DIURNAL VARIATION OF ANIONIC SURFACTANTS AND FORMS OF PHOSPHORUS IN A POLLUTED STREAM (RIO DE JANEIRO, BRAZIL)

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ABSTRACT

The concentrations of anionic surfactants and forms of phosphorus were investigated in two weather conditions in a sub-tropical polluted stream, flowing into a coastal lagoon. Diurnal variation was monitored hourly on an august 1991 day (considered dry condition) and on a January 1992 day (considered wet condition). The stream (Arrozal river) water samples collected during dry condition, showed concentrations ranging 1.90 $mg.L^{-1}$ - 4.90 $mg.L^{-1}$ for anionic surfactant, 0.10 µM - 6.05 µM for polyphosphate, 13.29 µM - 29.07 µM for phosphate and 30.58 µM - 44.22 µM for total phosphorus. Under wet conditions the ranges were 0.10 $mg.L^{-1}$ - 0.29 $mg.L^{-1}$ for anionic surfactants, 3,33 µM - 24.30 µM for phosphate and 15.45 µM - 26,28 µM for total phosphorus. The importance of human activities on concentrations of surfactants and forms of phosphorus has been established. Furthermore, the great variability of all parameters during the day (wet and dry) show the importance of the sampling scheme adopted.

INTRODUCTION

Even though detergents have largely been considered biodegradable pollutants, the lag of time necessary for degradation in some types of environments can be long enough to cause accumulation (Okpokwasil & Nwabuzor, 1988). On the other hand, products of degradation of detergents like phosphates can also be considered as harmful to the environment, increasing eutrophication rates (Devey & Harkness, 1973).

Even though many works have been done on surfactants in the environment (e.g. Adachi et al., 1983; Adachi et al., 1984; Urano et al., 1984a; Urano et al., 1984b; Sueishi et al., 1988), very little is known about their dynamics in the different environments. This is partly due to the fact that the studies concerning surfactants in the environment just consider the absolute concentrations present in the system as means of large range of variations. The question of how and why do the variations take place, has not yet been studied.

For some types of environments like small coastal basins, associated to coastal lagoons, a parallel can be stated between surfactants and phosphate, because they are usually dissolved, and originated from raw domestic sewage. Thus, the variations should be monitored on a diurnal basis, under wet and dry conditions (since the response time to short term events is immediate).

The aim of this study was to assess diurnal variation of anionic surfactants and the forms phosphorus: phosphate, polyphosphate and total phosphorus in a small stream flowing into a coastal choked lagoon subjected to high levels of eutrophication. One day under wet weather condition and one day under dry weather condition was monitored.

METHODS

The Study Area:

The Arrozal river is a tributary of the Piratininga lagoon, Niterói, some 20 Km from Rio de Janeiro (figure 1). Its drainage basin has been subjected to human occupation during the late 20 years, increasing considerably the amount of raw sewage entering the system (rivers and lagoon) bringing about large eutrophication problems, as stated in a number of publications (FEEMA, 1988; Knoppers, Kjerfve and Carmouze, 1991; Carneiro, 1992; Souza, 1992).

The lagoon itself has been classified as choked, with water turn-over time of 16 days (Kjerfve, 1986; Knoppers, Kjerfve and Carmouze, 1991), a small surface area of 2.89

Km^2 and a mean depth of 0.7 m. This has amplified the eutrophication problem (FEEMA, 1988).

Sampling

The diurnal variation was monitored in the sampling site of figure 1. Samples of water were collected every hour from 6:00 until 19:00 on 22 August 1991 (dry day) and on 22 January 1992 (rainy day). Aliquots of the water samples were filtered for analysis of the dissolved phase. Both filtered and unfiltered samples were preserved at 4° C until analysis (allways undertaken within the week of sampling). Measurements of water temperature and rough estimates of the flow rates were made at the time of sampling.

Analytical

Analysis of anionic surfactants were executed on filtered samples following the methylene blue method as described by APHA (1985). Calibration curves were obtained carrying the same analysis on FEEMA (Fundação Estadual de Engenharia do Meio Ambiente) LAS (Linear Alkylbenzene sulfonate) standards that were calibrated with EPA-US LAS standard.

The analyses of phosphate and polyphosphate were carried out on filtered samples following the method described by Grasshoff et al. (1983). Total phosphorus analysis was carried outusing unfiltered samples, following the method described by Grasshoff et al. (1983).

RESULTS AND DISCUSSION

The Physical Parameters

Table 1 show variation of temperature and water flux during the dry and wet day. It can be observed that even though during the dry day there is no rainwater input at all, an increase of water flux is observed in the afternoon. This is probably due to the fact that the quantity of natural water entering the river is so small that human inputs can increase the volume of water by a factor of 2. Such a trend is not observed in the wet condition since input of rain water was an order of magnitude higher than human inputs. It is of interest to note that temperatures in wet condition are higher because this occurred during sumer.

Surfactants

The Figures 2 and 3 show the surfactant concentrations under dry and wet conditions. As shown in these figures, the range of concentrations are quite different during both conditions, being low under wet (range 0.10 through 0.29 mg.L^{-1}) and strikingly raising under dry conditions (range 1.90 through 4.90 mg.L^{-1}). The low concentrations in wet conditions are not only due to dilution but also due to the fact that inhabitants of the area do not wash garments. This can be confirmed by the estimations of the total amount of surfactant passing through a section of the river per day calculated from the hourly concentrations and corresponding flow rates (table 2). As shown in table 2 the total amount of surfactants released to the system daily show an almost 2 fold reduction in the utilization of surfactants.

For both conditions, peak concentration occurred around noon (12:00/1:00 PM under dry and 11:00 AM under wet). In another short term study in Japan river, Adachi et al. (1983) have shown that maximum surfactant levels are attained at 10:30 AM, which seem comparable to ours, since diurnal variations seem to be controlled by human activities. Although, the concentrations observed in the study of Adachi et al. (1983) are significantly lower (ranging from circa 0.03 till 2,00 mg.L^{-1}) than those found in this study, both environments appear to be similar and subjected to heavy sewage pollution.

In this study the measurements started at 6:00 AM, it was assumed that very little surfactant input would take place earlier, and the concentrations found at this time would be considered the lowest of the day. For the humid day after 3:00 PM, the concentrations decay steeply until 6:00 PM and then stabilize to a probable background level. This steep fall in concentrations is probably due to high wash out rate of the system, sweeping all surfactants introduced during the day. Nevertheless, under dry conditions, when low flow rates are observed, wash out can be slower and probably goes on through the night, not attaining background levels, as stated by the high concentrations found early in the morning.

Forms of Phosphorus

Figures 4 and 5 show the variations in concentrations of phosphate (PO_4), Polyphosphate (POLY-P) and Total Phosphorus during dry and rainy days.

One should expect some correlation between surfactants and and the harmful degradation product of detergents, phosphorus (initially as Polyphosphate and subsequently as phosphate). Regardless of this fact, due to the existence of a number of other sources of phosphorus, in the environment studied, this correlation was not observed. And it is likely that the many other sources (mostly human originated, in the environment studied) are more important than the detergents themselves.

As stated in other studies made in the same area (Carneiro, 1992), the behaviour of the forms of phosphorus is also controled by human activities (since those are the main sources in this environment), however, these activities seem somewhat different from those controling surfactants, resulting in a less marked rise in concentrations during the day.

Under dry conditions, the concentration of total phosphorus and dissolved phosphate constantly increases during the day, and will, probably constantly, decrease after 10:00 or 12:00 PM (although data is not available). Even though polyphosphate concentrations are low, it is possible to observe, under dry condition, an antagonistic behaviour as compared to surfactants. This is confirmed by good negative correlation ($p < 0.01$) observed between these two variables. The absence of polyphosphate between 12:00 and 15:00 may be explained by the increase in use of liquid detergents for dish washing, that do not contain polyphosphates. It should also be considered that degradation of polyphosphates has been shown to be fast, no longer than some hours (Devey & Harkness, 1973), while degradation of surfactants (LAS) can last one or two days (Berna et al., 1991). this seem the only plausible explanation for the high levels found early in the morning and late in afternoon.

Under wet conditions, the concentrations of forms of phosphorus were half of those found under dry conditions. For the forms of phosphorus, dilution is a major process, since the sources should be continuously supplying this element to the environment at a rate wich does not depend on rainfall. It can be inferred that detergents are not an important source of phosphate, since the reduction in the surfactant concentration under wet is about ten fold and the reduction in phosphorus forms (except polyphosphate) is just 2 fold.

As under dry conditions, no marked time trends were detected under wet conditions, and variations seem arbitrary, indicating that no accumulation along the day time is occurring due to constant wash out.

The polyphosphate concentrations that were small under dry conditions become almost undetectable under wet condition and few conclusions should be stated.

CONCLUSIONS

The concentrations of anionic surfactants as well as forms of phosphorus has been shown to vary significantly along the day establishing the importance of the approach of diurnal variation. In this study it should be concluded that surfactant concentrations are strictly controled by human activities and dilution from rain water. The forms of phosphorus did not present significant correlation with surfactants, on the one hand because many sources of phosphorus (other than degradation of detergents) are present, and on the other hand, because polyphosphates degrade much faster than surfactants.

Even though very small quantities of natural surfactants exist, which probably are hardly detectable, sources other than direct anthropogenic input should be further studied, such as underground waters, soils and sediments. Underground water soils and sediments should be treated as a reservoirs capable of retaining relatively high amounts of surfactants, what should be released during heavy rains, or as result of any physico-chemical transformation in such reservoirs. In the studied area, some preliminary data colected from wells neighboring the studied river as well as lagoonar sediments showed high levels of surfactants placing those reservoirs as potential important ones.

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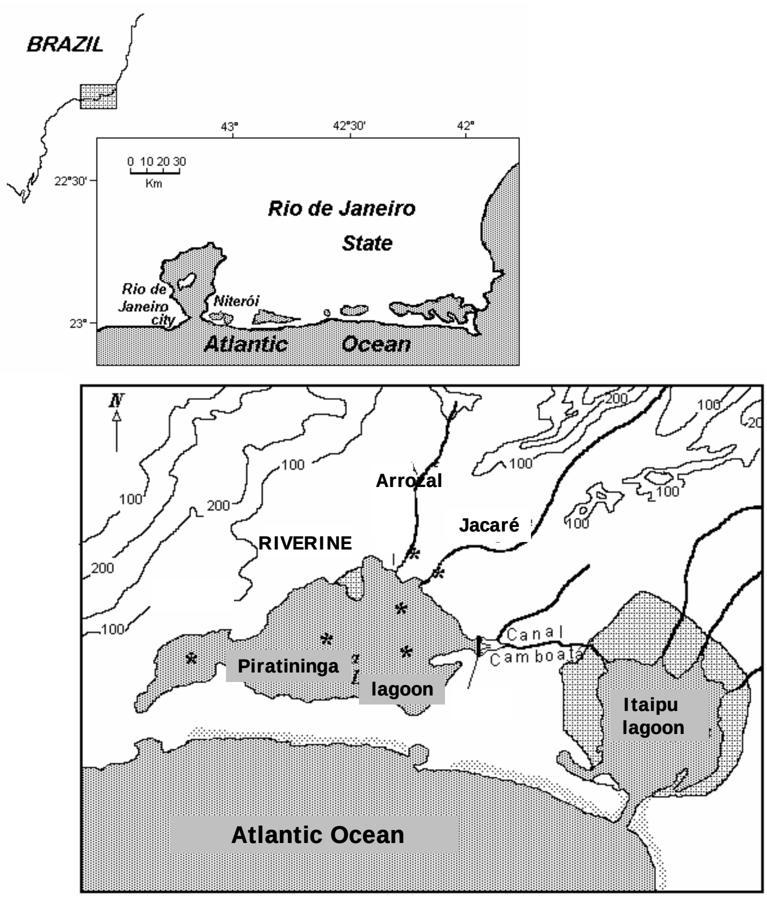

Figure 1: Location of study area and diurnal monitoring site

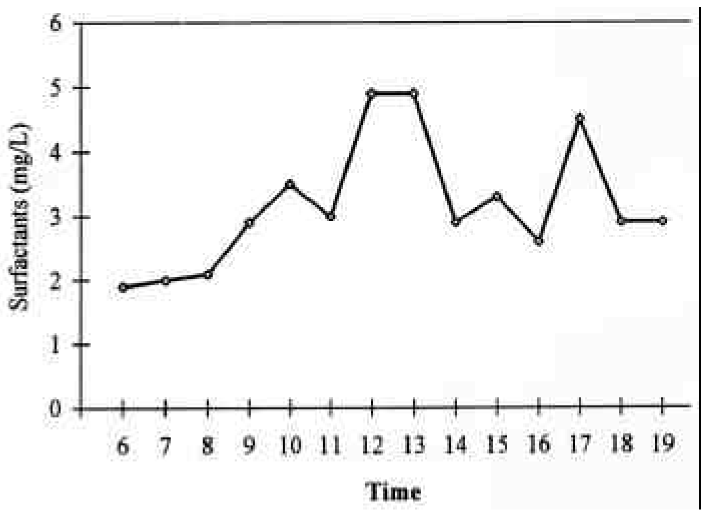

Figure 2: Surfactants during a dry day.

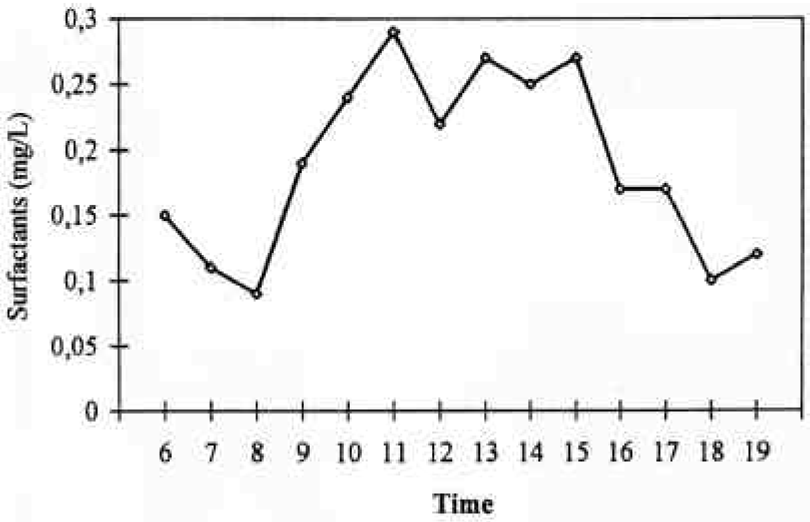

Figure 3: Surfactants during a wet day.

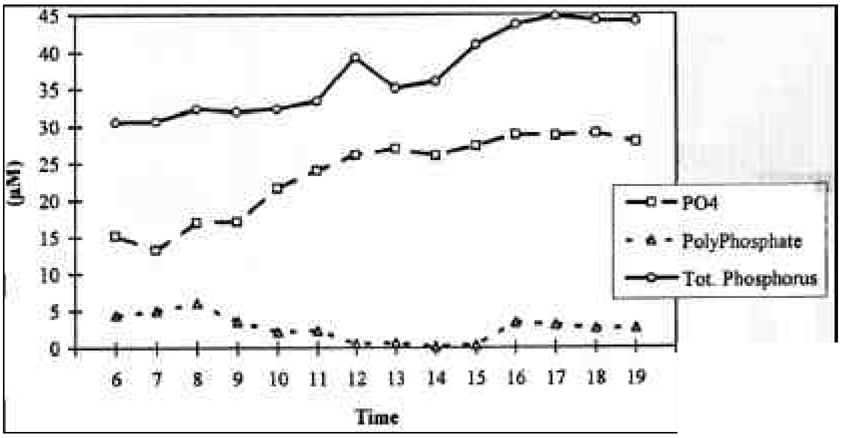

Figure 4: Forms of phosphorus during dry day

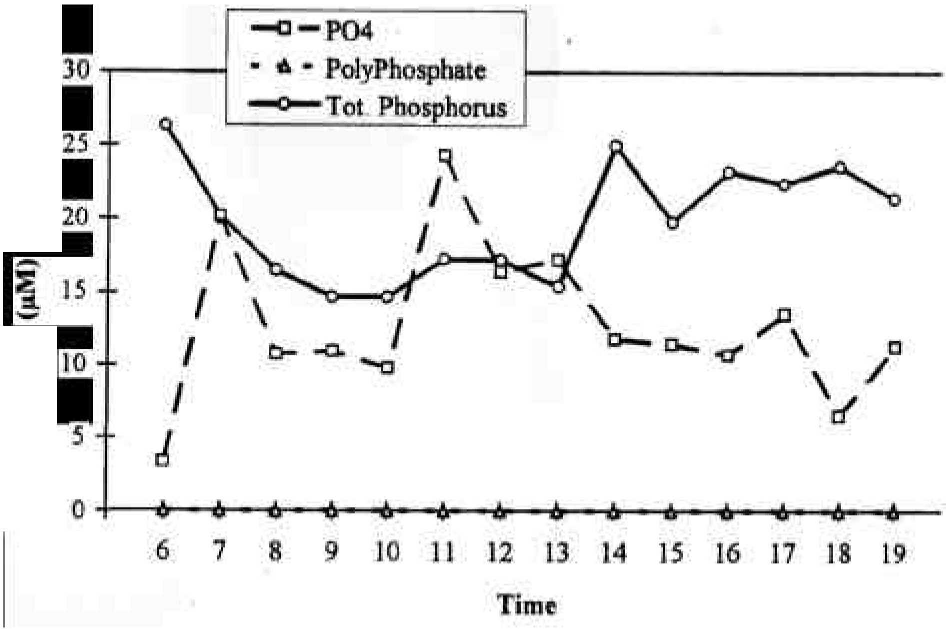

Figure 5: Forms of phosphorus during wet day.

Table 1: Temperature and fluxes during wet and dry conditions

	DRY		WET	
TIME	Temp °C	Flux ($m^3.s^{-1}$)	Temp °C	Flux ($m^3.s^{-1}$)
6:00	19.0	0.01	25.0	0.16
7:00	19.2	0.01	25.0	0.13
8:00	20.6	0.01	25.0	0.17
9:00	22.0	0.01	25.0	0.15
10:00	22.3	0.01	25.0	0.19
11:00	23.5	0.01	25.0	0.17
12:00	23.7	0.01	26.5	0.17
13:00	24.2	0.02	25.7	0.15
14:00	24.5	0.02	26.0	0.13
15:00	23.8	0.02	25.4	0.17
16:00	23.6	0.02	25.0	0.15
17:00	23.2	0.02	24.8	0.13
18:00	22.5	0.02	24.7	0.13
19:00	21.9	0.02	24.0	0.13

Table 2: Mass balance of the input of surfactants in the river water

Time	DRY Surfactants ($Kg.h^{-1}$)	WET Surfactants ($Kg.h^{-1}$)
6:00	0.07	0.09
7:00	0.07	0.05
8:00	0.08	0.06
9:00	0.10	0.10
10:00	0.13	0.16
11:00	0.11	0.18
12:00	0.18	0.13
13:00	0.35	0.15
14:00	0.21	0.15
15:00	0.24	0.17
16:00	0.19	0.09
17:00	0.32	0.08
18:00	0.21	0.05
19:00	0.21	0.05
$Kg.day^{-1}$*	3.17	2.01

* The lowest values were used as extrapolation for the hours when there was no sampling.