# EFFECTS OF URBAN SEWAGE ON DISSOLVED OXYGEN, DISSOLVED INORGANIC AND ORGANIC CARBON, AND ELECTRICAL CONDUCTIVITY OF SMALL STREAMS ALONG A GRADIENT OF URBANIZATION IN THE PIRACICABA RIVER BASIN

## MARIELY H. B. DANIEL, ALEXANDRA A. MONTEBELO, MARCELO C. BERNARDES, JEAN P. H. B. OMETTO, PLINIO B. DE CAMARGO, ALEX V. KRUSCHE, MARIA V. BALLESTER, REYNALDO L. VICTORIA and LUIZ A. MARTINELLI\*

Centro de Energia Nuclear na Agricultura, Av. Centenário 303, 13416-000, Piracicaba-SP, Brazil (\* author for correspondence, e-mail: zebu@cena.usp.br, fax: 55 193 429 4610)

(Received 12 July 2000; accepted 18 April 2001)

Abstract. In Brazil most of the urban sewage is dumped without treatment into rivers. Because of this, it is extremely important to evaluate the consequences of organic matter rich sewage on the structure and functioning of river ecosystems. In this study we investigated the effects of urban sewage on the dissolved oxygen (O<sub>2</sub>), dissolved inorganic (DIC) and organic carbon (DOC), and electrical conductivity (EC) in 10 small streams of the Piracicaba River basin, southeast region of Brazil. In the Piracicaba River basin, which is one of the most developed regions of the country, only 16% of the total sewage load generated is treated. These streams were classified into two groups, one with heavy influence of urban sewage and another with less influence. Both concentrations and seasonal variability were distinct between the two groups. The streams that received sewage effluent had a combination of low O<sub>2</sub> with high DIC, DOC, and EC. In the polluted streams, concentrations of dissolved carbon forms and EC were higher and O<sub>2</sub> concentration lower during the low water period. In the less polluted streams seasonal variations in concentrations were small. We also investigated the efficiency of a sewage treatment plant installed two years ago in the catchment of one of these streams. It was observed an increase in the  $O_2$  concentration after the beginning of the treatment, and a decrease of DIC and DOC concentrations especially during the low water period. However, no significant change was observed in the EC, suggesting that the concentrations of major ions is still unaltered, and that a secondary treatment is necessary in order to reduce ion load into the stream.

Keywords: Brazil, effluents, Piracicaba, pollution, sewage, streams, rivers

## 1. Introduction

Urban sewage has affected river and estuarine ecosystems around the world (e.g. Yung *et al.*, 1999; Singh *et al.*, 1999; Lampman *et al.*, 1999). The structure of biotic communities and water biogeochemistry has been severely affected by sewage (VanderPeek and VanGaans, 1997; Dauba *et al.*, 1998; Noppe *et al.*, 1999; Goni-Urriza *et al.*, 1999; Wass and Leeks, 1999; Naden and Cooper, 1999; Koning and Ross, 1999). Besides disruption of natural process, urban sewage has been a source to aquatic systems of heavy metals (Sanudo-Wilhelmy and Gill, 1999), pathogens



Water, Air, and Soil Pollution **136**: 189–206, 2002. © 2002 Kluwer Academic Publishers. Printed in the Netherlands. (Roll and Fujioka, 1997; Higuti *et al.*, 1998; Donnison and Ross, 1999), and drugs (Ternes, 1998), including carcinogenic compounds (Ono *et al.*, 2000). In Brazil, most of cities have no sewage treatment and untreated wastes are dumped directly into rivers. In the Piracicaba River basin, located in the São Paulo State, one of the most developed areas in Brazil, only 16% of the urban sewage are treated. As a consequence, most of major rivers in this basin have already altered their basic functioning by the large load of urban sewage and industrial effluents dumped in their waters (Krusche *et al.*, 1997; Martinelli *et al.*, 1999a; Ballester *et al.*, 1999). In this region, sewage wastes are preferentially dumped in small streams, instead of being directly loaded to major rivers. The impact of the sewage load on these streams has not been investigated, we however suggest that it may be severe because water volume of these streams is not large (Robson and Neal, 1997). A preliminary study in one of these streams heavily affected by urban sewage has shown that the O<sub>2</sub> concentration decreased to near zero during the low water period (Ometto *et al.*, 2000).

One of the strategies that the Piracicaba River Basin Committee is using is to encourage sewage treatment plants to treat urban sewage in small catchments. One example was the treatment plant installed in the Piracicamirim catchment (130 km<sup>2</sup>), which has a population of 60 000 inhabitants. Two years ago, approximately 150 L s<sup>-1</sup> of sewage was directly dumped in the Piracicamirim stream. Now, more than 90% of this load is collected in a sewage plant that primarily removes the organic load. In order to fully evaluate this strategy, it is necessary to understand the impact of sewage (Robson and Neal, 1997), and the effectiveness of sewage treatment plants in removing organic matter from these small streams (Ternes, 1998; Kosmala *et al.*, 1999; Koning and Roos, 1999; Noppe *et al.*, 1999; Ono *et al.*, 2000).

First we investigated the impact of sewage load on the dissolved oxygen (DO), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and electric conductivity (EC) of 10 small streams because these parameters are good indicators of sewage loading, and rates of production and consumption of organic matter in aquatic systems. Electrical conductivity was chosen as a proxy of ion content in the water. Secondly, we investigated the impact caused by the effluents of a sewage treatment plant by sampling two sites in the Piracicamirim river, one before the sewage effluents input (P1) and other after (P2). In order to test the effectiveness of this sewage treatment plant, we compared concentrations of the above parameters at P2 site before and after the installation of the sewage treatment plant. Finally, we also examined the correlations between the percentage of urbanized area in each catchment and water quality parameters. This search is important, since financial resources are always limited in our region, and water managers of the Piracicaba River basin have to select, among hundreds of small catchments, the most impacted ones in order to provide sewage treatment plants. Monitoring of hundreds of small streams is time demanding and expensive. An alternative is to search for correlations between land-use attributes, easily measured by geoprocessing tools,

and water quality. If a good correlation is found, the land-use attribute can be used to identify impacted small catchments in the basin. Such relationships have been investigated mainly in temperate developed countries (Peierls *et al.*, 1991; Hunsaker and Levine, 1995; Puckett, 1995; Howarth *et al.*, 1996; Allan *et al.*, 1997), focusing mainly in nitrogen and phosphorus (Vitousek *et al.*, 1997). Much less of these relationships are known in tropical developing countries (Ometto *et al.*, 2000).

## 2. Study Area

The streams investigated in this study belong to the Piracicaba River basin (12 400 km<sup>2</sup>), which is a developed meso-scale basin located in the state of São Paulo, southeast region of Brazil (Figure 1). The main river of this basin is the Piracicaba, which is formed by the junction of Atibaia and Jaguari (Figure 1). The average discharge of the Piracicaba River in its final reach is approximately 160 m<sup>3</sup> s<sup>-1</sup> (Moraes *et al.*, 1998). The annual average precipitation of the basin is approximately 1400 mm, most of it falling from November through March (Moraes *et al.*, 1998).

The Piracicaba basin is one of the most developed areas of Brazil, generating approximately 10% of the national gross internal product. Approximately 3 million persons live in this area, producing an urban sewage load equivalent to 90 tBOD day<sup>-1</sup>. Almost 85% of this effluent is dumped into rivers and streams without any treatment, causing severe pollution problems (Krusche *et al.*, 1997; Martinelli *et al.*, 1999a). Although most industries treat their effluents, the total volume is so high that their final BOD input is comparable to that from domestic sewage (São Paulo, 1994). Because more than 50% of domestic and industrial sewage is generated in the central region of the Piracicaba River basin (20% of the total basin area), the upstream reaches of its rivers are less impacted than downstream ones (Martinelli *et al.*, 1999a). Land use is intense, with almost 30% of the basin covered with sugar cane, 45% with pasture, 5% with agroforest, and approximately 5% are occupied with urban centers. Less than 10% is covered with the original forest vegetation. Pastures and agroforest dominate in the eastern side, while the western side is dominated by sugar cane (Martinelli *et al.*, 1999b).

#### 3. Methods

Ten streams where most of the pollution is generated mainly by domestic sewage were sampled in their final reach, before the junction with a major river (Figure 1). Number of samples and sampling periods for each stream are shown in Table I. These streams were approximately 1 m in depth and 2 to 12 m in width. In two of them, more than one site was sampled. In the Cabras stream we sampled two



Figure 1. Study area showing the main Piracicaba River and sampled streams.

IABLE I
---------

Stream	Area (km <sup>2</sup> ) <sup>a</sup>	% Urbanized <sup>a</sup>	N	Sampling
Cabras C1	11	1	14	02/97 to 06/98
Cabras C2	52	1.9	13	02/97 to 06/98
Tatu	192	19	11	06/98 to 03/99
Quilombo	417	31	11	06/98 to 03/99
Toledo	253	10	11	06/98 to 03/99
Tijuco	95	4	11	06/98 to 03/99
Piracicamirim P0 (before) <sup>b</sup>	20	7	27	02/97 to 06/98
Piracicamirim P1 (after) <sup>b</sup>	130	13	18	07/98 to 12/99
Piracicamirim P2 (before) <sup>b</sup>	130	13	29	02/97 to 06/98
Piracicamirim P2 (after) <sup>b</sup>	130	13	18	07/98 to 12/99
Enxofre	18	50	11	06/98 to 03/99
Guamium	65	3	11	06/98 to 03/99

Physical characteristics of stream sampling sites, and number (N) and sampling period

<sup>a</sup> For methodology details see Ometto et al. (2000).

<sup>b</sup> Before and after the installation of the sewage treatment plant.

sites, one near the headwaters (C1) and other in its final reach (C2). For detailed description of these sites see Ometto *et al.* (2000). In order to evaluate the effects of the effluent from the sewage treatment plant, which started its activity in June 1998, three sites were sampled in the Piracicamirim stream. One site at the less urbanized Piracicamirim headwaters (P0), approximately 20 km upstream from the output of the sewage effluent and other in the more urbanized area of the basin, approximately 200 m upstream (P1) of the sewage effluent output. Finally, a third site (P2) was sampled approximately 100 m downstream of the sewage effluent output. For trend analysis we have included data from P2 sampled before (02/97 to 06/98) the installation of the sewage treatment plant (Ometto *et al.*, 2000). We also included, for comparison, data from two major rivers of the basin, the Atibaia River, which was sampled in its headwater and is considered a less polluted river and the Piracicaba River near its end, considered one of the most polluted reach of this river (Martinelli *et al.*, 1999a).

Water samples for chemical analysis were collected in the middle of the channel at the surface using a Niskin bottle. 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. Samples were filtered after collection through precombusted glass-fiber filters for analysis. Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were determined with a Shimadzu TOC-5000A (Skirrow, 1975). Oxygen and  $CO_2$  (calculated from pH and dissolved inorganic carbon) concentrations are expressed as either mg L<sup>-1</sup> or as their departure from atmospheric equilibrium (apparent oxygen utilization (AOU) for oxygen and Excess-CO<sub>2</sub> for carbonic gas) and are defined as:

$$AOU = [O_2]_{eq} - [O_2] \tag{1}$$

$$Excess-CO_2 = [CO_2] - [CO_2]_{eq}, \qquad (2)$$

where  $[O_2]_{eq}$  and  $[CO_2]_{eq}$  are the equilibrium values and  $[O_2]$  and  $[CO_2]$  are the observed values of oxygen and carbon dioxide expressed in  $\mu$ M, respectively. Atmospheric equilibrium values were calculated based on Henry's law for gas-liquid equilibrium in aqueous media, using *in situ* temperature and pH values (Stumm and Morgan, 1996). Similarly, free dissolved CO<sub>2</sub> was calculated using the equilibrium constants for the carbonate system and *in situ* temperature and pH values (Skirrow, 1975). The higher the AOU, the more O<sub>2</sub> is depleted in water (Richey *et al.*, 1988; Devol *et al.*, 1995). In contrast, the higher the Excess-CO<sub>2</sub>, the CO<sub>2</sub> is enriched in water. Values of Excess-CO<sub>2</sub> and AOU higher than 200  $\mu$ M indicate the predominance of anaerobic decomposition process.

The percent of the catchment area covered with urban centers was estimated using LANDSAT TM images for 1997 and ARC-INFO geoprocessing software (Ometto *et al.*, 2000). Two assumptions were that the population density in these urban areas are the same (Brasil, 1991), and that the sewage produced in one catchment is dumped in the channel of this catchment.

Differences among streams were tested using the parametric Tukey Honest test for unequal variance. Temporal differences in the Piracicamirim-P2 site were tested using the non-parametric test Mann-Whitney U test, since populations were not statistically independent. To test for correlations between percent of urbanized area in each catchment and water quality the parametric Pearson correlation was used. Statistical differences at 1% level of probability is indicated in the text by P < 0.01.

### 4. Results

The concentrations of O<sub>2</sub>, DIC, DOC, and EC were highly variable in the streams of the Piracicaba Basin (Table II). Based on DO measurements, we identified 2 groups; one encompassing those streams with almost no urbanization (Cabras C1 and C2, Piracicamirim P0, Guamium and Tijuco) or with sewage treatment in their catchments (Piracicamirim), and the high urban streams, encompassing those streams with heavy urbanization in their catchments and without sewage treatment (Toledo, Tatu, Quilombo, Itapeva, and Enxofre) (Table I). The average DO concentrations of the lower urban group range from 5.6 to 9.1 mg L<sup>-1</sup> (Table II) and were higher (P < 0.01) than the average concentrations of the high urban that range from 1.8 to 2.9 mg L<sup>-1</sup> (Table II). The differences in the DIC average concentrations

### TABLE II

Average concentration and standard-deviation of O<sub>2</sub> (mg L<sup>-1</sup>), DIC (mg L<sup>-1</sup>), DOC (mg L<sup>-1</sup>), and EC ( $\mu$ S cm<sup>-1</sup>) in investigated streams and rivers

Stream	O <sub>2</sub>	DIC	DOC	EC
Cabras C1	9.1±0.6	16.8±2.3	3.1±1.7	53.5±5.6
Cabras C2	$7.7 {\pm} 2.0$	$26.4{\pm}4.6$	$2.9{\pm}1.3$	81.6±19.2
Piracicamirim P0	$6.7 \pm 0.3$	$28.9 {\pm} 7.4$	$3.9{\pm}1.7$	$81.6 {\pm} 16.8$
Tijuco	$6.7 \pm 0.6$	43.1±17.9	5.7±1.3	$159.2 \pm 54.7$
Guamium	$6.3 \pm 2.4$	$25.4 \pm 9.4$	$6.0{\pm}2.1$	$151.2 \pm 44.9$
Piracicamirim P1 (after) <sup>a</sup>	$5.7 \pm 2.0$	$52.4{\pm}21.0$	$6.3 \pm 2.6$	$219.0 \pm 83.4$
Piracicamirim P2 (after) <sup>a</sup>	$5.6 \pm 1.4$	$62.9 {\pm} 30.0$	$6.6 {\pm} 1.5$	$272.6 {\pm} 108.2$
Toledo	$2.9{\pm}2.1$	32.3±15.8	$7.0{\pm}2.6$	$131.2 \pm 64.7$
Tatu	$2.8{\pm}2.5$	$52.0{\pm}24.8$	47.7±43.9	376.7±166.4
Quilombo	$2.4{\pm}1.5$	$56.4{\pm}22.5$	$11.3 \pm 5.2$	$294.7 \pm 107.1$
Enxofre	$1.8{\pm}1.6$	$164.7 {\pm} 47.6$	$21.2 \pm 14.5$	597.5±159.3
Atibaia	$8.3{\pm}0.8$	$15.1 \pm 1.9$	$2.7{\pm}0.8$	$54.6 {\pm} 9.6$
Piracicaba	2.7±1.7	34.9±9.9	4.9±1.7	191.3±69.1

<sup>a</sup> Average concentrations obtained after the installation of the sewage treatment plant.



Figure 2. Relation between AOU and Excess-CO<sub>2</sub>.

were not as large between the two groups as they were for  $O_2$ . Only the Itapeva and Enxofre streams had significantly higher concentrations (P < 0.01) in relation to other streams (Table II). Concentrations of DOC and EC were higher in the high urban group, however, only the streams Tatu, Itapeva and Enxofre (P < 0.05) had significantly higher concentrations than the others (Table II). Generally, the  $O_2$ depletion observed in some streams was followed by an increase in dissolved  $CO_2$ . As a consequence, the more polluted streams appear to be operating, at least part of the time, under anaerobic conditions (Figure 2).

In order to show seasonal changes we selected one stream from each group: a low urban catchment (Tijuco), and a high urban catchment (Tatu), taking into account that the other streams showed similar behaviors in their respective groups. Seasonal variation was more pronounced in the high urban streams (e.g. Tatu) in relation to low urban streams (e.g. Tijuco) (Figure 3). The O<sub>2</sub> concentration in high urban streams decreased abruptly during the low water relative to the high water period. This decrease was followed by a increase in the DIC concentration. On the other hand, in low urban streams  $O_2$  concentration was practically constant during year-round (Figure 3). Overall, the DOC concentration in high urban streams was also higher during the low water in relation to high water, but again practically constant in non-polluted streams. The highest concentrations were observed during July and August, with an abrupt decrease in September and a second peak in the end of the low water period (Figure 3). The EC followed a similar trend in polluted tributaries, however, the second peak in the end of the low water period was higher than concentrations observed in the beginning of the same period (Figure 3). Once more variability was much smaller in non-polluted streams with highest values occurring in the middle of the low water period (Figure 3). These seasonal trends created an inverse correlation between DOC and O2, and a direct correlation between DOC and EC (Figure 4). When more DOC enters into streams via sewage, more ions are carried associated with it and more O2 is consumed to decompose this extra input of organic matter. The relation between DOC and DIC is not so clear due to the fact that after approximately 40 mg  $L^{-1}$  of DOC, the DIC concentration starts to decrease (Figure 4). Most probably due to anaerobic conditions, other compounds, such as  $CH_4$ , start to be formed instead of  $CO_2$ .

In order to test if the effluents from the sewage treatment plant has caused changes in its chemical composition of the Piracicamirim, we sampled this stream in two different sites, one upstream of the sewage effluent input into the stream (P1) and other downstream from the sewage effluent input (P2). There were no statistical differences between concentrations observed in P1 and P2. Therefore, the input of treated sewage is not altering the parameters investigated in this study. A second test made in this study was to compare the concentration of  $O_2$ , DIC, DOC and EC in the Piracicamirim before and after the installation of the sewage treatment plant. For this, we have been collecting water samples at P2 since the beginning of 1997 (one year and a half before the beginning of the sewage treatment). We also sampled at the Piracicamirim headwaters (indicated as P0 in Figure 1), before



*Figure 3.* Seasonal variation of  $O_2$ , DIC, DOC, and EC in the Tijuco ( $\bigcirc$ ) and Toledo ( $\bigcirc$ ) streams. Open and full bars at the top of the graphics indicate low and high water, respectively.



Figure 4. Relation between DOC versus O<sub>2</sub>, DIC, and EC for sampled streams.



*Figure 5.* Seasonal variation of  $O_2$ , DIC, DOC, and EC in the site P2 at Piracicamirim stream ( $\bigcirc$ ) and in the site P0 ( $\bullet$ ). The vertical line in the graphics indicates the beginning of the sewage treatment.

#### M. H. B. DANIEL ET AL.

#### TABLE III

Average concentration and standard-deviation of O<sub>2</sub> (mg L<sup>-1</sup>), DIC (mg L<sup>-1</sup>), DOC (mg L<sup>-1</sup>), and EC ( $\mu$ S cm<sup>-1</sup>) of low and high water periods before (02/97 to 06/98) and after (07/98 to 12/99) the installation of the sewage treatment at P2. For comparison, it was included the average concentrations found at Piracicamirim headwaters (P0 – Figure 1). Different letters indicate that the difference between averages is significant at *P* < 0.05

	O <sub>2</sub>	DIC	DOC	EC
Low water				
Headwater (P0)	6.8±0.3c	30.2±6.6c	3.2±0.9c	82.7±14.1c
Before (P2) After (P2)	1.9±1.7a 5.4±2.0b	82.7±23.6a 64.0±21.4b	11.4±5.3a 6.7±1.4b	309.4±18.9a 273.4±71.1a
High water				
Headwater (P0)	6.6±1.3c	27.6±8.2c	4.6±2.0c	80.7±19.7c
Before (P2)	2.7±2.0a	57.1±15.5a	8.7±4.0a	213.9±56.5a
After (P2)	5.9±2.0b	51.7±28.8a	6.5±2.9a	214.6±114.0a

it enters in the urban area of Piracicaba city, where this stream is relatively clean (Ometto et al., 2000). We compared concentrations of low water and high water periods before and after the treatment (Table III). Major differences were found for O<sub>2</sub> and carbon forms, especially during the low water period, when the impact of the sewage was higher due to the lower water volume available to dilute the sewage load (Figure 5). Dissolved oxygen average concentration during the low water was at least two times higher (P < 0.01) after sewage treatment, and DOC and DIC concentrations decreased (P < 0.05) after treatment (Table III). On the other hand, the sewage treatment had no effect on EC either during low or high water periods (Figure 5). During the high water, only  $O_2$  had concentrations significantly distinct before and after sewage treatment (Table III). Probably because, even before the sewage treatment, DIC and DOC concentrations increased during this period due the dilution of sewage water by precipitation and runoff (Figure 5). In comparison with the less impacted headwater region, concentrations observed at P2 after sewage treatment were intermediate between headwaters and P2 before sewage treatment. Therefore, it was an improvement especially in the oxygen status of the water, and dissolved forms of carbon. However, not comparable yet with concentrations observed in more pristine reaches of this stream. The values of EC found in P2 after sewage treatment are still similar to the ones found in P2 before sewage treatment and well above the values found in more pristine headwater regions of the Piracicamirim (Figure 5).



*Figure 6.* Relation between percentile of urbanized area versus O<sub>2</sub>, DIC, DOC, and EC for each sampled stream.

We found an inverse (P < 0.05) correlation between urbanized area and average concentration of O<sub>2</sub> (r = 0.82), and a direct and significant (P < 0.05) correlation with DIC (r = 0.91), and EC (r = 0.93) (Figure 6). The most urbanized catchment was the Itapeva, however its catchment could not be precisely measured because it was entirely in the limits of the Piracicaba city. The less urbanized were Cabras-C1 and C2, and Piracicamirim P0 (Table I). The others catchments had an intermediate urbanization process varying from approximately 10 to 50% (Table I). In these analysis we only included the Piracicamirim for correlation between EC and urbanized area, since the other parameters were affected by the sewage treatment. The correlation between urbanized area and average concentration of DOC was not significant mainly due the fact that Tatu creek had a very high DOC average concentration. In 3 samplings during the low water period, the DOC concentration in this creek was higher than 90 mg L<sup>-1</sup>. Excluding this creek from the analyzes, the correlation become significant with a r value equal to 0.90.

## 5. Discussion

Point source pollution, mainly through urban sewage and industrial effluents, has the most acute impact in rivers and streams in developing countries like Brazil (São Paulo, 1991). Although it is a very common problem in Brazil, the consequences of such impacts on water bodies have not been fully evaluated. In the Piracicaba River Basin it has been shown that water quality of its main rivers are rapidly deteriorating due to sewage inputs (Krusche et al., 1997). As it was hypothesized before, the impact of sewage load was even more severe on small stream than in the main rivers of the basin. For instance, the maximum DOC concentration in the more polluted reach of the Piracicaba River was 8 to 9 mg  $L^{-1}$ . In some streams, like the Tatu, we found DOC concentration as high as 100 mg  $L^{-1}$ . Electrical conductivity and DIC were almost 3 times higher in most polluted streams when compared with the Piracicaba River (Table II). Not only concentrations of these parameters were altered but also their seasonality. In less disturbed streams the seasonal variability of O<sub>2</sub>, dissolved carbon forms and EC was much less pronounced than in polluted river (Figure 3). In addition, stream metabolism was also altered, because in less disturbed streams carbon was originally metabolized only under aerobic conditions, while in polluted streams most of the time anaerobic conditions prevailed (Figure 2). As a consequence of these changes macroinvertebrates benthonic fauna were impoverished in one of these streams (Ometto et al., 2000).

One of the possible solutions in order to improve the overall conditions of these streams is treatment of urban sewage. Our temporal series of the Piracicamirim stream have shown that there was a significant improvement in its water quality after sewage treatment (Figure 5). Dissolved oxygen significantly increased either during low and high water periods, and DOC and DIC concentrations decreased especially during the low water period (Table III). On the other hand, no significant improvement was observed in electrical conductivity. This fact is suggesting as expected that concentration of major cations and anions did not change with sewage treatment. Therefore, a secondary system, devoted to hold this excess of ions, have to be set in order to better improve water quality of these small streams. Similarly, the concentration of PO<sub>4</sub> also did not decrease in the Hudson River estuary after more than 20 yr of the Clean Water Act of the United States (Sanudo-Wilhelmy and Gil, 1999). Based on the parameters investigated in this study, the impact of the sewage effluent into the Piracicamirim stream was not significant. However, other parameters related to water quality have to be tested, since it has been shown in the literature that sewage effluents from treatment plants may influence abiotic and biotic composition of streams (VanderPeek and VanGaans, 1997; Donnison and Ross, 1999; Kosmala et al., 1999; Koning and Roos, 1999).

Several authors pointed out the importance of finding land-use attributes that can be used to predict water quality (Field *et al.*, 1996; Siver *et al.*, 1996; Allan *et al.*, 1997; Jonhson *et al.*, 1997; Jordan *et al.*, 1997; Robson and Neal, 1997; Herlihy *et al.*, 1998). The finding of these relations would enhance our capability to

predict further scenarios (Robson and Neal, 1997), and is considered a requirement to achieve a comprehensive assessments of river conditions (Norris and Thoms, 1999; Fairweather, 1999). Most of studies relating land-use attributes and water chemistry where conducted in more developed temperate countries, and few were conducted in tropical and sub-tropical regions of developing countries. In these regions, land-use and other attributes, like sewage management, are different than in developed countries (Ometto et al., 2000). Therefore, attempts to find this kind of relationship in our region would be important not only for local water managers but also to allow comparisons with temperate catchments. In an early attempt we successfully correlated land-use attributes with water chemical composition along the Piracicamirim and Cabras streams (Ometto et al., 2000). One of the conclusions of that study was that the area occupied by urban centers was a significant predictor of water quality (Ometto et al., 2000). Here we also found significantly correlations between the percentile area covered by urban centers in each catchment and average concentrations of O2, DIC, DOC, and EC (Figure 5). Soils in the Piracicaba basin are mainly composed by leached, nutrient-poor tropical soils. Consequently, the EC is low in the low urban development streams and rivers of the basin (Table I). At the more urbanized sites, EC increases significantly, as a result of sewage load (Martinelli et al., 1999a) (Figure 4). In addition, EC is the most conservative parameter among the ones analyzed in this study.

Based on these facts, we choose EC to estimate critical values of urbanized area for the purpose of locating future sewage treatment plants in this region. The most pristine waters of the Piracicaba basin had average EC between 50 and 100  $\mu$ S cm<sup>-1</sup>, and the most disturbed waters had an average EC between 400 and 600  $\mu$ S cm<sup>-1</sup> (Table II). Using the equation yield from the correlation between EC and percentile of urbanized area (EC = 9.9 \* %urb + 79), we estimated that, for the most preserved streams (with an EC of 100  $\mu$ S cm<sup>-1</sup>), would correspond an urbanized area of approximately 2.1%. For the most disturbed rivers (an EC of 400  $\mu$ S  $cm^{-1}$ ), would correspond an urbanized area of approximately 32.4%. Assuming an EC of 250  $\mu$ S cm<sup>-1</sup> as an intermediate value, a corresponding urbanized area of 17.3% would be obtained. Based on these estimates, catchments with an urbanized area larger than 32% would be the first candidates to receive a sewage treatment plant, followed by catchments with an urbanized area varying between 17 to 32% and finally catchments with less than 17% of urbanized area. As an example of the application of this methodology, the criteria described above were applied in catchments with areas larger than 50 km<sup>2</sup> in the central part of the basin (Figure 7). From the 21 selected catchments, 2 had urbanized areas larger than 32% (Figure 7) and, hence, should be of first priority for sewage treatment plant construction. Three other catchments had urbanized areas between 17 and 32%, qualifying as a second level of priority to receive investments. Finally, there were 16 catchments with lower urban areas (<17%), which were classified, in terms of investments, as a third level of priority.



*Figure 7.* Piracicaba River basin showing selected catchments of the central part of the basin with an area larger than  $50 \text{ km}^2$  and classified according to the size of urban areas in their catchments. Low – urban area < 17%; Medium – urban area between 17 and 32%; High – urban area > 32%.

#### EFFECTS OF URBAN SEWAGE

### 6. Conclusions

Sewage effluents severely altered concentrations of  $O_2$ , DIC, DOC and EC in small streams of the Piracicaba River basin. However, an improvement of  $O_2$  concentration, followed by a decrease in DIC and DOC concentrations, was obtained after a treatment plant was installed in one of the catchments (Piracicamirim). This is suggesting that, unlike most of the watersheds with relatively high pollution problems in developed countries, the major problem in our catchments seems to be the discharge of point sources to streams and rivers. Nevertheless, water EC did not change after sewage treatment at the Piracicamirim catchment, indicating that nutrients, such as nitrogen, are still high. Since there are several known effects of nitrogen excess in aquatic systems (Vitousek *et al.*, 1997), it is essential that future sewage treatment plants also contemplate the removal of nutrients. Otherwise, the current efforts to minimize sewage influence on streams of the Piracicaba basin may not produce completely satisfactory results.

The combination of water quality parameters with land-use attributes, through geographical information systems, allowed us to propose to the Piracicaba River Basin Committee a simple way to select catchments for which investments in sewage treatment plants are most needed. This methodology will be most accurate in catchments where the main source of pollution is domestic sewage. Several catchments will follow in this situation, since the biggest industries discard their effluents mainly in the main rivers of the basin, and not in small streams, like we investigated in this study.

## Acknowledgements

We thank Linda Deegans for comments and suggestion on the manuscript. This research was partially funded by: Fapesp (Grants 94/0529-9, 95/9311-9 and 97/06140-4); PADCT/CNPq (Grant 62.0363/92.4) and ESSO BRASILEIRA DE PETRÓLEO.

### References

Allan, J. D., Erickson, D. L. and Fay, J.: 1997, Freshw. Biol. 37, 149.

- Ballester, M. V., Martinelli, L. A., Krusche, A. V., Victoria, R. L., Bernardes, M. and Camargo, P. B.: 1999, *Water Res.* **33**, 2129.
- Dauba, F., Lek, S., Mastrorillo, S. and Copp, G. H.: 1997, Arch. Environ. Contam. Toxicol. 33, 277.

Devol, A. H., Quay, P. D., Richey, J. E. and Martinelli, L. A.: 1987, Limnol. Oceanogr. 32, 235.

Donnison, A. M. and Ross, C. M.: 1999, New Zealand J. Mar. and Freshw. Res. 33, 119.

Fairweather, P. G.: 1999, Freshw. Biol. 41, 211.

Goni-Urriza, M., Capdepuy, M., Raymond, N., Quentin, C. and Caumette, P.: 1999, Can. J. Microbiol. 45, 826.

Herlihy, A. T., Stoddard, J. L. and Johnson, C. B.: 1998, U.S., Water, Air, and Soil Pollut. 105, 377.

- Higuti, I. H., Macena, I. R., Masunari, S., Branco, M. D., Blaskowiski, M. M. M. and do Nascimento, A. J.: 1998, *Brazilian Arch. Biol. Techn.* 41, 417.
- Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendese, F., Freney, J., Kudeyarov, V., Murdoch, P. and Zhao-Liang, Z.: 1996, *Biogeochemistry* 35, 75.
- Hunsaker, C. T. and Levine, D. A.: 1995, BioScience 45, 193.
- Johnson, L. B., Richards, C., Host, G. E. and Arthur J. W.: 1997, Freshw. Biol. 37, 193.
- Jordan, T. E., Correl, D. L. and Weller, D. E.: 1997, J. Environ. Qual. 26, 836.
- Koning, N. and Roos, J. C.: 1999, Water SA 25, 285.
- Kosmala, A., Charvet, S., Roger, M. C. and Faessel, B.: 1999, Water Res. 33, 266.
- Krusche, A. V., Carvalho, F. P., Moraes, J. M., Camargo, P. B., Ballester, M. R. V., Hornink, S., Martinelli, L. A. and Victoria, R. L.: 1997, J. Amer. Wat. Res. Assoc. 33, 1117.
- Lampman, G. G. and Caraco, N. F. and Cole J. J.: 1999, Estuaries 22, 285.
- Martinelli, L. A., Krusche, A., Victoria, R. L., Camargo P. B., Bernardes M. C., Ferraz E. S., Moraes J. M. and Ballester M. V.: 1999a, *Water, Air and Soil Pollut.* 110, 67.
- Martinelli, L. A., Ballester, M. V., Krusche, A., Victoria, R. L., Camargo, P. B., Bernardes, M. and Ometto, J. P. H. B.: 1999b, *Limnol. Oceanogr.* 44, 1826.
- Moraes, J. M., Pellegrino, G. Q., Ballester, M. V., Martinelli, L. A., Victoria, R. L. and Krusche, A. V.: 1998, *Water Res. Manag.* 12, 295.
- Naden, P. S. and Cooper, D. M.: 1999, Hydrol. Proc. 13, 1011.
- Nope, K., Prygiel, J., Coste, M. and Lepetre, A.: 1999, J. Freshw. Ecol. 14, 161.
- Norris, R. H. and Thoms, M. C.: 1999, Freshw. Biol. 41, 197.
- Ometto, J. P. H. B., Martinelli, L. A., Ballester, M. V., Gessner, A., Krusche, A., Victoria, R. L. and Williams, M.: 2000, *Freshw. Biol.* 44, 327–337.
- Ono, Y., Somiya, I. and Oda, Y.: 2000, Water Res. 34, 890.
- Peierls, B. L., Caraco, N. F., Pace, M. L. and Cole, J.: 1991, Nature 350, 386.
- Puckett, L.: 1995, Environ. Sci. Technol. 29, 408A.
- Richey, J. E., Devol, A. H., Wofsy, S. C., Victoria, R. and Ribeiro, M. N. G.: 1988, *Limnol. Oceanogr.* 33, 551.
- Robson, A. J. and Neal, C.: 1997, Sci. Tot. Environ. 195, 173.
- Roll, B. M. and Fujioka, R. S.: 1997, Water Sci. Technol. 35, 179.
- Sanudo-Wilhelmy, S. A. and Gill, G. A.: 1999, Environ. Sci. Technol. 33, 3477.
- São Paulo: 1994, Estabelecimento de metas ambientais e reenquadramento dos corpos d'água, Bacia do Rio Piracicaba, Secretaria do Meio Ambiente, p. 81.
- Singh, H. P., Mahaver, L. R. and Mishra, J. P.: 1999, J. Environ. Biol. 20, 279.
- Skirrow, G.: 1975, 'The Dissolved Gases-Carbon Dioxide', in J. P. Riley and G. Skirrow (eds), *Chemical Oceanography*, Vol. 2, 2nd ed., Academic, New York, pp. 1–192.
- Stumm, W. and Morgan, J. J.: 1996, Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters, 3nd ed., John Wiley & Sons, New York, p. 1021.
- Ternes, T. A.: 1998, Water Res. 32, 3245.
- VanderPeek, M. and VanGaans, P. F. M.: 1997, Water, Air, and Soil Pollut. 96, 107.
- Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Shcindler, D. W., Schlesinger, W. H. and Tilman, D. G.: 1997, *Ecol. Appl.* 7, 737.
- Yung, Y. K., Yau, K., Wong, C. K., Chan, K. K., Yeung, I., Kueh, C. S. W. and Broom, M. J.: 1999, *Mar. Pollut. Bull.* 39, 315.
- Wass, P. D. and Leeks, G. J. L.: 1999, Hydrol. Process. 13, 935.