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Effects of land use on water chemistry and macroinvertebrates in two streams of the Piracicaba river basin, south-east Brazil

JEAN PIERRE H. B. OMETO*, LUIZ A. MARTINELLI*, MARIA VICTORIA BALLESTER†, ALAÍDES GESSNER*, ALEX V. KRUSCHE*, REYNALDO L. VICTORIA* AND MICHAEL WILLIAMS*
**CENA, Av. Centenário 303, Piracicaba-SP, 13416–000, Brazil*
†Universidade Federal de São Carlos, São Carlos-SP, Brazil

SUMMARY

1. Several studies have shown that land use has a strong influence on river chemistry and its biotic components. Most of these studies focused on nitrogen in temperate American and European catchments. Much less is known about the relationship between stream conditions and land use in tropical areas of developing countries.
2. Besides climate, there are three important differences between attributes of temperate and tropical catchments: non-point sources are the dominant contributor of pollution in USA, whereas point source pollution is the most important in our study; use of fertilizer is much smaller in developing countries, and the type of agriculture and management practices are distinct.
3. We test whether the chemical composition of streams and their macroinvertebrate communities can be related to land use. Accordingly, we compared the variability of chemical composition and macroinvertebrate communities in the streams of two catchments (Pisca and Cabras) belonging to the same ecoregion, but having different types of land use.
4. The main land use in the Pisca catchment in 1993 was sugar cane (62%), followed by pasture (22%) and urban centres (10%). In contrast, the main land use in the Cabras catchment was pasture (60%), followed by annual crops (13%) and forest (10%); urban centres occupied only 2% of the catchment.
5. In the Cabras catchment, most of the parameters correlated with a land use index (LUI) (Fig. 2). However, only conductivity, major cations and major anions (with exception of sulfate) had a statistically significant correlation coefficient. More than 90% of the variance was explained for these parameters. DIC, NO_3 and richness of invertebrates (RI) also strongly correlated with LUI (R^2 = 0.75), although these correlation coefficients were not significant. Total suspended solids (TSS) had a significant correlation with LUI (R^2 = 0.98), but, the correlation was inverse. In the Pisca catchment, conductivity, major cations (with exception of potassium), major anions, and DIC, DO, and DOC had a strong and statistically significant correlation with LUI. Correlation coefficients were also high for respiration rate, although the correlation was not statistically significant.

Keywords: land use, pollution, water chemistry, macroinvertebrate, streams, Piracicaba, Brazil

Introduction

Several studies have shown that land use has a strong influence on river chemistry (e.g. Peierls *et al*., 1991; Hunsaker & Levine, 1995; Puckett, 1995; Howarth *et al*., 1996; Allan *et al*., 1997), and its biotic compo-

Correspondence: Jean Pierre H.B. Ometo, CENA, Av. Centenário 303, Piracicaba-SP, 13416-000, Brazil.
E-mail: zebu@cena.usp.br

nents (e.g. Allan & Flecker, 1993; Richards *et al*., 1996). For instance, total N and nitrate concentrations were well correlated with the percentage of cropland in catchments of the Coastal Plain of Chesapeake Bay (Jordan *et al*., 1997). Regarding habitat quality and biotic integrity, agricultural land area was considered the best predictor of these attributes in the Rasin River in south-eastern Michigan (Allan *et al*., 1997).

Many of these studies focused on nitrogen and phosphorus, and were conducted in developed countries mostly under temperate conditions (American and European catchments) (Vitousek *et al*., 1997). Much less is known about the relationship between stream conditions and land use in tropical areas of developing countries. Besides climate, there are three important distinctions between attributes of temperate and tropical catchments: (1) although point source pollution is still important in some regions of developed countries, like the north-east region of the United States, non-point sources are the dominant contributor of pollution (Newman, 1995; Puckett, 1995). In most developing countries like Brazil, point source pollution, mainly through urban sewage, has the strongest impact in rivers and streams (São Paulo, 1991). (2) The use of fertilizer is much smaller in developing countries than in developed countries. For example, several agricultural crops in Brazil receive less fertilizer than they need; therefore, they are net sinks of nutrients like N, P and K (T. Yamada, personal communication). In contrast, in developed countries like the United States, agricultural fields are net sources of nutrients (Puckett, 1995; Carpenter *et al*., 1998). (3) The crops cultivated and the management practices are distinctly different between tropical developing countries compared to temperate developed countries.

Like nearly half of the states in the USA (Pelley, 1997), the state of São Paulo approved a law in 1991 recognizing river basins as physical entities for planning and management, in an attempt to promote better management of its water resources and reverse their progressive deterioration. One of the first steps towards better water management is to establish in our study the impacts of different land uses to streams and rivers. This kind of investigation, relating environmental attributes, such as land-use, with water quality and biological communities, can be used to better protect water resources and is a requirement to achieve holistic assessments of river conditions, current denominated 'river health' (e.g. Fairweather, 1999; Norris & Thoms, 1999).

In this study, we propose to test whether the chemical composition of streams and their macroinvertebrate communities can be related to land use, as in temperate developed countries. In order to test this, we compared the variability of chemical composition and macroinvertebrate communities along streams of catchments belonging to the same ecoregion, but having different land uses.

Methods

Study area

Both catchments (Cabras and Pisca) are located in the Piracicaba River basin, which is a 12400-km^2 basin located in the state of São Paulo, south-east region of Brazil (Fig. 1). Detailed information about the Piracicaba River basin can be found elsewhere (Krusche *et al*., 1997; Moraes *et al*., 1998; Martinelli *et al*., 1999).

Table 1 Characteristics of the channel and topographical characteristics of the subcatchments of the Cabras and Pisca catchment

Sampling station	Length (km)	Channel average width (m)	Channel average depth	Drainage area (km^2)	Average altitude (m)
P1	6.5	2.0	0.5	19	587
P2	1.8	4.0	1.0	19	593
P3	2.0	5.8	0.7	57	591
P4	4.0	3.5	1.3	10	572
P5	7.2	6.0	4.3	25	571
Catchment	21.5	0.9	1.0	130	583
C1	5.0	2.0	0.3	11	925
C2	5.2	3.0	0.7	13	861
C3	8.8	2.7	1.0	19	768
C4	1.7	3.5	1.2	11	762
Catchment	20.7	2.8	0.8	54	829

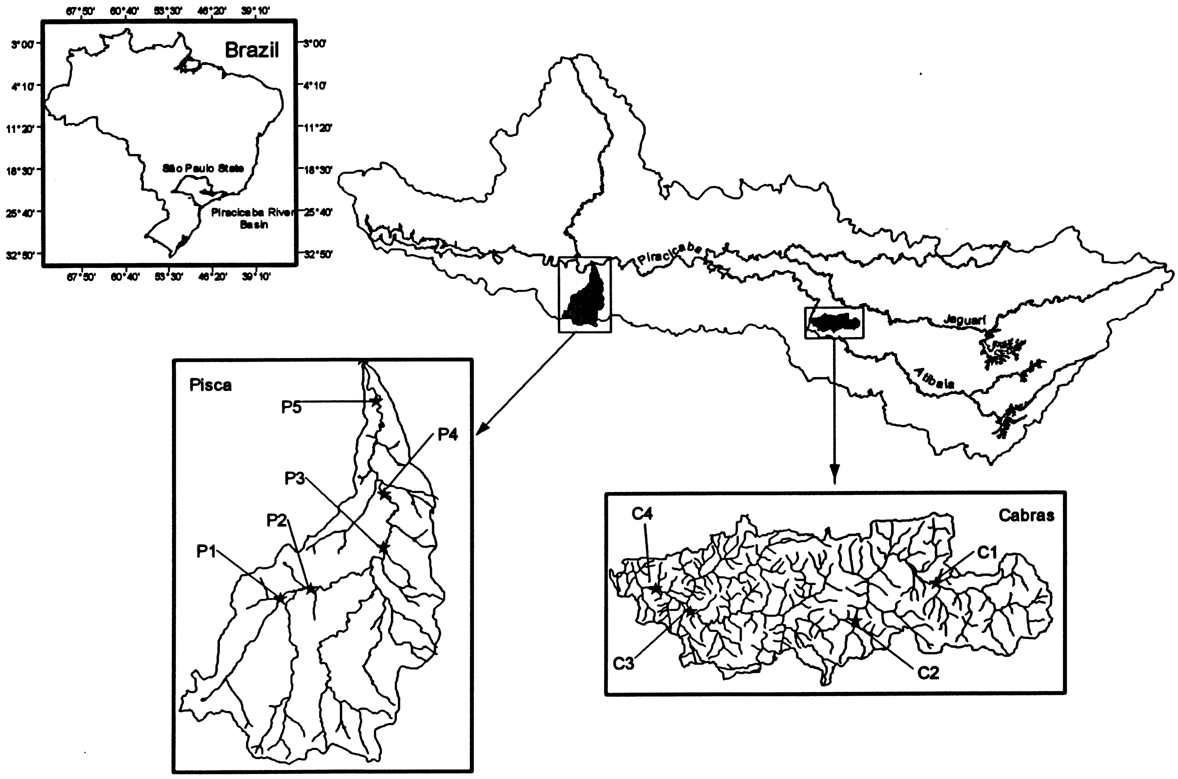

Fig. 1 Location of Pisca and Cabras catchments and sampling sites in Brazil.

The Cabras stream is a tributary of the Atibaia River (a main river of the Piracicaba basin); its catchment has an area of ≈ 50 km^2, an average altitude of 830 m, and is located in the less polluted region of the basin. The Pisca catchment has an area of nearly 130 km^2 with an average altitude of 580 m (Table 1). Its main stream is a tributary of the Piracicaba River and this catchment is located in the most polluted region of the basin. The dominant soil types in each catchment are Ultisols and Oxisols (weathered tropical soils). The average annual precipitation in the Cabras and Pisca catchments is about 1400 mm. The wet season occurs between October and March, while dry season occurs from April to September. The Cabras and the Pisca catchments were divided in 4 and 5 subcatchments, respectively, and a sampling site was placed in the downstrem end of each subcatchment. The channel and topographic characteristics of each subbasin are in Table 1.

Both catchments have a similar historical land use. Both were deforested after 1850 and coffee plantations replaced the forest. In the Pisca catchment, coffee was replaced by sugar cane in the second decade of this century. On the other hand, in the Cabras catchment, coffee was replaced by pasture, mainly in the 1960s though today there are still remnants of these coffee plantations in some areas of the catchment.

From February 1997 to July 1998, a total of 28 water samples were collected at each of five sites along the Pisca stream and a total of 19 water samples were collected at each of 4 sites along the Cabras stream (Fig. 1). Water samples for determination of sediment concentration, and respiration rates were collected only in three sites in the Pisca (P1, P3, and P5), and in the Cabras (C1, C2, and C3) catchments. Water samples for chemical analysis were collected from the surface and in the middle of the channel using a Niskin bottle. Samples were filtered after collection through precombusted glass-fiber filters for DOC analysis and cellulose acetate (nominal pore size of 0.45 μm, type GF/F) for inorganic analysis. In the field, pH was measured with an Orion 250A meter, conductivity with an Amber Science 2052 meter, and dissolved oxygen and temperature with an Yellow Springs 58 meter. For the determination of respiration rates (expressed as μM h^{-1}) six 350 mL glass-stoppered BOD bottles were filled in the field. Three bottles (controls) were immediately preserved and the other three were incubated in the dark for 2–6 h at ambient temperatures. Subsequently, incubated bottles were preserved and oxygen concentrations determined by Winkler titration within 1 h. Respiration rates were calculated as the average difference in O_2 concentrations between incubated and control bottles (zero time oxygen).

Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) were determined with a Shimadzu TOC-5000A (Skirrow, 1975). Alkalinity (Alc) was determined by micro-Gran tritation. Nitrate, sulphate and chloride were determined within 6 h of sample collection using an ion chromatograph model Shimadzu LC-10AD. Aliquots were preserved with $HgCl_2$ (50 μM) for later analysis of calcium, magnesium, sodium, potassium and ammonium by ICP-AES (Jarrel-Ash Atomcomp, model 975).

Water samples for total suspended solids (TSS) were collected in the middle of the channel with a depth-integrating sampler. After homogenization through a US Geological Survey splitter, 1–2 L of water was collected for TSS determination. In the laboratory, 0.5–1.0 L of water was passed through a preweighed filter. After drying the filter to a constant weight, sediment concentration was determined gravimetrically.

Macroinvertebrates were surveyed in sites P1, P3 and P5, and sites C1 to C3, at the Pisca and Cabras catchments, respectively, in the months of March, June, September and December 1997, and March 1998. The macroinvertebrates were collected using a D-frame (Merrit & Cummins, 1984) aquatic net (250 μm) to sample an approximately one square meter area from three depositional habitats in each sampling site. The pools were never deeper than 50 cm. The three collections were combined into a single collection. The samples were washed in the field and taken to the laboratory for final sorting procedures. All the individuals collected were identified and counted. The insects were dominant, and the level of taxonomic identification achieved was to Family for most individuals, and Subfamily for *Chironomide.* Non-insects were mostly identified to Order and Class.

The depositional areas were chosen for sampling in each site because they were common at all study sites, consequently comparisons between sites were easier to make. In addition, the D frame sampler was easier to handle in such areas, avoiding escape of animals. However, it should be noted that pools can present a degraded system due to sediment loading, but they can provide richer information than a riffle environment (Fore *et al*., 1996).

The increasing interest for qualitative approaches to macroinvertebrate studies in water quality monitoring programs (Resh & Jackson, 1993) support our choice for the sampling protocol adopted in this work. In our region there is no index correlating the macroinvertebrate communities and the local environment, or any water-quality index using benthic fauna. Consequently we used the richness index by Margalef (1982), defined as:

$$RI = \frac{NT - 1}{\ln(NO)}$$

where, RI is the richness index, NT is the number of taxa, and NO the number of organisms.

We performed spatial analysis on data compiled as layers in Arc-Info GIS. For this analysis we used the following data layers: (1) elevation, derived from a 20-m vertical resolution digital elevation model (DEM) obtained from the Brazilian Institute of Geography and Statistics (IBGE); (2) river network derived from 1 : 50000 maps from IBGE, and (3) land use/cover data sets for the study area obtained from aerial photographs from 1993. The mapping scale for these data was 1 : 25000, with a minimum lateral dimension of 150 m. Nine classes were identified: forests, wetlands sugarcane, pasture, silviculture, citrus, annual and perennial crops, and urbanization. The remaining area was classified as 'other uses'.

In order to statistically correlate river water chemistry and macroinvertebrate richness with land use, we developed a landscape metric, called land use index (LUI). This index is the sum of the weighted percentage area occupied by the most important land

Table 2 Land use types and weight of each land use type used to calculate the land use index

Land use	Weight
Forest	0
Wetlands	0
Perennial	0.15
Citrus	0.15
Pasture	0.20
Annual	0.25
Silviculture	0.30
Sugar cane	0.50
Urban	5.00

use types in the subcatchments in relation to the total subcatchments areas. The LUI's are cumulative values, which means that LUI for a donwstream site S_I is the sum of the LUI of subcatchment S_I plus the LUI of the upstream subcatchments. The weight of each land use type (Table 2) is an arbitrary value given by us based on two criteria: (1) we considered that point source pollution caused by domestic sewage is the most influential type of pollution, since only 10% of sewage has been treated in the Piracicaba River basin. Urban sewage plus industrial effluents dumped into the rivers of the Piracicaba basin was estimated as ≈ 170 tBOD day^{-1}, while the loading generated by diffuse runoff from agricultural fields was estimated as only 20 tBOD day^{-1} (São Paulo, 1994). As the population density for small catchments like Cabras and Pisca is not available, we chose to use the extent of urban area to estimate the LUI, assuming that the populational density is not significantly different between the urban areas of the two catchments (Brasil, 1991). In order to check if the calculated LUI was correctly describing the landscape composition, it was correlated with the landscape metric dominance. Dominance metric has been used as a landscape diversity measurement because it determinates the equality of the portion of types of land cover in the landscape. High dominance indicates that few land cover types dominate the landscape. On the contrary, low dominance indicates that several land cover types have nearly equal proportions in the landscape (O'Neill *et al*., 1988; Turner *et al*., 1989). Lower values of dominance were associated with higher LUI values (R^2 = 0.98 for Pisca Creek and R^2 = 0.88 for Cabras Creek) (2) we ranked the aggressiveness of the agricultural practices as a function of soil losses using the Universal Soil Losses Equation and GIS techniques (C.E. Cerri, unpublished data). Hence, land use impact is proportional to rank (Table 2).

Correlation analyses were used to investigate interactions between water chemistry and macroinvertebrate richness with downstream distance and LUI. Sampling water along rivers implies that downstream water composition is dependent of upstream water composition. Therefore, in such cases, parametric statistics can not be used (Motulsky, 1995). For this reason, we choosed to use Spearman rank correlation, which is a non-parametric test equivalent to Pearson parameteric correlation (Motulsky, 1995). Differences between catchments were tested by grouping all variables together, regardless sampling site position along the streams, using Mann–Whitney, also a non-parametric test, which is equivalent to unpaired *t* parametric test (Motulsky, 1995).

Results

Land use

Sugar cane covered ≈ 62% of the total area in the Pisca catchment, being considered the most important land use type (Table 3). Among the subcatchments, P5 had the smallest area covered with sugar cane and the largest urbanized area. Pasture occupied the second largest area in the Pisca catchment. However, the area occupied by pasture was more variable between subcatchments than sugar cane (Table 3).

In the Cabras catchment, pasture was the main land use type, covering ≈ 60% of this catchment in 1993. There was not a single second largest land use.

Table 3 Size of the area (%) in 1993 under different land uses in the Pisca (P1 – P5) and Cabras (C1 – C4) subcatchments and whole catchment. The size of the area of the whole catchment (%) was estimated by the sum of the weighted percentage area occupied by the most important land use types in each subcatchments

	P1	P2	P3	P4	P5	Whole catch.	C1	C2	C3	C4	Whole catch.
Forest	3.5	2.2	3.0	8.8	5.8	4.0	8.7	10.8	8.4	9.3	9.0
Wetland	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Perennial	0.4	0.4	0.2	0.0	0.0	0.2	4.4	6.7	9.4	13.2	8.6
Citrus	0.1	0.3	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Pasture	14.5	15.7	21.0	10.4	39.0	21.9	58.7	62.0	60.9	56.5	58.9
Annual	0.0	0.7	0.5	0.0	0.2	0.4	12.5	12.1	13.8	14.9	14.1
Silviculture	0.1	0.3	1.6	9.8	0.1	1.5	14.6	6.9	5.8	4.2	7.8
Sugar cane	78.3	71.3	71.5	64.2	18.9	61.9	0.0	0.0	0.0	0.0	0.0
Urban	2.9	9.1	1.9	6.4	36.1	10.0	1.1	1.4	1.6	2.0	1.5

Table 4. Land use area index (LUI) for 1993, macroinvertebrates richness index (RI), and average concentration of parameters of the Cabras (C) and Pisca (P) sampling sites. *N* – number of samples, DO – dissolved oxygen, *R* – respiration rate, DOC – dissolved organic carbon, alc – alkalinity, DIC – dissolved inorganic carbon, TSS – total suspended solids

Sampling site	C1	C2	C3	C4	P1	P2	P3	P4	P5
Downriver distance (km)	0	5.2	14.0	15.6	0	1.8	3.9	7.9	15.0
LUI	25	44	64	84	56	140	190	259	454
RI	3.1	3.1	2.9		2.3		3.0		0.2
N	19	19	19	19	28	28	28	28	28
Con (μS cm^{-1})	55.5	56.3	72.5	81.6	81.6	153.2	163.5	182.2	272.8
DO (mg L^{-1})	7.9	9.1	8.6	7.7	7.8	6.6	7.2	4.8	2.1
R (μg L^{-1} h^{-1})	8.1	16.1	12.9		6.6		12.2		660.2
DOC (mg L^{-1})	2.6	2.9	3.0	2.9	3.9	5.3	4.4	5.1	10.5
alc (μM)	422.2	429.0	576.9	637.1	728.9	1216.0	1193.6	1351.8	1858.5
DIC (μM)	453.8	413.9	542.9	598.9	657.8	991.0	1051.9	1192.9	1636.4
NH_4 (μM)	0.0	15.8	10.5	12.0	0.0	2.5	5.0	67.9	331.0
NO_3 (μM)	32.0	51.1	69.3	62.2	5.65	10.0	27.3	37.0	17.5
SO_4 (μM)	8.9	7.1	9.3	12.3	36.6	91.2	96.0	89.1	191.8
Cl (μM)	55.5	64.3	71.2	84.3	87.3	172.8	138.8	138.1	143.7
Na (μM)	168.0	161.9	201.5	239.2	136.0	273.5	346.1	385.0	766.2
Ca (μM)	79.4	85.9	110.7	125.3	192.6	335.9	334.0	347.9	398.1
Mg (μM)	54.3	60.6	79.4	88.9	132.7	230.7	270.7	279.5	305.0
TSS (mg L^{-1})	59.4	37.0	34.2		50.6		26.8		55.0

Annual and perennials crop, and silviculture were the second most important types of land use. Sugar cane was virtually absent in this catchment and the area covered by forest was twice as large as in the Pisca catchment. Urban centres covered a maximum of 2% in the Cabras subcatchment (Table 3).

Chemical composition

Average solute concentrations were higher in the Pisca than in the Cabras catchment (Table 4). This difference was statistically significant for NO_3, DO, DOC, DIC, alc, SO_4, Cl, Na, Ca, and Mg. NO_3 had a statistically higher average concentration in the Cabras than in the Pisca catchment. The highest averages of solute concentrations were generally observed in the most donwstream sites of each stream (Table 4). Comparing these dowstream sites to each other, most of the averages solute concentrations were 2–3 times higher in the Pisca stream. For instance, SO_4 and NH_4 had concentrations 16 and 28 times higher in the Pisca, respectively (Table 4).

Macroinvertebrate community and the richness index

The *Insecta* class dominated the benthic fauna in both streams. The taxonomic groups distribution among the sampling sites showed a richer diversity in the Cabras than in the Pisca. Besides *Insecta*, other taxonomic groups like *Oligochaeta, Mollusca, Crustacea, Octopoda, Hirudinea* and *Tubellaria* were found in the Cabras. In the Pisca, the 'non *Insecta*' organisms were limited to *Oligochaeta*. Along the Cabras stream, richness was maintained downstream (Table 4). On the other hand, there was a sharp decrease in richness in the Pisca as the stream was affected by the urban area (Table 4).

Correlation between chemical composition, RI and LUI

We tested correlations between river water chemical composition and RI against LUI obtained in 1993 for each catchment. In the Cabras catchment, conductivity, major cations and major anions (with the exception of Na, SO_4 and NO_3) had a direct significant correlation with LUI (Fig. 2). TSS had an inverse and significant correlation with LUI (Fig. 2).

In the Pisca catchment, conductivity, major cations (with the exception of K) and major anions had a strong and statistically significant correlation (Fig. 3). In addition, DIC and DO showed a significant correlation with LUI. As already mentioned, the weightings for the calculation of LUI were arbitrary. Therefore, it is important to check if changing weights in the LUI calculation would not affect the correlation's outputs. The largest weight was attributed to

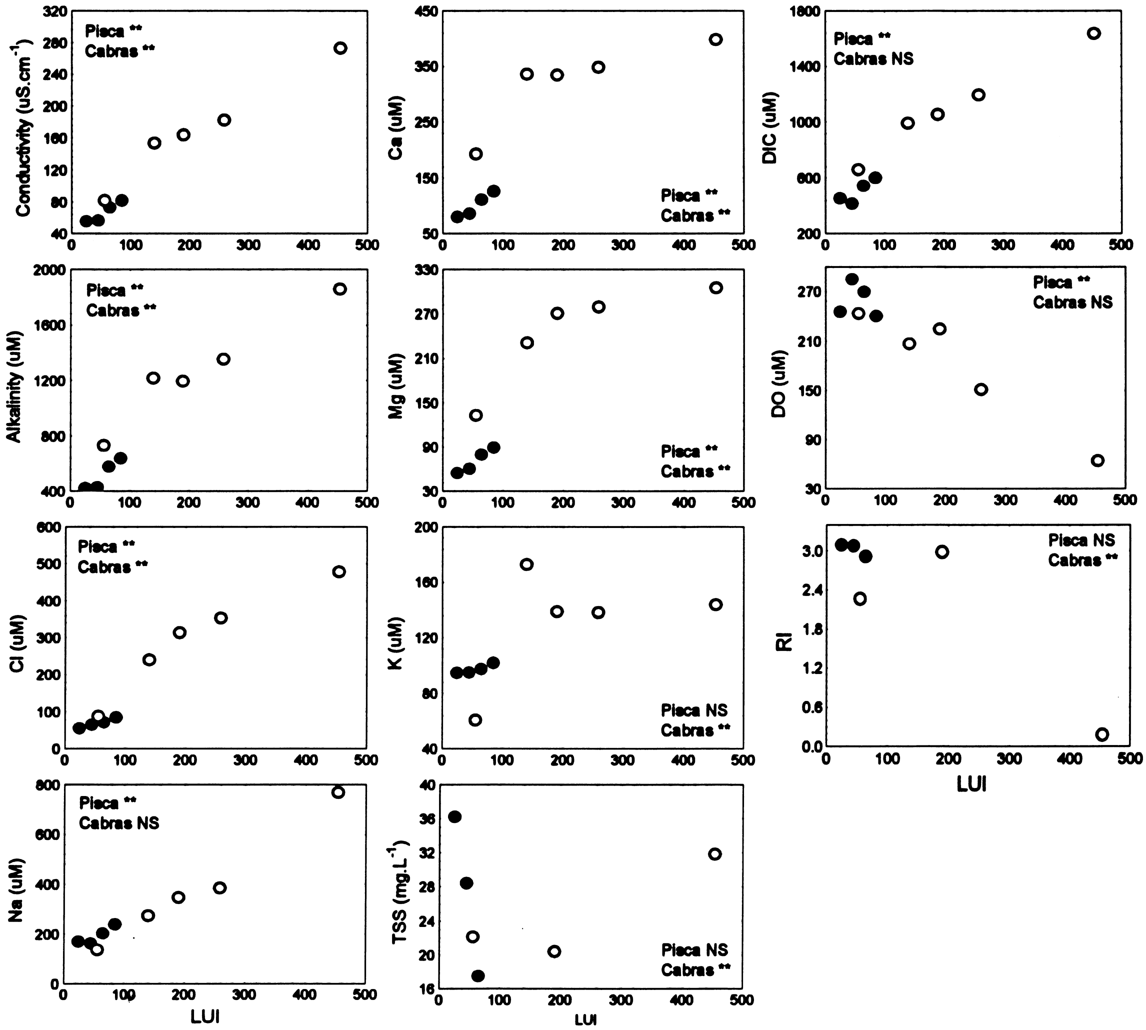

Fig. 2 Relationships between variables and LUI (land use index) for the Cabras (closed circle) and Pisca (open circle) catchments. Both catchment were pooled together in this figure, however, statistical tests were performed separately for each catchment.

urban areas (Table 2). In order to check the sensitivity of our analysis, we attributed one smaller (1) and one larger (10) weight to urban areas and calculated new land use indexes based on these new weights. The outputs of regressions involving these new LUIs and river water variables were practically unaltered in comparison with the original correlations.

Discussion

The fact that Cabras and Pisca catchments have different land uses (pastures vs. sugar-cane, low urbanization vs. high urbanization) may have important implications to streams conditions, due to the higher extent of impact caused by sugar-cane and urban sewage. For instance, sugar cane is burned and harvested each year and each 5–6 years the plants are removed and cultivated again. This type of management requires heavy traffic of machinery in the field and each year a portion of the plantation is replaced, exposing bare soils for months. On the other hand, pasture is only renewed every 8–10 years and is not harvested each year. Consequently, the erosion risk in a sugar cane field is much higher than in a pasture (C. E. Cerri, unpublished data). Moreover, sugar cane receives much more fertilizer than pasture. Annually sugar cane receives an average of 80–100 kg of nitrogen per hectare, while pasture in most of the area is not fertilized at all. As domestic sewage is almost always dumped into the rivers of the Piracicaba basin without treatment, the impact of cities is directly proportional to their sizes. Therefore, the

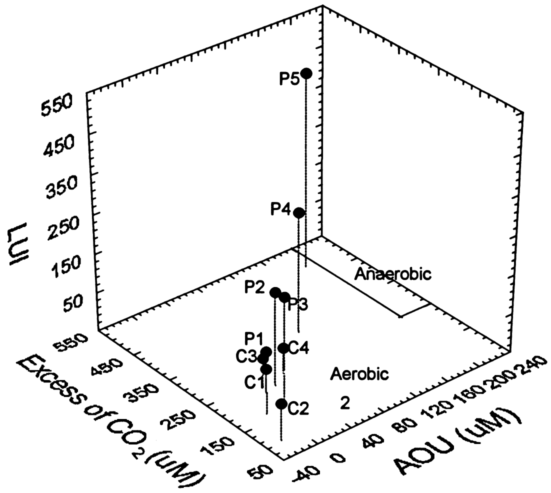

Fig. 3 Tridimensional plots of LUI, against AOU and excess-CO_2 for the Cabras and Pisca catchments.

urbanization impact in the Pisca catchment was larger than in the Cabras catchment. As a consequence, solute concentrations in the Pisca were generally higher than in the Cabras catchment. The largest difference was SO_4 with an average concentration ≈ 12 times higher in the Pisca catchment.

Predicting river water chemistry from land use is well documented in temperate catchments (e.g. Field *et al.*, 1996; Siver *et al.*, 1996; Allan *et al.*, 1997; Johnson *et al.*, 1997; Jordan *et al.*, 1997; Herlihy *et al.*, 1998). In general, our results are in agreement with these investigations. However, it is important to understand the processes in our catchments that cause changes in river water composition as a result of land use, since they may be different than those operating in temperate regions. For instance, several studies have shown that the increase in Cl and Na in river waters is a result of salt used in road de-icing operations (Prowse, 1987; Mattson & Godfrey, 1994; Siver *et al.*, 1996), which is not used in Brazil. In more urbanized areas, like subcatchment P5 of the Pisca, a clear source of Cl and Na is the human sewage that is added to the Pisca stream in the city of Piracicaba (Herlihy *et al.*, 1998). In rural areas of the Pisca and Cabra catchments, the increase of Na and Cl concentration in stream water is not easily explained, since there are no clear point sources, but instead potential diffusive sources from agricultural fields. Herlihy *et al.* (1998) also failed to find a specific cause for the increase in Cl concentration as a function of land use changes in more than 360 streams sampled in the mid-Atlantic region of the United States. They concluded that Cl is a 'general indicator of any non-forested land'.

Alkalinity is another parameter that frequently increases in association with agricultural activities and urbanization process (Siver *et al.*, 1996). The soils in both catchments (Pisca and Cabras) are typically very leached and acidic (C.E. Cerri, unpublished data). For agricultural purposes the pH of these soil types have to be raised; consequently the use of limestone is a common practice in this region. The two typical minerals used for this purpose are calcite ($CaCO_3$) and dolomite ($MgCO_3$). Consequently, besides CO_3, Ca and Mg are also added to the soil and possibly to the rivers. Indirect evidence that liming is causing an increase in alkalinity, Ca and Mg is that there was a strong and significant correlation between alkalinity and Ca and Mg in river waters of both catchments. Artificially limed streams in mid-Wales had significantly higher Ca concentration in relation to non-limed streams (Rundle *et al.*, 1995).

Although in general our results are in agreement with other investigations relating river water composition and land use, there are three major differences between this work and others. Land use was not a good predictor of TSS and NO_3 concentrations, or macroinvertebrate richness. It is important to remember that TSS concentration had a significant inverse correlation with LUI in the Cabras catchment. As there was large variability in altitude among the subcatchments, we tested the correlation between TSS concentration and altitude of each subbasin. There was a strong correlation between these two parameters, indicating that TSS in the Cabras catchment is controlled by physical characteristics, such as altitude, and not by land use.

In both catchments there was a tendency for higher NO_3 concentration to be associated with higher LUI (Table 4); however, the correlation was not significant. One possible explanation is that in our catchments, in contrast to lime application, nitrogen fertilizers are not widely used as in developed countries. For instance, U.S.A farmers apply ≈ 25–40% more fertilizers than crops really require (Puckett, 1995). In the Cabras catchment, pasture dominates and fertilizers are not added. Consequently, the runoff of fertilizer excess from the land to streams is probably smaller than that of U.S.A. farmlands.

Another possible explanation for the absence of a relationship between NO_3 concentration and LUI is that in heavily urbanized areas the domestic sewage load is so high that the dissolved oxygen concentration decreases abruptly; a good example is the P5 sampling site. As a consequence, NO_3 is transformed (denitrification) to a gas and lost to the atmosphere (Howarth *et al*., 1996). The total N loss in the heavily polluted Scheldt River in Europe corresponded to ≈ 50% of the total N inputs (Billen *et al*., 1985, cited by Howarth *et al*., 1996). In the main stem of the Piracicaba River the average NO_3 concentration did not statistically differ from the less polluted sites, probably due to N loss via denitrification (Martinelli *et al*., 1999). However, none of these possible explanations justify the higher NO_3 concentration observed in the Cabras catchment. We would expect to see higher concentrations in the Pisca catchment, since NO_3 is generally higher in catchments where the anthropogenic input of N is higher (Turner & Rabalais, 1994; Justic *et al*., 1995; Jordan & Weller, 1996). Atmospheric deposition could be a significant source of N to catchments (Howarth *et al*., 1996; Jaworski *et al*., 1997; Carpenter *et al*., 1998) and may explain the higher NO_3 concentration found in Cabras catchment. However, wet deposition estimates for areas near both catchments revealed similar N depositions (4.5 kg N ha^{-1} $year^{-1}$) (L.L. Lara, unpublished data). Animal manure can also be an important source of N (Puckett, 1995). The livestock population in the Cabras is higher than in the Pisca catchment and may also help to explain the higher NO_3 concentration found in the former catchment.

As for NO_3 concentration there was a trend between macroinvertebrate richness and LUI for both catchments; however, the correlation coefficients were not significant in both cases. In both catchments the second sampling sites were richer than the first sampling sites, while a decrease in RI values was observed at the third sampling sites, especially in the Pisca catchment (Figs 2 and 3). Although the macroinvertebrate sampling was done in pools to homogenize habitat conditions, the second sampling sites of both catchments were much more complex in terms of habitats than the first sampling sites, particulary because of the presence of more dense riparian vegetation and higher number of rocks in the stream bed. As only three sites in each stream were sampled, the fact that one site with a higher LUI had a higher RI due to local conditions was enough to make the correlation between RI × LUI non significant. This suggests that local stream conditions may exert an important influence on richness (Richards *et al*., 1996) and only abrupt changes in land use can offset local stream conditions. On the other hand, Allan *et al*. (1997), found in their investigation that habitat quality and biotic integrity were better predicted by regional land use than local stream conditions.

A set of parameters also investigated in this study were those related to river metabolism: dissolved oxygen (DO), dissolved inorganic carbon (DIC) and respiration rate (R). We observed a decreasing trend in DO and an increasing trend of DIC and respiration rate with the increase of LUI. Although not all of these trends had a statistically significant correlation, they suggest that the carbon oxidation pathway may be altered as a function of LUI. In order to test this possibility the excess-CO_2 was plotted against apparent oxygen utilization (AOU) (Richey *et al*., 1988; Devol *et al*., 1995; Ballester *et al*., 1999) defined as:

$$\mathrm{AOU} = [O_2]_{eq} - [O_2]$$

$$\mathrm{excess-CO_2} = [CO_2] - [CO_2]_{eq}$$

where $[O_2]_{eq}$ and $[CO_2]_{eq}$ are the equilibrium values calculated based on Henry's law for gas diffusion in aqueous media, using *in situ* temperature and pH values (Stumm & Morgan, 1996). $[O_2]$ and $[CO_2]$ are the observed values of dissolved oxygen concentration and dissolved carbon dioxide, respectively. The dissolved carbon dioxide concentration was calculated from pH and DIC (Skirrow, 1975). A higher AOU value indicates that the water is more depleted in dissolved O_2, whereas a higher excess-CO_2 value indicates that the water is more enriched in dissolved CO_2. Aerobic waters are characterized by excess-CO_2 concentration lower than 250 μM and AOU lower than 200 μM (Richey *et al*., 1988). As the LUI increased the excess-CO_2 and AOU became higher, leaning toward the anaerobic field (Fig. 4). This was especially the case of sampling site P5 in the Pisca catchment. In this site, the respiration rate increased since there was possibly more labile material available (high DOC concentration), consequently dissolved oxygen decreased and more CO_2 was generated.

Overall our results indicated that urbanization caused a higher impact in the river water than sugar cane, which in turn caused more impact than pasture. The fact that different crops caused distinct impacts to streams emphasizes that in our study land use cannot simply be grouped as agricultural or nonagricultural, but the type and intensity of land use have also to be addressed. Clearly efforts should be made towards urban sewage treatment, which is a major point source pollution. Although the economic situation in Brazil poses a major constraint, there is already available technology to solve this problem. The non-point source pollution caused mainly by sugar-cane is more difficult to resolve. According to Puckett (1995), the USA has already spent US$ 540 billion since 1972, when the Clean Water Act was approved, and 20 years later ≈ 44% of river miles tested still had pollution problems mainly attributed to nonpoint source pollution.

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