%). The Frutal Basin shows a high rate of agriculture (63%).

Of the drainage basins analyzed, Frutal is the one with the greatest drainage area, with 242 km². By subdividing the basins into smaller units from the monitoring points, the smallest area observed is in the Canha Basin, with 0.93 km². Table 1 shows the drainage area upstream, the land use ratio, and the number of samples and biome in each drainage basin.

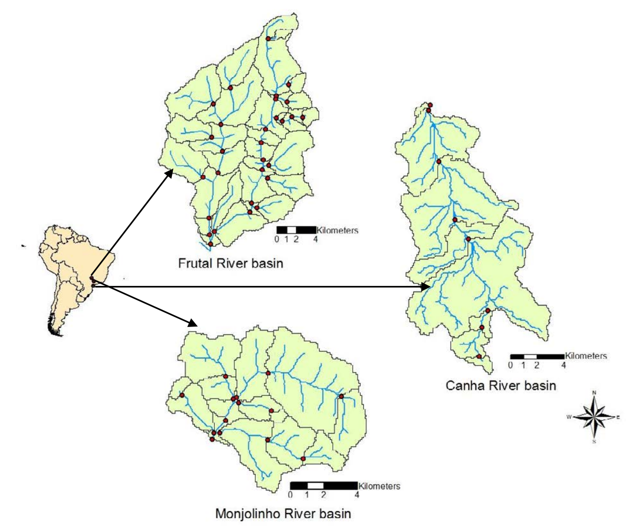

Figure 1: Drainage basins under study and their location in South America

Qualitative and quantitative aspects of the watercourses analyzed

Qualitative water analysis of the water bodies was performed by calculating the pollutant loads obtained by the product between the concentration of a particular pollutant and the river flow. The qualitative and quantitative data relating to the river Canha were obtained by Bottino [25]. The data of the Monjolinho basin were obtained by Pehovaz and Zaffani [26,27], while the data for the Frutal basin are in Zaffani [28]. Of the quality variables analyzed by these authors, we show here data on the quality variables Dissolved Oxygen, Total Suspended Solids, Biochemical Oxygen Demand (BOD$_{5,20}$), Total Coliforms, Nitrogen and Chlorophyll *a*.

Spatial variation of diffuse pollution

The spatial variation of the generation of diffuse loads was analyzed by subdividing the study basins into smaller and nested units and characterizing the soil types and activities at each site. With the characterization of the basins and the availability of empirical data, the spatial patterns analysis looks for diffuse load generation patterns according to the different LULC in the drainage basin, per unit area.

Ground cover: The Canha Basin is inserted in the Atlantic Forest biome, which includes mountains, plateaus and plains. The predominant vegetation is dense ombrophilous forest (dense tropical rain forest) with tall trees and hot and humid climate [29]. The Monjolinho basin is located in a transition area of Atlantic Forest to Cerrado, and the Frutal basin is in the Cerrado. In the Brazilian Cerrado there is a predominance of savanna formations with hot and sub-humid tropical climate, with dry and rainy seasons. In this biome there are regions of gallery forests and riverine forest [29]. Cambisols are the predominant soil type in the Canha river watershed [25], and in the Monjolinho and Frutal watersheds the dominant soil type are red-yellow and dark red latosols [30].

The land uses were identified and classified with the satellite images of the study areas. The three pre-determined categories were: urban,

NCE	Drainage Area (km²)		Land use (%)			Seasonal NCE Samples	Biome
	Min	Max	Forest	Agric	Urban		
Canha	0,9	125,9	82	16	2	8; 8; 8; 8	Atlantic Rainforest
Monjolinho	2,0	75,6	6	48	46	3; 3; 3; 3; 14	Atlantic Rainforest and Cerrado
Frutal	1,5	75,6	20	75	5	28	Cerrado

Table 1: Characterization of the drainage basins under study

mixed farming and forestry. The mixed farming use was employed to identify areas with varied cultivations and also pasture areas. The cultivation of banana, corn and cassava are prevalent in the Canha Basin, while sugarcane is prevalent in the Monjolinho basin. The Frutal Basin, however, has sugarcane and pineapple cultivation areas. Natural or restored landscapes were considered in the Forestry use category, which has higher species density.

Although three categories were identified to apply the methodology proposed here, only two were considered. Thus, the "forestry" and "mixed farming" uses were united into a single use, designated "rural".

Mass balance and pollution generation coefficient: With the satellite images the land uses were classified and the mass balance methodology was applied to identify the diffuse pollution sections of each use. The mass balance conducted for each sampling point is represented by the general equation

$$C_i . Q_i = C_{i-1} . Q_{i-1} + (Y_{rural} . A_{rural,i} + Y_{urban} . A_{urban,i}) + error_i \qquad (1)$$

In the equation above the term C_i. Q_i is the load on the i-th collection point, which coincides with the discharge of the sub-basin in question. The term C_{i-1} . Q_{i-1} is the sum of all upstream loads of the sub-basin, that is, all loads entering the sub-basin. The terms Y_{rural} and Y_{urban} represent the specific rural and urban load generation coefficients, respectively. Lastly, the terms $A_{rural,i}$ and $A_{urban,i}$ are the urban and rural use areas, respectively, the sub-basin *i*.

For sub-basins with only one type of land use, the solution of this equation is simple, obtaining the unknown (Y) load generation. The sub-basins with two types of uses were grouped in pairs to solve a system of two equations. The criterion used to group the sub- basins in pairs was their similarity in terms of LULC. The result is a specific rural and urban load generation coefficient for each sub-basin. To calculate the average, only non-negative values found for Y were used, since negative values indicate no generation but rather a load consumption/sink. The coefficients can have seasonal variations, observed at locations where more than one collection was performed [25,26]. It can also have spatial variation, observed by comparing the different drainage basins.

To analyze the spatial variation of pollutant loads, the Monjolinho and Frutal catchments were subdivided, because some collection points were not located in the main river channel, but rather in one of its tributaries. The catchment area of the Canha River (CAN) does not have this division because all collection points were located along the main river channel. The Monjolinho drainage basin was subdivided in two ways: for the data of Pehovaz [26] it was separated in Gregório (GRA) and Monjolinho (MJA), where GRA is the sub-basin of MJA, and for the data of Zaffani [27], the Monjolinho drainage basin (MJB) was separated into the sub-basins of the rivers Santa Maria do Leme (SML), Mineirinho (MIN), Tijuco Preto (TPR) and Gregório (GRB). For Frutal the drainage basin was divided into the sub- basins Bebedouro (BEB), Frutal (CFR) and Frutal Urbano (FRU), where FRU is the sub- basin of CFR.

The rationale to apply this methodology includes: 1) the loads generated for each type of LULC can vary seasonally, but it is assumed that the generation rate is the same for this occupation throughout the drainage basin and over time; 2) the load rates are similar to increased areas over the left and right margin of the drainage basin and/or any pollution source located at a relative distance from the main channel; 3) in the case of negative mass balances, that is with load sinks, the hypothesis cannot be used to detect the load potential or the types of load degradation during transport. In this case, the longitudinal balance is estimated, without estimating the contributions of each use with the coefficients; 4) point- source loads that can influence the mass balance are disregarded because its precise definition is practically impossible with only the collection data.

Temporal variation of polluting loads: The temporal variation analysis of the production of diffuse loads was performed using qualitative and quantitative data collected in different seasons. In the works of Bottino [25] 4 campaigns were performed, with 3 campaigns in the dry season and 1 in the rainy season, and in Pehovaz [26], 3 in the rainy season and 1 the dry season. The data of Zaffani [27] were collected in the rainy season (January/2012), after 15 consecutive days of precipitation. The Frutal data were collected in September, characterized as the dry season (Figure 2).

Results and Discussion

Generation of pollutant loads in areas under different land uses

Figure 2 shows the percentage of each use in the sub-basins studied, and to facilitate interpreting the conditions of the drainage basins under study, the empirical data in this figure is as follows: the area, the number of nested catchments, the number of collections and weather conditions (Area/Nested Catchment/Samples-Weather Conditions). For example, the symbol "128/8/4-dddw" means a river catchment with drainage area of 128 km², using 8 NCE, during 4 seasonal experimental gauging, under three dry conditions (ddd) and under one wet conditions (w). Since the GRA and GRB catchments are identical, differing only in the number of sampling points, they were represented in this figure only as GR. The same is true for the Monjolinho drainage basin, represented by MJ. The BEB basin has the highest agricultural use rate, in addition to being the only one that has no urban use. The CAN basin is the most forested (82%), with reduced urbanization, around 1.5%. The CFR basin has a predominance of agricultural use, however the 10% of urbanization has profound effects on the water quality, as seen below. The FRU drainage basin refers to the portion of the Frutal basin located in the Frutal urban area, explaining the highest urban occupation rate (82%) when compared to other uses. The other catchments represented (SML, GR, MIN and TPR) belong to the Monjolinho drainage basin, in which most of it is predominantly for urban use. In these catchments the downstream regions are intensely urbanized and the upstream regions are used for agricultural and forestry activities, predominantly agricultural.

The comparison of the different areas shows different behaviors in the generation of specific loads (Table 2). The Frutal Basin has the highest average value for chlorophyll *a* (4693 g/yr/km²) and for DO (5365 kg/yr/km²). The highest mean values for the variables coliform

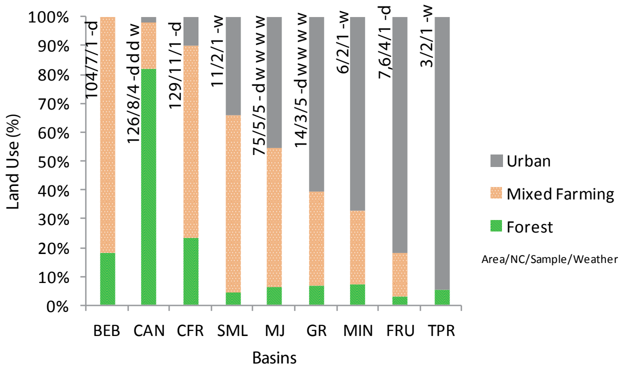

Figure 2: Land use and characterization of nested catchments

(5.18E+09 Most probable number - MPN/yr/km²), BOD (3731 kg/yr/km²) and nitrogen (17985 kg/yr/km²) were found for MJ. These values show the load differences due to the LULC in each catchment. The drainage basin with the predominant use of mixed farming (CAN), has the highest value for the variable total dissolved solids (8322 kg/yr/km²), explained by the non-impervious soil cover, which contributes to higher sediment loads transported to the river. As for the drainage basins with predominantly urban occupation, MJ showed higher values of variables associated with effluent discharge, such as total coliforms (5.18E+09 MPN/yr/km²), nitrogen (17985 kg/yr/km²) and $BOD_{5,20}$ (3731 kg/yr/km²).

For the variable DO, for example, the highest value found for the Canha river (13168 kg/yr/km²) was observed in rural areas, while for the Monjolinho basin the highest value refers to the urban area (14783 kg/yr/km²). Regarding the variable $BOD_{5,20}$, the highest value (26658 kg/yr/km²) was for the MJ basin, at an urban occupation point. When nested basins are studied, they are subject to scale effects and the influences that different land uses can have on the generation of pollutants. Therefore, a pollution generating coefficient for LULC can help to understand the dynamics of load generation and provide assistance to soil planning and managing water resources.

Signs of hydrological impacts resulting from land use changes

LULC changes are recognized as a relevant impact factor on water resources [1,31], including quality and quantity. These changes affect the flow dynamics and influence the generation of polluting loads. Diffuse and punctual pollution are the greatest sources of surface waters degradation [10,22,32-34]. The figures below show the differences in the generation of pollutant loads for NCEs. Figures 3 to 5 show the pollution produced for each of these areas that demonstrate the loads (kg/year) depending on the upstream drainage area (km²) of each point analyzed.

Observing the basins in question, we note the increase in $BOD_{5,20}$ upstream-downstream in all campaigns (Figure 3). Since the areas near the sources are covered by forest or native vegetation, it is concluded that LULC changes, due to agricultural or urban uses, have significant effects on the material generated that needs to be stabilized by aerobic organisms. The catchment of the Canha river, campaign 4 (CAN4), conducted in the rainy season, has the highest $BOD_{5,20}$ values (613917 kg/yr), while the smallest values can be seen in campaign 3 in CAN3 (10879 kg/yr), conducted in the dry season, autumn. The highest load recorded in Monjolinho (MJA2) was also observed in the rainy season, accounting for more than 1.4E+07 kg/yr).

The Canha drainage basin has a total area of 56 km² and mostly for forest use, and when the values obtained in this area are compared with data from another basin with forest and agricultural use (Canha Basin, with an area of 71 km²), a similar load generation behavior was observed in the variable $BOD_{5,20}$. In the Canha basin, the highest value obtained in the rainy season is of 54872 kg/yr, resembling that seen in the Canha basin in CAN4.

It can be observed that the $BOD_{5,20}$ values are in line with a well-defined range of values (548 ≤ DBO5,20 ≤ 6.14E+05 kg/yr/km²), and the increase tendency is of approximately 1450 km/yr/km². However, some drainage basins do not fit this pattern, such as GRA2, GRA3, GRA4, TPR and MJA2. The values located at these points vary between 63 and 1.56E+07kg/yr and are outside the range of the others in the area identified for the remaining ones. These results are due to unusual situations, and have to be individually analyzed case by case. The GRA series in collections 2, 3 and 4, are points out of the tendency range, showing high loads and confirming the influence of urbanization and seasonality on the generation of organic matter to be degraded in this drainage basin. In the case of the TPR basin, there is an increase approximately 12.5 times higher than the tendency, with values raging between 63 kg/yr and 2.52E+04 kg/yr. This is because this drainage basin is highly urbanized, which increases the generation of diffuse urban loads.

With regards to the MJA2 series, the condition of intense storm is highlighted, which influenced the generation of $BOD_{5,20}$ to a higher range than the tendency. Another indication of how seasonality influences the generation of pollutant loads is the behavior observed in MJA1, which shows an upstream to downstream load decrease. Comparing the MJA1 data with other MJA series showed that only in the first case, in the dry period, there was a downstream-upstream load decrease. However, there was an increase in the load generated for the other ones. Such behavior can be explained based on the seasonal influence, which increases the behavior uncertainty in terms of the polluting loads generated.

The MJB basin shows an increase about 6.2 times higher than the pattern from the second point shown in the graph, reaching the value of 3.41E+05 kg/yr. This is because, just upstream from this point, the river receives one of its tributaries, the river of the GRB drainage basin, which is intensely urbanized, causing this significant load increase in the river. The drainage basins TPR, SML, MIN and GRB are tributaries of MJB. In the basins TPR, MIN and GRB with significant urbanization rates, the load generation rates were higher than the tendency identified for $BOD_{5,20}$, with values of 18059 kg/yr/km², 7571 kg/yr/km² and 4336 kg/yr/km², respectively. However, the SML drainage basin, which has most of its territory occupied by agriculture, showed a rate of 512 kg/yr/km².

Chlorophyll *a* is a hydrobiological variable, characterized by a pigment responsible for photosynthesis. Chlorophyll *a* represents approximately 1% to 2% of the dry weight of planktonic algae, therefore an indicator of algal biomass or the trophic state of the aquatic environment [35].

Figure 4 shows a tendency pattern of increased loads of chlorophyll *a*, which is of approximately 0.39 kg/yr/km². Of the different campaigns in the Canha River, the highest load of chlorophyll *a* was for CAN1, in the upstream section (1.32 kg/yr) and in CAN4 in the downstream section (513 kg/yr). This result shows the influence of precipitation and runoff on the load generation of this variable, since the first CAN1 collection corresponds to the dry season and for CAN4 it corresponds to

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		DO	T. Coliforms	Chlorophyll	BOD	NTK	TSS
		(kg/yr/km²)	(MPN/yr/100L)	a (g/yr/km²)	(kg/yr/km²)	(kg/yr/km²)	(kg/yr/km²)
	Average Value	4502	-	1181	1806	1208	8322
	Standard Deviation	3320	-	1324	1911	665	10063
CANHA	Median	3374	-	500	900	925	4500
	Min	1252	-	100	100	400	1000
	Max	13168	-	5500	8000	3250	39000
	Average Value	5191	5.18E+09	-	3731	17985	55
	Standard Deviation	2864	2.24E+10	-	6065	15885	32
MJ	Median	5205	3.46E+07	-	1701	11342	48
	Min	0	0.00E+00	-	0	83	0
	Max	14783	1.03E+11		26658	41684	111
	Average Value	5365	8.19E+04	4693	-	-	-
	Standard Deviation	8567	1.11E+04	11302	-	-	-
FRUTAL	Median	2547	9.83E+02	983	-	-	-
	Min	0	3.62E+01	36	-	-	-
	Max	36709	5.51E+04	55077	-	-	-

Table 2: Polluting loads observed in the experimental basins

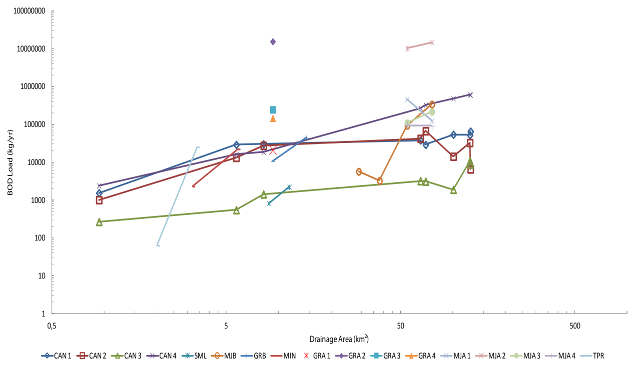

Figure 3: BOD5,20 load related to the drainage area

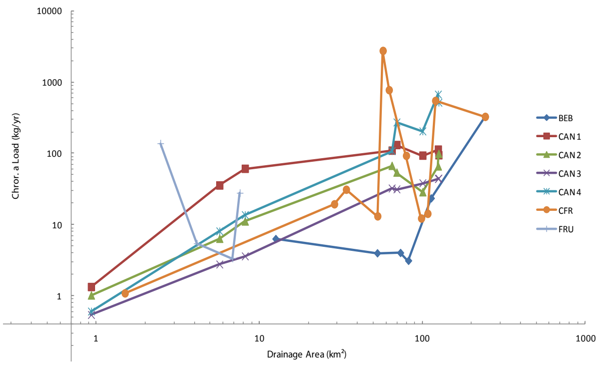

Figure 4: Chlorophyll *a* load related to the catchment area

the rainy season. The downstream region of that basin is characterized by the presence of urban centers, contributing to the entry of nutrients that favor the development of algae. A change in the load behavior is clearly observed from the fourth point of the analysis in the CAN series. In the campaigns CAN1 and CAN4 there is an increase after point 4 and later, after point 6. The production of diffuse loads from rural land use is evident in the fourth collection of this drainage basin (CAN4), showing a load increase of chlorophyll *a* between collection points 4 and 5. There is a significant percentage increase in the soil covered by agricultural use between these points, and the fourth collection was the only one performed in the rainy season, enabling to clearly observe this phenomenon, not seen in the collections performed in the dry season.

The analysis of chlorophyll *a* in the CFR section, which is under the influence of the urban area, corroborates the influence of urbanization. In this section, there was a significant chlorophyll *a* load increase (from 13 kg/yr to 2738 kg/yr) at the point located downstream of the sewage treatment plant, which due to operational problems discharges much of the untreated waste into the watercourse. The increased amount of nitrogen and phosphorous in the sewer increases the trophic level of that water environment, hence increasing the algae population and consequently increasing the load of chlorophyll *a*. In this section, the increase tendency is 1700 times higher than the average, which indicates that it is probably point source pollution, and not diffuse pollution. In the FRU urban stretch, there is an upstream- downstream reduction. However, in the final stretch between the last two points, there is a chlorophyll *a* load increase (from 3 kg/yr to 27 kg/yr). This behavior can be explained by analyzing the load of total coliforms, which also increased, indicating the entry of point source pollution that contributes to the entry of nutrients into the watercourse. The high chlorophyll *a* value in the starting point of FRU (136 kg/yr) can be attributed to the area's declivity, which favors the supply of nutrients to the channel.

Despite the obvious influence of urban areas, observing the BEB section that exhibits agricultural and forestry use, an increase in chlorophyll *a* load is also noticed in the downstream direction (from 6 kg/yr to 23 kg/yr). However, the values observed for the loads of that variable are lower than those observed for the urban areas, and that is probably because in rural areas there is a lower input of nutrients, which promotes the growth of aquatic photosynthetic organisms [35,36].

The graphic related to chlorophyll *a* indicates an increase in the

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uncertainty of the relationship between the load generated and its catchment area. This uncertainty can be associated with the influence land use has on the load generation of this variable. In places with higher drainage areas there is greater LULC changes, and therefore different factors that contribute to calculating chlorophyll *a*.

Figure 5 shows the data distribution results for total coliforms, which indicates greater data reliability. The average load generation for this variable is of 3.74E+06 MPN/yr/km². The TPR drainage basin exhibits the highest rate of the sections analyzed (1.04E+05 MPN/yr/km²), this is also the area that has the highest degree of urbanization, explaining the highest generation of coliforms in the receiving body. Despite the apparent change along the CFR stretch, it has the lowest pollutant generation rate, corresponding to 1.12E+04 MPN/yr/km².

The analysis of total coliforms shows the high load values (between 4.71E+03 MPN/yr and 9.02E+08 MPN/yr) for catchments with smaller drainage areas (between 2 km² and 14km²) such as TPR, MIN, FRU, GRB and SML. These catchment areas have intense urbanization, therefore the high total coliform values can be explained by the entry of loads from human activities. In the catchments with larger drainage areas and greater number of sampling points, such as BEB and CFR, there was a load increase in the upstream-downstream direction (6.76E+03 MPN/yr to 2.70E+06 MPN/yr and, 5.83E+02 MPN/yr to 2.70E+06 MPN/yr, respectively), and in the CFR stretch the higher loads are because this section is under the influence of the urban area.

The Canha basin shows occupation characteristics similar to that observed in BEB, mainly with agricultural and forestry use. This drainage basin also has increased upstream- downstream coliform loads, with values ranging between 9.54E+02 MPN/yr and 1.02E+04 MPN/yr. As in BEB, the values are smaller than in CRF due to the occupation characteristic of the basin. The values observed in the Canha basin are within the combined results of the three drainage basins analyzed.

The SML catchment exhibits a different behavior from the others, since besides having the greatest amount of upstream total coliforms, there is a reduction in the load of this variable from upstream to downstream (9.02E+08 MPN/yr to 9.18E+05 MPN/yr). The value measured in the area near the source is 982 times higher than that measured downstream. In the upstream region the use is predominantly agricultural, and activities related to this use, such as soil movement, can favor the entry of large amounts of sediments that carry total coliforms. Another factor that may have influenced this value is the precipitation of the previous days, contributing to soil leaching and material containing coliform transported to the channel. In the UK, despite improvements in the wastewater treatment system, it was found that the coliform values higher than that allowed still occur, attributed to the flow generated in agricultural areas during precipitation events [37-39].

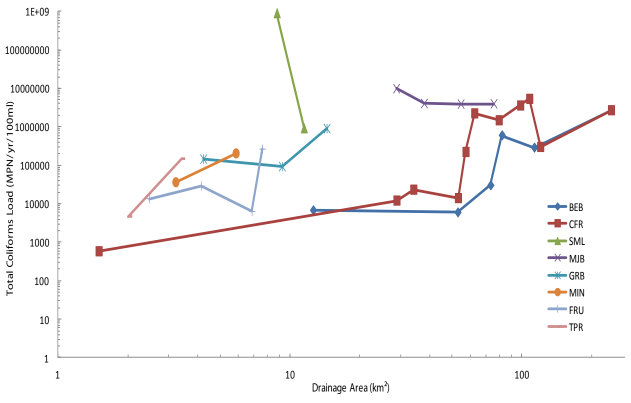

Figure 5: Total coliform loads related to the catchment area

In the FRU drainage basin the same behavior previously described for the variable chlorophyll *a* is also observed. At the third point of the urban area there is a decrease of coliform loads, with a subsequent increase at the last point, which may be due to the influence of more intense urbanization downstream of the basin.

Mass balance applied to reduce uncertainties in the generation of diffuse pollution

Table 3 shows the application of the mass balance methodology to look for patterns in pollution generation, resulting in the specific load generation coefficients (Y). The average value of the coefficients were calculated considering different amounts of data, since in some cases the values were negative, which does not characterize pollutant generation.

With regard to generating $BOD_{5,20}$ loads, in the CAN basin the mean generation coefficient in the urban area (Yurb) has a value almost 20 times higher than the coefficient in the rural area (Yrural) of the same field campaign. The analysis of the seasonal variation of the coefficients found shows that the MJA basin, the Yrural found in the rainy season (campaign 2), is about 105 times higher than in the dry season. However, in CAN the rural use coefficient in the rainy season (campaign 4) has a value close to that observed in campaign 2, in the dry period,

6726 kg/yr/km² and 6065 kg/yr/km², respectively. The comparison between the urban (Yurb) and rural (Yrural) coefficients was conducted by setting up two groups "A" and "B". The first one includes situations in which Yrural was greater than Yurb; and for "B" Yurb is greater than Yrural. The last column of the tables below show that most of the drainage basins analyzed exhibit Yurb greater than Yrural, thus classified as "B". However, it can be seen that a basin can have a different behavior depending on the variable in question. The MJB basin is classified as A in relation to $BOD_{5,20}$ and Total coliforms, but fits in B when it regards DO.

The pollution generation coefficients obtained in the NCEs analyzed showed no pattern or tendency behavior for the areas and variables studied. It was observed that in many nested catchments in CAN, MJA, MJB, BEB and CFR there is some type of sink load that is not accounted for with the methodology used. In some NCEs the output load was higher than the balance that determined the inputs and production by the land uses. According to Hannah et al. [17], what was observed as discharge in the NCEs is the result of integrating inputs in the drainage basins and storage and transfer processes. Thus, the different coefficients for similar conditions in one NCE confirms the hypothesis of Rothwell et al. [22], that for variables influenced by point sources, it is difficult to find patterns and trends taking into consideration only the drainage basin's characteristics. Thus, the mass balance based on the qualitative and quantitative data measured in the water body without monitoring and determining the punctual entries and the depuration of pollutant loads is a limitation of the methodology used. Considering the interaction that takes place between different processes in the natural environment, another possibility for the different coefficients found is the occurrence of synergism or antagonism in these processes [40].

BOD							
NCE (Forest -Farm -Urban)	**Nº of Data**	**Average Yrural (kg/yr/km²)**	**Yrural [min-max]**	**Nº of Data**	**Average Yurb (kg/yr/km²)**	**Yurban [min-max]**	**Type ratios Y's**
MJB (6,2% - 48,2% - 45,6%)	4	90 793	[8 853 - 172 732]	12	28 246	[667 - 215 421]	A
MJA (6,2% - 48,2% - 45,6%)	*	-	-	2	20 884	[20 884 - 20 884]	A
	2	12 183 875	[12 183 875 - 12 183 875]	*	-	-	
	2	199 075	[199 075 - 199 075]	*	-	-	
	2	115 911	[115 911 - 115 911]	*	-	-	
CAN (82,2% - 16,1% - 1,7%)	5	1 772	[138 - 5 785]	2	34 770	[34 770 - 34 770]	B
	7	6 065	[258 - 13 671]	*	-	-	
	6	627	[31 - 1 515]	*	-	-	
	8	6 726	[1 007 - 12 672]	*	-	-	
DO							
NCE (Forest -Farm -Urban)	**Nº of Data**	**Average Yrural (kg/yr/km²)**	**Yrural [min-max]**	**Nº of Data**	**Average Yurb (kg/yr/km²)**	**Yurban [min-max]**	**Type ratios Y's**
BEB (20,8% - 79,2% - 0,0%)	11	6 760	[695 - 25 016]	2	7 538	[7 538 - 7 538]	B
CFR (25,4% - 63,0% - 11,6%)							
MJB (6,2% - 48,2% - 45,6%)	6	29 423	[2 143 - 68 463]	11	34 573	[7 140 - 66 699]	B
MJA (6,2% - 48,2% - 45,6%)	*	-	-	3	9 445	[885 - 13 725]	A
	2	1 299 329	[1 299 329 - 1 299 329]	*	-	-	
	*	-	-	3	7 934	[5 491 - 9 156]	
	*	-	-	3	10 747	[10 093 - 12 057]	
CAN (82,2% - 16,1% - 1,7%)	8	3 887	[271 - 14 994]	0	-	-	A
	8	5 955	[714 - 12 512]	*	-	-	
	7	2 294	[1 279 - 3 747]	*	-	-	
	8	20 679	[1 592 - 54 918]	*	-	-	
CHLOROPHYLL-*a*							
NCE (Forest -Farm -Urban)	**Nº of Data**	**Average Yrural (kg/yr/km²)**	**Yrural [min-max]**	**Nº of Data**	**Average Yurb (kg/yr/km²)**	**Yurban [min-max]**	**Type ratios Y's**
BEB (20,8% - 79,2% - 0,0%)	10	1	[0,04 - 2,9]	3	7 838	[32 - 11 741]	B
CFR (25,4% - 63,0% - 11,6%)							
CAN (82,2% - 16,1% - 1,7%)	7	6,4	[0,9 - 10,2]	*	-	-	B
	4	1,3	[1,0 - 1,9]	2	84	[84 - 84]	
	7	0,9	[0,04 - 2,9]	2	2	[2,0 - 2,0]	
	7	34,9	[0,6 - 101]	*	-	-	
TOTAL COLIFORMES							
NCE (Forest -Farm -Urban)	**Nº of Data**	**Average Yrural (MPN/yr/100ml)**	**Yrural [min-max]**	**Nº of Data**	**Average Yurb (MPN/yr/100ml)**	**Yurban [min-max]**	**Type ratios Y's**
BEB (20,8% - 79,2% - 0,0%)	19	25	[0,14 - 222]	4	529	[9 - 883]	B
CFR (25,4% - 63,0% - 11,6%)							
MJB (6,2% - 48,2% - 45,6%)	2	927 855	[927 855 - 927 855]	11	177 913	[7 - 975 892]	A

Legend: *mass balance equation not applied

Table 3: Estimated pollution generation coefficients (Y's) based on the mass balance of nested catchments

The variable $BOD_{5,20}$, for example, shows the relationship of synergy with the presence of heavy metals in the water, in other words, the presence of metals has an inhibitory effect on the $BOD_{5,20}$, which influences the measurement.

Since the study of nested catchments is limited by the variation of input and generation of pollutants in the drainage basins [41], it was decided to calculate the pollution generation coefficient in the headwater catchment of the Canha river. Because it is a headwater catchment and as it does not receive upstream contribution, the pollutant load measured in the mouth of the basin refers exclusively to the load generated within it. As the land use in this drainage basin is exclusively rural and considering the different collections performed in this area of 0.93 km², it is expected that the pollution generation coefficient (Y) is the same in different events. However, Table 4 shows that the coefficients obtained were different. It is observed that even for collections in the dry season (1, 2 and 3), the coefficients found range between 288 kg/yr/km² and 1662 kg/yr/km², showing a variation that is 7 times the value of the concentration of $BOD_{5,20}$ in the same sampling point, while for the variable chlorophyll *a* there is variation of up to 3 times, with values between 1.09 kg/yr/km² and 2.88 kg/yr/km². The values found in the rainy campaign (4) are even higher, 2577 kg/yr/km² for $BOD_{5,20}$ and 0.64 kg/yr/km² for chlorophyll *a*. The causes behind the coefficient variation are the river flow measurements and the concentration of the variables in question.

Moreover, the climate variations in the different collection sites can influence the final result, reinforcing the idea that despite numerous studies and efforts in understanding the factors that influence the hydrological processes, there are still challenges when addressing the uncertainties of that relationship [42-44].

Conclusions

Catchments under LULC are more vulnerable to conditions of increased pollutant loads and biodiversity loss due to the geomorphological changes that take place when the occupation site undergoes adaptation. The analysis of the experimental data, together with the assessment of the characteristics of the nested catchments in question indicate upstream-downstream degradation in the three rivers analyzed. Although the generation of higher flow and pollutant loads in urban areas is due to the intense changes in these areas, reduced quality was also observed in the rural areas. Given the negative impacts due to different land uses, the mass balance methodology was proposed in order to look for pollution generation coefficients for each land use. Determining a coefficient associated with each use can help to better understand the factors involved in the generation of pollution, thus assists in the management and planning of water resources in areas that exhibit the same characteristics. However, there were limitations in the application of this method to identify the pollution generating coefficients. For this methodology to be effective, we suggest greater control in the identification and/or correction of the agricultural activities prior to the collections, rainfall variations and other factors. Furthermore, a large number of samples under different climatic conditions, as heavily dry or wet season, can favor the identification of a tendency or pattern in the generation of diffuse loads. So, it is important to increase the number of continuous monitoring points and set a data basis. Lastly, it was noted that the presence of sinks and pollution sources have significant limiting effect on the effectiveness of the proposed methodology. Thus, if these variables are identifiable and quantifiable, it is suggested to incorporate them in the mass balance.

Acknowledgements

This work is partially granted by HidroEX/FAPEMIG (17.049/2011), FAPESP (2012/22013-4); CNPq 307637/2012-3.

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Campaigns	Flow	BOD			Chlorophyll a		
		C (mg/L)	Load (kg/ano)	YY (kg/yr/km²)	C (mg/L)	Load (kg/ano)	Y (kg/yr/km²)
1	0,01	3,5	1545	1662	0,03	1,32	1,42
2	0,02	2	1009	1085	0,02	1,01	1,09
3	0,02	0,5	268	288	0,01	2,68	2,88
4	0,02	4	2397	2577	0,05	0,6	0,64

Table 4: Estimates of seasonal pollutant loads in the catchment of the river Canha

Citation: Zaffani AG, Cruz NR, Taffarello D, Mendiondo EM (2015) Uncertainties in the Generation of Pollutant Loads in Brazilian Nested Catchment Experiments under Progressive Change of Land Use and Land Cover. J Phys Chem Biophys 5: 173. doi:10.4173/2161-0398.1000173

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